SUPPORTING INFORMATION

Synthetic Musk Fragrances in Lake Erie and Lake Ontario Sediment Cores

Aaron M. Peck[1,2], Emily K. Linebaugh[1,3] and Keri C. Hornbuckle[1*]

[1] Department of Civil and Environmental Engineering, University of Iowa, Iowa City, IA 52242

[2] Current address: National Institute of Standards and Technology, Hollings Marine Laboratory, 331 Fort Johnson Road, Charleston, SC 29412

[3] Current address: Veenstra & Kimm, Inc., 860 22nd Avenue, Coralville, IA, 52241

*Corresponding Author: keri-hornbuckle@uiowa.edu, Phone: 319-384-0789, Fax: 319-335-5660

9 Pages

1 Figure

5 Tables

Table S1. Synthetic Musk Fragrances

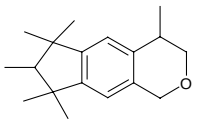
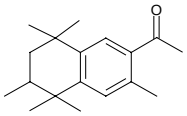
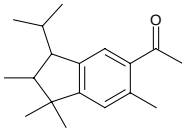
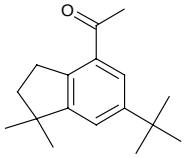
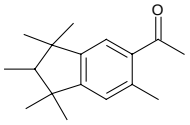
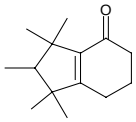
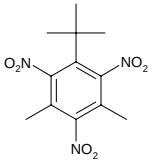
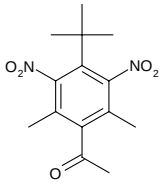
Compound	CAS RN	Structure	IUPAC Name	Trade Name
HHCB	1222-05-5		1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran	Galaxolide
AHTN	1506-02-1		7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene	Tonalide
ATII	68140-48-7		5-acetyl-1,1,2,6-tetramethyl-3-isopropyl-dihydroinden	Traseolide
ADBI	13171-00-1		4-acetyl-1,1-dimethyl-6-*tert*-butyldihydroindene	Celestolide
AHMI	15323-35-0		6-acetyl-1,1,2,3,3,5-hexamethyldihydroindene	Phantolide
DPMI	33704-61-9		6,7-dihydro-1,1,2,,3,3-pentamethyl-4(5H)-indanon	Cashmeran
Musk Xylene	81-15-2		2,4,6-trinitro-1,3-dimethyl-5-*tert*-butylbenzene	-
Musk Ketone	81-14-1		4'-*tert*-butyl-2',6'-dimethyl-3',5'-dinitroacetopheneone	-

Table S2. Synthetic Musk Fragrance Physical-Chemical Properties

Compound	**MW (g/mol)**	**Solubility (mg/L)**	**Henry's Law Constant (Pa m^3/mol)**	**Vapor Pressure (Pa)**	**log K_{ow}**
HHCB[a]	258.4	1.75	11.3	0.073	5.9
AHTN[a]	258.4	1.25	12.5	0.068	5.7
ATII[b]	258.4	0.085	85.1	1.2	8.1
ADBI[b]	244.3	0.015	1801	0.020	6.6
AHMI[b]	244.3	0.027	646	0.024	6.7
DPMI[b]	206.3	0.17	9.9	5.2	4.9
Musk Xylene[c]	297.2	0.49	0.018	0.00003	4.9
Musk Ketone[c]	294.3	1.9	0.0061	0.00004	4.3

[a] Physical-chemical properties from (*1*).
[b] Physical-chemical properties from (*2*).
[c] Physical-chemical properties from (*3*).

Table S3. Characteristics of Lake Ontario Sediment Core Sections
(Sedimentation Rate = 0.027 g/cm^2-yr)

Section	Depth (cm)	Cumulative Dry Mass (g/cm^2)	Dry Mass (g)	Water Content (%)	Midpoint Year
1	0-2	0.25	11.61	0.86	1999.0
2	2-4	0.57	14.49	0.83	1988.4
3	4-6	0.92	15.76	0.83	1976.1
4	6-8	1.33	18.92	0.83	1962.0
5	8-10	1.83	22.84	0.76	1945.0
6	10-12	2.53	31.53	0.71	1923.0
7	12-14	3.33	36.54	0.71	1895.3
8	14-16	3.87	24.99	0.71	1870.3
9	16-18	4.59	32.44	0.71	1847.0
10	18-20	5.28	31.47	0.71	1821.0
11	20-22	5.90	28.44	0.75	1796.7
12	22-24	6.61	32.29	0.68	1772.1
13	24-26	7.51	41.17	0.64	1742.2
14	26-28	8.47	43.58	0.64	1707.8
15	28-30	9.25	35.70	0.68	1675.6
16	32-34	10.02	35.34	0.69	1646.8
17	34-36	10.86	38.32	0.66	1616.9
18	36-38	11.67	36.63	0.67	1586.4
19	38-40	12.60	42.40	0.64	1554.3
20	40-42	13.46	39.28	0.63	1521.2
21	42-44	14.27	36.99	0.61	1490.2
22	44-46	14.96	31.68	0.63	1462.3
23	46-48	15.82	39.26	0.61	1433.5

