Synthetic Fragrances in the Aquatic Environment: Overview of Chemistry, Monitoring, and Significance

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Overview

- Synthetic musk compounds!
- What are they?
- The chemistry
- Monitoring methods
- Data evaluation
- Summary
- Conclusion

What are synthetic musk compounds

- Polycyclic musks are acetylated and highly methylated pyran, tetralin, and indane skeletons.
- Nitro musks are methylated, nitrated, and acetylated benzene ring.
- They have the characteristic odor of natural musks, hence the name synthetic musk compounds.
- Detergents, shampoo, bar soap, body lotion, and additives for perfumes.

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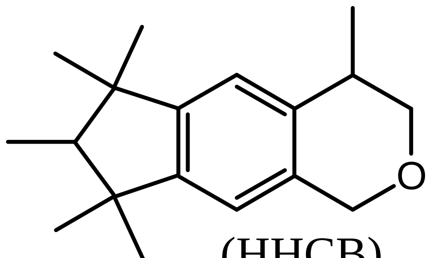
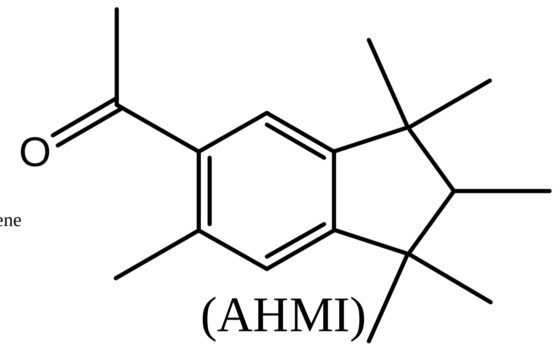
Chemical Structures of Synthetic Polycyclic Musks



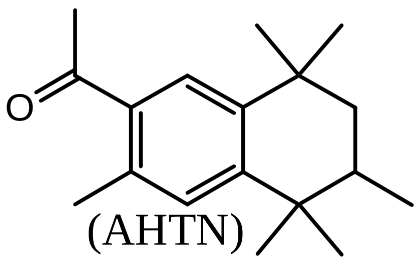
(HHCB)

1,1,2,3,3,8-Hexamethyl-1,2,3,5,7,8-hexahydro-6-oxa-cyclopenta[*b*]naphthalene



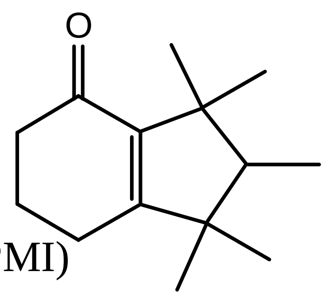
(AHMI)

1-(1,1,2,3,3,6-Hexamethyl-indan-5-yl)-ethanone



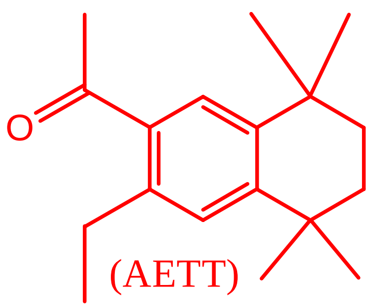
(AHTN)

1-(3,5,5,6,8,8-Hexamethyl-5,6,7,8-tetrahydro-naphthalen-2-yl)-ethanone



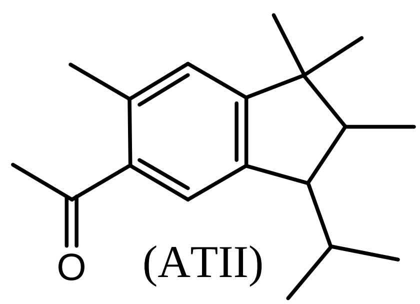
(DPMI)

1,1,2,3,3-Pentamethyl-1,2,3,5,6,7-hexahydro-inden-4-one



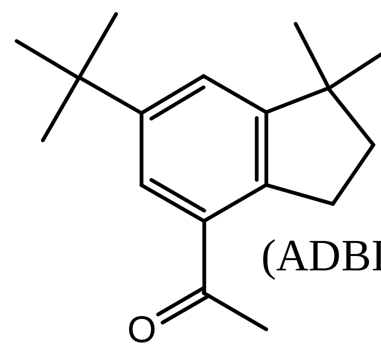
(AETT)

1-(3-Ethyl-5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-naphthalen-2-yl)-ethanone



(ATII)

