

1 Manuscript number: B913229E.

2 Manuscript title: Fate and distribution of the octyl- and nonylphenol ethoxylates and some
3 carboxylated transformation products in the Back River, Maryland

4 Corresponding author: Jorge E. Loyo-Rosales

5

6 **Supplementary Information**

7

8 **Analytical methods**

9 *Samples 2001.* Samples collected in January and February 2001 were analyzed for NP, OP,
10 NP1EO, NP2EO, NP3EO, OP1EO, OP2EO, and OP3EO. A complete description of these
11 procedures can be found in Loyo-Rosales et al ¹ and Rice et al ². Briefly, 4 L of water were
12 filtered with 1 µm Multigrade GMF 150 filters in series with 0.7 µm GF/F filters (both from
13 Whatman Inc., Clifton, NJ, USA). Samples were extracted using ENV+ solid-phase extraction
14 (SPE) cartridges (500 mg/6 mL from International Sorbent Technology Ltd., Hengoed, UK)
15 previously rinsed with 12 mL dichloromethane (DCM), 12 mL acetone, and 12 mL carbon-free
16 water on a vacuum manifold. After passing the water through the cartridges, they were dried
17 with N₂ and stored at -20°C until elution. Analytes were eluted with 6 mL DCM into a 15-mL
18 centrifuge tube; DCM was then exchanged to hexane by evaporation with a N₂ stream, and the
19 resulting extracts derivatized with PFBC, and analyzed by negative chemical ionization GC/MS
20 according to Datta et al ³, using PCB 204 (10 µL) as internal standard. Recoveries for all
21 compounds were above 80% and results were not corrected for recovery.

22

1 *Samples 2004 and 2005.* Samples collected in 2004 and 2005 were analyzed quantitatively for
2 NP, NP1EO to NP16EO, OP, OP1EO to OP5EO, NP1EC, NP2EC and OP1EC in the dissolved
3 fraction; and for the same analytes, except for the APECs, in suspended particulate matter.
4 Additionally, NP3EC, NP4EC and OP2EC were monitored qualitatively in the dissolved
5 fraction. The analytical methods have been published in a separate report ⁴. Briefly, water
6 samples were filtered and extracted on SPE cartridges as described above; however, a mixture of
7 [¹³C₆]-labeled compounds⁵ was added to this set of samples before extraction in order to use an
8 isotope dilution mass spectrometry (IDMS) approach for quantitation of the APEOs. After
9 drying, SPE cartridges were eluted with 10 mL DCM, 10 mL methanol, and 12 mL acetone,
10 which were pooled and reduced to 0.5 mL methanol in a nitrogen evaporator. After adding 0.5
11 mL water, the mixture was filtered through a 0.2 μm PVDF membrane (Acrodisc LC 13-mm
12 syringe filter, Pall Gelman Laboratory, Ann Harbor, MI, USA), and volume was adjusted to 1.5
13 mL. For the analysis of APEOs in particulate, the filters above were Soxhlet-extracted with
14 methanol, reduced to 0.5 mL and filtered as the water extracts above. Extracts from both the
15 dissolved and particulate fractions were analyzed by multiple-reaction monitoring in an
16 LC/MS/MS (Waters 2690 XE separations module with a Micromass Quattro LC triple
17 quadrupole mass spectrometer) with an electrospray ionization source.
18 APECs were extracted from filtered water samples with DCM, exchanged to methanol and
19 analyzed by LC/MS/MS. Recoveries were above 90% for the three APECs analyzed, and results
20 were not corrected for it. Quantitation for the APECs was done using an external standard
21 method followed by standard additions because no [¹³C₆]-labeled APECs were available for
22 IDMS.
23

1
2 **Model**
3 Back River was modeled as an incompletely mixed system at steady state using a control-volume
4 approach⁶. The estuary was divided into $n = 1200$ segments with constant length, $dx = 10$ m,
5 and surface area calculated for every segment. The mass balance equation for segment i is:

$$6 \quad 0 = W_i + Q_{i-1,i} \left(\frac{c_{i-1} + c_i}{2} \right) - Q_{i,i+1} \left(\frac{c_i + c_{i+1}}{2} \right) + E'_{i-1,i} (c_{i-1} - c_i) + E'_{i,i+1} (c_{i+1} - c_i) - k_i V_i c_i \quad \text{Eq. 1}$$

7 where c is the concentration of the chemical in the corresponding segment [mmol/m^3], W the
8 mass loading of the chemical to the segment [mmol/d], Q is the flow rate [m^3/d], E' the bulk
9 dispersion coefficient [m^3/d], k a lumped first-order reaction rate constant for the chemical [d^{-1}],
10 and V the volume of the segment [m^3].