Table S4. Characteristics of Lake Erie Sediment Core Sections
(Sedimentation Rate = 0.73 g/cm^2-yr)

Section	Depth (cm)	Cumulative Dry Mass (g/cm^2)	Dry Mass (g)	Water Content (%)	Midpoint Year
1	0-1	0.15	6.87	0.73	2003.5
2	1-2	0.45	13.78	0.72	2003.1
3	2-3	0.86	18.77	0.68	2002.6
4	3-4	1.30	19.98	0.64	2002.0
5	4-5	1.71	18.69	0.65	2001.5
6	5-6	2.16	20.36	0.64	2000.9
7	6-7	2.59	19.57	0.65	2000.4
8	7-8	3.07	22.13	0.64	1999.8
9	8-9	3.49	19.19	0.62	1999.2
10	9-10	4.03	24.43	0.60	1998.6
11	10-11	4.51	21.90	0.59	1998.0
12	11-12	5.02	23.11	0.62	1997.3
13	12-13	5.45	19.86	0.63	1996.8
14	13-15	6.28	37.89	0.63	1995.7
15	15-16	6.85	25.67	0.62	1995.0
16	16-17	7.36	23.59	0.61	1994.3
17	17-18	7.72	16.42	0.63	1993.9
18	18-19	8.14	19.02	0.64	1993.4
19	19-21	8.64	22.76	0.63	1992.7
20	21-22	9.03	18.01	0.63	1992.2
21	22-23	9.50	21.44	0.64	1991.6
22	23-24	9.96	20.87	0.64	1991.1
23	24-25	10.39	19.63	0.63	1990.5
24	25-26	10.76	16.56	0.64	1990.1
25	26-27	11.23	21.58	0.64	1989.5
26	27-28	11.70	21.54	0.65	1988.9
27	28-29	12.02	14.69	0.63	1988.5
28	29-30	12.49	21.50	0.61	1987.9
29	28-30	13.39	40.82	0.63	1986.7
30	30-32	14.11	32.62	0.63	1985.8
31	32-34	15.01	41.22	0.62	1984.7
32	34-36	16.03	46.71	0.61	1983.4
33	36-38	16.89	39.05	0.61	1982.3
34	38-40	17.86	44.05	0.61	1981.1
35	40-42	18.71	38.92	0.62	1980.0
36	42-44	19.64	42.51	0.60	1978.8
37	44-46	20.55	41.45	0.60	1977.7

Table S5. Quantification and Confirmation Ions

Compound	GC/MS Analysis		GC/MS/MS [2]	
	Quantification Ion	**Confirmation Ion [1]**	**Parent Ion**	**Daughter Ion**
ADBI	229	244	229	173
AHMI	229	244	229	187
HHCB	243	213	243	213
Pentachloronitrobenzene (IS)	237	-	237	141
ATII	215	258	215	173
Musk Xylene	282	297	282	91
AHTN	243	258	243	159
Musk Ketone	279	294	279	118
fluoranthene-d_{10} (Surrogate)	212	-	212	212