1-(3-Isopropyl-1,1,2,6-tetramethyl-indan-5-yl)-ethanone



(ADBI)

1-(6-*tert*-Butyl-1,1-dimethyl-indan-4-yl)-ethanone

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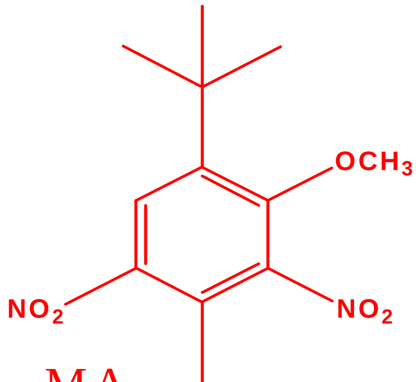
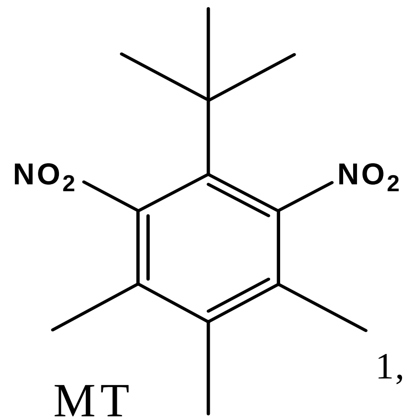
Chemical Structures of Synthetic Nitro Musks