11
12 Dirichlet boundary conditions were used to for the first, 0 , and last, n , segments. At segment 0 ,
13 the interface with the tributaries was assumed to be advective only; i.e. no dispersive mass
14 transport occurred; whereas the boundary of cell n with the Chesapeake Bay was treated as an
15 open boundary, with the concentration in the Bay assumed to be 0 . The system of n equations
16 was solved using MatLab Version 6.5.0.1924 Release 13 (The MathWorks, Inc., Natick, MA).

17
18 *Model parameters*

19 *Estuary dimensions*—The total length of the Back River was calculated from topographic maps
20 and rounded to 12000 m. Depths were calculated for each segment of the model assuming
21 geometric dimensions for the estuary (Fig. S1), and depths of 1.5 m at the head of the estuary,
22 2.7 m at 6000 m, and 7.6 m at the mouth⁷. For a segment situated at length x , if $x \leq 6000$, depth,
23 $h(x)$, was calculated as

1
$$h(x) = \frac{(2.7-1.5)}{6000}x + 1.5$$
 Eq. 2a

2 and for $x > 6000$,

3
$$h(x) = \frac{(7.6-2.7)}{6000}x + 2.7$$
 Eq. 2b

4 Widths were calculated in an analogous manner, assuming that the estuary was 800, 1000, 1500,
5 1600, 1700, and 1800 m at a distance of 0, 2000, 3000, 6000, 8400, and 12000 m respectively
6 from the estuary head.

7

8 *Flow rate*—Net estuary flow, $6.5 \times 10^5 \text{ m}^3/\text{d}$, was assumed to be the sum of the WWTP
9 discharge, 110 mgd ($4.2 \times 10^5 \text{ m}^3/\text{d}$) plus the average watershed discharge, $2.3 \times 10^5 \text{ m}^3/\text{d}$, which
10 was assumed to occur mainly through Back River's tributaries ⁸.

11

12 *Mass loadings*—Total APE mass loadings to the Back River were estimated using the water flow
13 rates above and APE concentrations measured in the WWTP effluent and the tributaries.

14

15 *Lumped reaction rate constant*—The first-order reaction rate constant k [d^{-1}] in this model is a
16 lumped parameter that includes all the processes other than advection and dispersion that may
17 affect the concentration of the chemical. Processes such as biotransformation, volatilization, and
18 photolysis were aggregated into a single rate constant, k_{transf} , which was the fitting parameter for
19 this model. When partition to solids was considered, k was the sum of k_{transf} and k_s ; the latter was
20 defined as:

21
$$k_s = \frac{V_s}{h}$$
 Eq. 3

1 where v_s corresponds to the apparent settling velocity of the particles [m/d], and h is the segment
2 depth as defined before. Note that elimination through settling with the solids applies only to the
3 fraction of the chemical sorbed to the particulate that is defined as

$$4 \quad F_p = \frac{K_d m}{1 + K_d m} \quad \text{Eq. 4}$$

5 where F_p is the fraction of the chemical in the particulate, K_d is the sorption coefficient for the
6 chemical [L/g], and m the suspended solids concentration [g/L]. Sorption was modeled using
7 weighted average values of the observed sorption coefficients, K_d , for the different APEOs along
8 with average suspended solids concentrations in Back River to calculate the fraction of the
9 NPEOs in the particulate, F_p . Because no data were available on the settling velocity, v_s , for the
10 river, a value of 0.25 m/d was chosen, which corresponds to the average value for phytoplankton
11 and organic solids⁶.