[1] Used for Lake Ontario core

[2] Used for confirmation of Lake Erie core

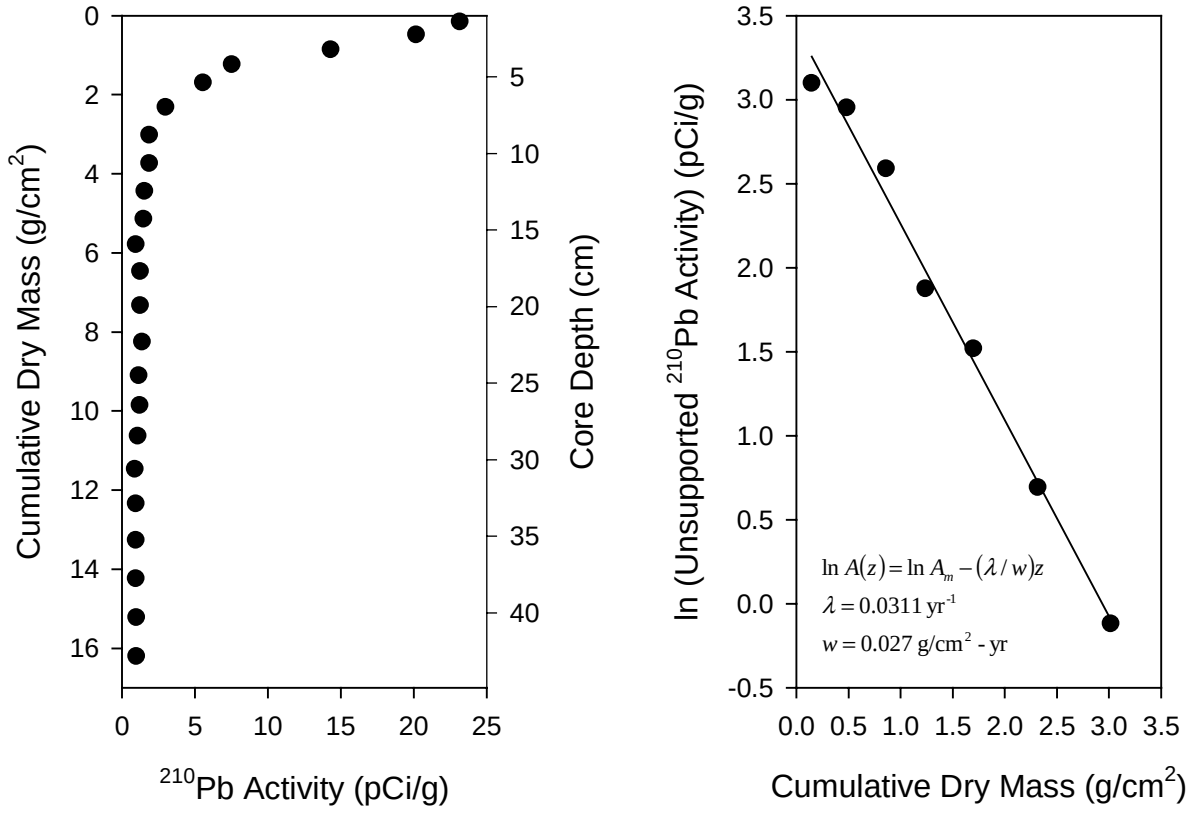

Cumulative Dry Mass (g/cm2)
Core Depth (cm)
210Pb Activity (pCi/g)
ln (Unsupported 210Pb Activity) (pCi/g)
Cumulative Dry Mass (g/cm2)
ln A(z) = ln Am – (λ / w)z
λ = 0.0311 yr-1
w = 0.027 g/cm2 - yr

Figure S1.

Notes on GC/MS/MS Method

Methods for the synthetic musk fragrance analysis using ion trap MS/MS have been previously reported (*4*,*5*), however, this is the first report of a triple-quadrupole method for these compounds. The dominant transitions identified for each compound are listed in Table SI-5. The 243→213 transition for HHCB corresponds to the loss of two additional methyl groups from the parent $[M-15]^+$ ion. The 215→173 transition for ATII corresponds to the loss of $-C_2H_3O$ from the parent $[M-43]^+$ ion. Similarly for AHTN, the 243→159 transition is the result of the loss of $-C_2H_3O$ and four methyl groups from the parent $[M-15]^+$ ion. The transitions for ADBI (229→173) and AHMI (229→187) result from the loss of an additional two and one methyl groups from the parent $[M-15]^+$ ions, respectively. The musk xylene transition (282→91) was due to the rearrangement of xylene resulting from the loss of all three nitro groups and the t*ert*-butyl group from the $[M-15]^+$ parent ion. The musk ketone transition (279→118) was due to the loss of $-C_2H_3O$ from the $[M-15]^+$ parent ion. Due to the stability of the parent ions for each compound, the yield for each transition was low and the sensitivity of the GC/MS/MS method was lower than that of the GC/MS methods used. Potential sensitivity gains due to the increased selectivity of this method were not seen because background interferences using GC/MS were already fairly low in these samples. The GC/MS/MS method was sensitive enough to confirm the presence and concentrations of HHCB in the Lake Erie core initially analyzed using ion trap GC/MS.

References

(1) Balk, F.; Ford, R. A. "Environmental risk assessment for the polycyclic musks AHTN and HHCB in the EU. I. Fate and exposure assessment," *Toxicol. Lett.* **1999**, *111*, 57-79.

(2) Paasivirta, J.; Sinkkonen, S.; Rantalainen, A. L.; Broman, D.; Zebuhr, Y. "Temperature dependent properties of environmentally important synthetic musks," *Environ Sci Pollut R* **2002**, *9*, 345-355.

(3) Tas, J. W.; Balk, F.; Ford, R. A.; van de Plassche, E. J. "Environmental risk assessment of musk ketone and musk xylene in the Netherlands in acccordance with the EU-TGD," *Chemosphere* **1997**, *35*, 2973-3002.

(4) Herren, D.; Berset, J. D. "Nitro musks, nitro musk amino metabolites and polycyclic musks in sewage sludges - Quantitative determination by HRGC-ion-trap-MS/MS and mass spectral characterization of the amino metabolites," *Chemosphere* **2000**, *40*, 565-574.

(5) Eschke, H. D.; Dibowski, H. J.; Traud, J. "Determination of polycyclic musk flavors in human fat and milk by using selective ion trap GC/MS/MS," *Deut Lebensm-Rundsch* **1995**, *91*, 375-379.