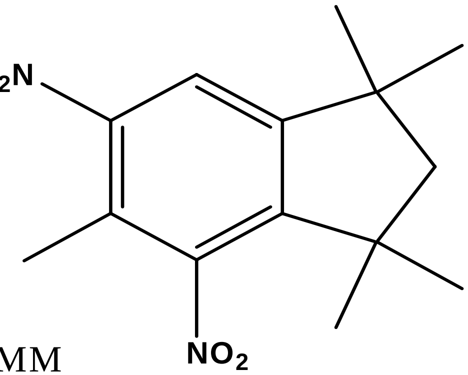
MA

2,6-dinitro-3-methoxy-4-tert-butyl toluene



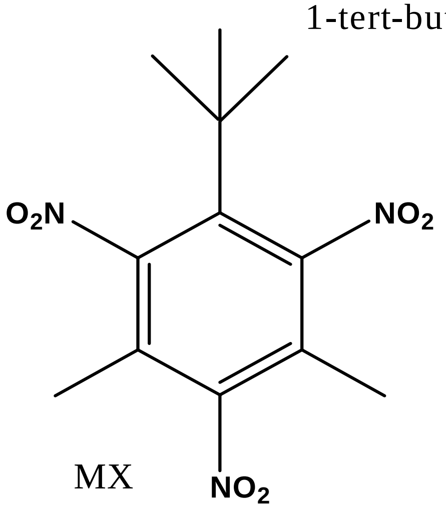
MT

1-tert-butyl-2,6-dinitro-3,4,5-trimethylbenzene



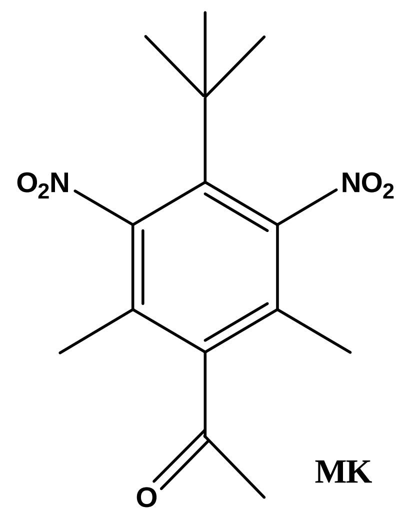
MM

1,1,3,3,5-Pentamethyl-4,6-dinitro-indan



MX

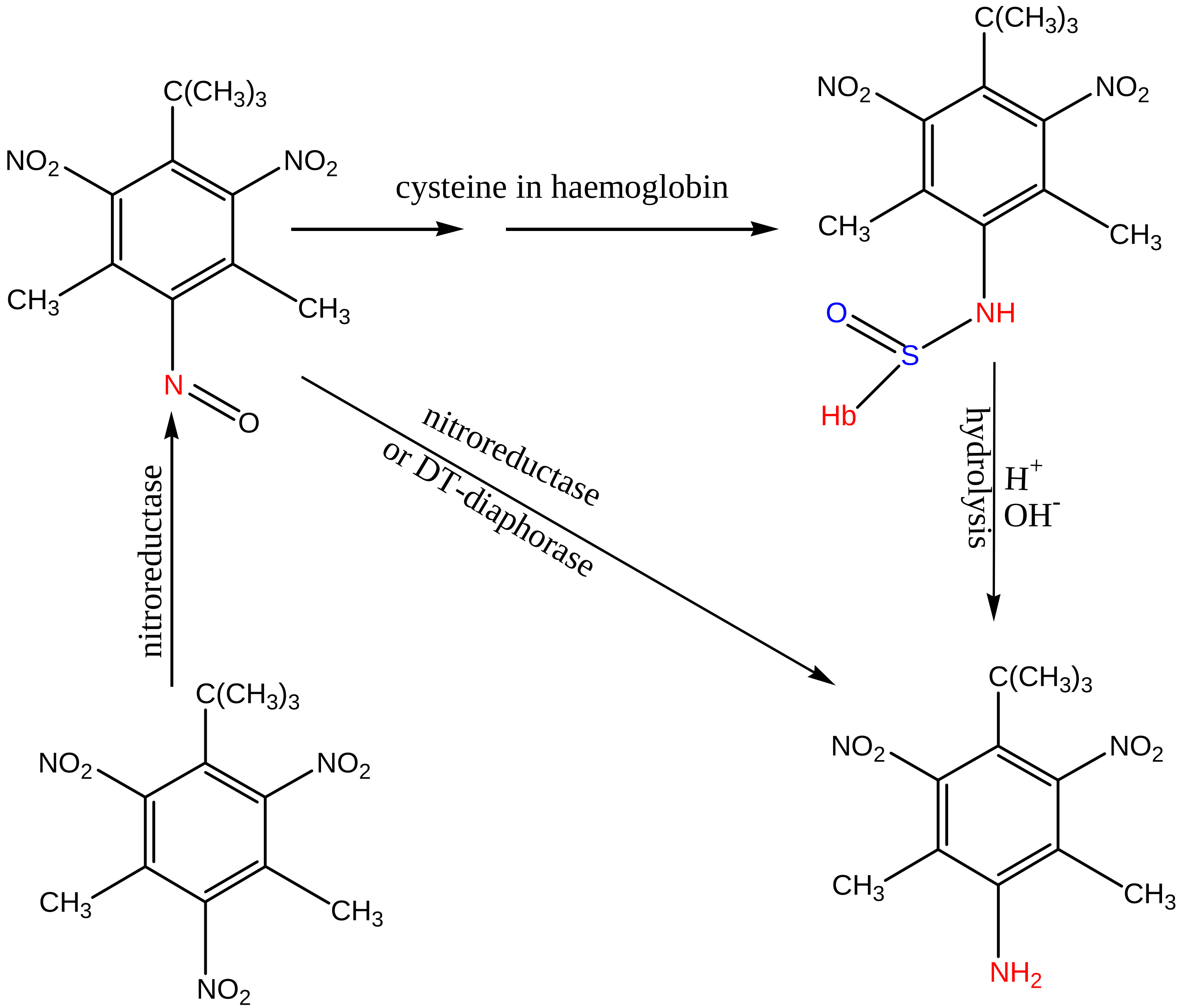
1-*tert*-Butyl-3,5-dimethyl-2,4,6-trinitro-benzene



MK

1-(4-*tert*-Butyl-2,6-dimethyl-3,5-dinitro-phenyl)-ethanone

MX Reactive metabolites



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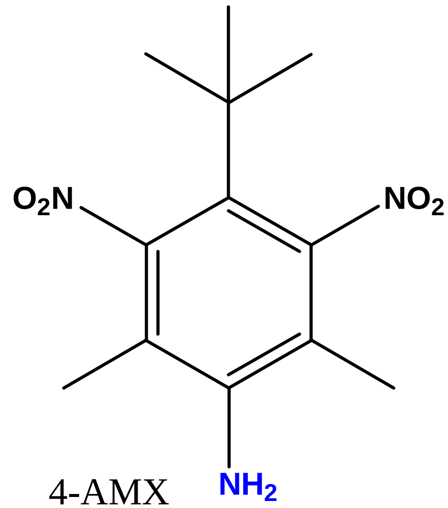
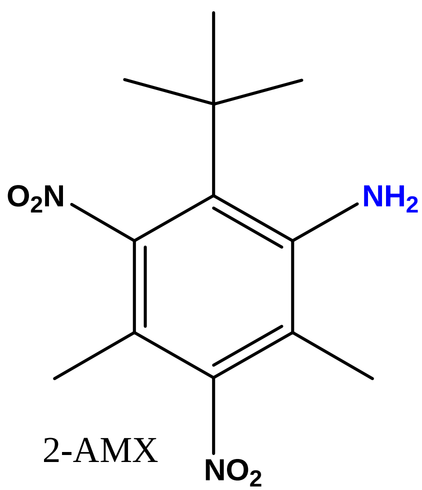
Chemical Structures of Synthetic Nitro Musk Metabolites