12
13 *Dispersion coefficient*—An average dispersion coefficient, E [m²d⁻¹] for Back River was
14 estimated assuming constant physical characteristics for the estuary and using the slope obtained
15 from a plot of the salinity data in Table 1 according to equation 5⁶

$$16 \quad \ln \frac{s}{s_0} = \frac{U}{E} x \quad \text{Eq. 5}$$

17 where s is the salinity [ppt] at distance x from the river's boundary with the Bay ($x = 0$), s_0 the
18 salinity at the boundary, and U the net estuarine velocity, 110 m d⁻¹. The latter was estimated
19 from the net estuary flow and the average cross-sectional area of the river, 5.8 x 10³ m².

20

21

22 **References**

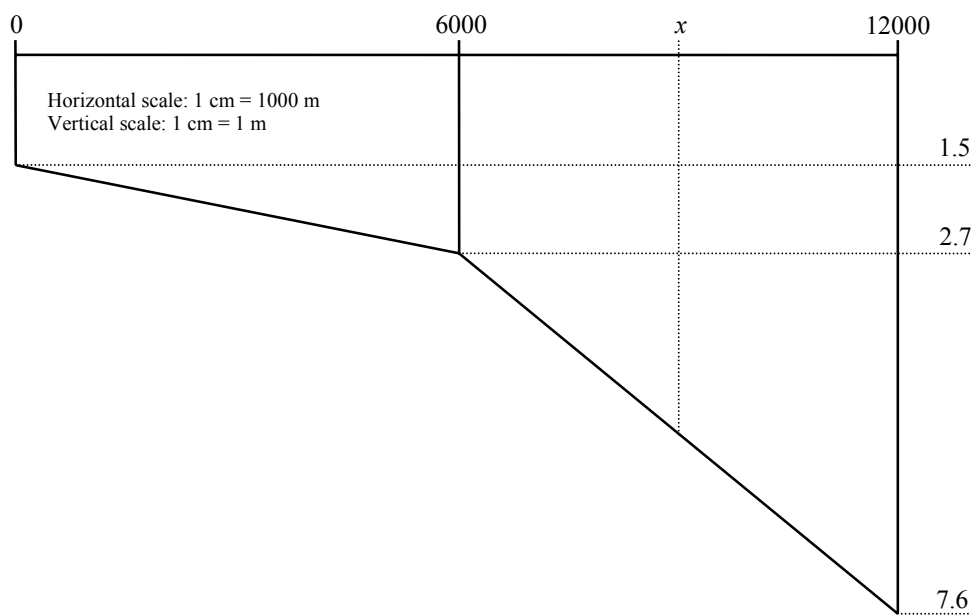
- 1 1. J. E. Loyo-Rosales, I. Schmitz-Afonso, C. P. Rice and A. Torrents, *Anal. Chem.*, 2003,
2 **75**, 4811-4817.
- 3 2. C. P. Rice, I. Schmitz-Afonso, J. E. Loyo-Rosales, E. Link, R. Thoma, L. Fay, D. Altfater
4 and M. J. Camp, *Environ. Sci. Technol.*, 2003, **37**, 3747-3754.
- 5 3. S. Datta, J. E. Loyo-Rosales and C. P. Rice, *J. Agric. Food Chem.*, 2002, **50**, 1350-1354.
- 6 4. J. E. Loyo-Rosales, C. P. Rice and A. Torrents, *Chemosphere*, 2007, **68**, 2118-2127.
- 7 5. P. L. Ferguson, C. R. Iden and B. J. Brownawell, *J. Chromatogr. A*, 2001, **938**, 79-91.
- 8 6. S. C. Chapra, *Surface Water-Quality Modeling*, McGraw-Hill, New York, NY, 1997.
- 9 7. MDE, *Total maximum daily loads of nitrogen and phosphorus for Back River in*
10 *Baltimore City and Baltimore County, Maryland*, Maryland Department of the
11 Environment, Baltimore, MD, 2005.
- 12 8. MDE, *Patapsco/Back River watershed SWMM model report*, Maryland Department of
13 the Environment, Baltimore, MD, 2003.
- 14
- 15

1

2 Figure S1. Schematic representation of the Back River used to estimate the estuary's depth at

3 distance x from the head of the estuary.

4



5

6