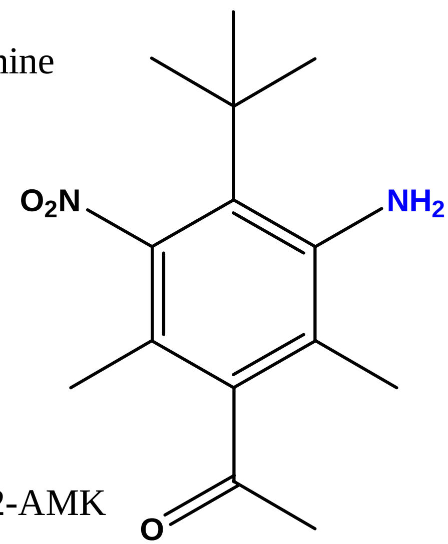
4-AMX

4-*tert*-Butyl-2,6-dimethyl-3,5-dinitro-phenylamine



2-AMX

2-*tert*-Butyl-4,6-dimethyl-3,5-dinitro-phenylamine



2-AMK

1-(3-Amino-4-*tert*-butyl-2,6-dimethyl-5-nitro-phenyl)-ethanone

Physicochemical Properties of Synthetic Musks

Acronym	$LogK_{OW}$	$LogK_{OC}$ (L/kg)	MWT (g/mole)	Empirical Formula	Water Solu. (mg/L)	Henry's Law Constant* (atm-L/mole)	Vapor Pressure (mPa)	BCF_L fish
HHCB	5.9[a]	4.80[a]	258.4	$C_{18}H_{26}O$	1.75[a]	7.56×10^{-4}	72.7[a]	33,200[h]
AHTN	5.7[a]	4.86[a]	258.4	$C_{18}H_{26}O$	1.25[a]	1.09×10^{-2}	68.2[a]	33,700[h]
AHMI	5.9[b]	3.90[d]	244.4	$C_{17}H_{24}O$	--	7.73×10^{-3}	--	33,400[h]
DPMI	5.9[b]	--	206.3	$C_{14}H_{22}O$	--	1.42×10^{-1}	--	1680[h]
ADBI	5.4[b]	4.00[d]	244.4	$C_{17}H_{24}O$	--	7.05×10^{-3}	--	13,300[h]
AETT	5.7[b]	3.72[d]	258.4	$C_{18}H_{26}O$	1.27[b]	9.96×10^{-3}	--	--
ATII	6.3[b]	4.33[d]	258.4	$C_{18}H_{26}O$	--	1.94×10^{-2}	--	--
MX	4.4[c]	4.21[d]	297.3	$C_{12}H_{15}N_3O_6$	0.49[c]	7.73×10^{-6}	--	4100[f]
MK	3.8[c]	3.23[d]	294.3	$C_{14}H_{18}N_2O_5$	1.9[c]	1.90×10^{-6}	--	1100[f]
MM	4.4[c]	--	278.3	$C_{14}H_{18}N_2O_4$	0.046[c]	1.54×10^{-4}	--	1300[g]
MA	4.0[c]	--	268.2	$C_{12}H_{16}N_2O_5$	0.79[c]	7.05×10^{-4}	--	646[g]
4-AMX	4.3[B]	--	267.3	$C_{12}H_{17}N_2O_4$	4.08[B]	3.79×10^{-7}	--	--
2-AMX	4.3[B]	--	267.3	$C_{12}H_{17}N_3O_4$	4.08[B]	3.79×10^{-7}	--	--
AMK	5.1[b]	--	264.3	$C_{14}H_{20}N_2O_3$	--	9.30×10^{-8}	--	--

a: Measured. Balk and Ford 1999
b: Estimated. Osemwengie and Steinberg 2001
B: Estimated. Behechti et al., 1998
c: Measured. Schramm 1996
d: Measured. Winkler et al., 1998
*: Estimated. US. EPA EPI Suite
f: Measured. Yamagishi et al.1983
g: Estimated Schramm 1996
h: Geyer et al., 1997

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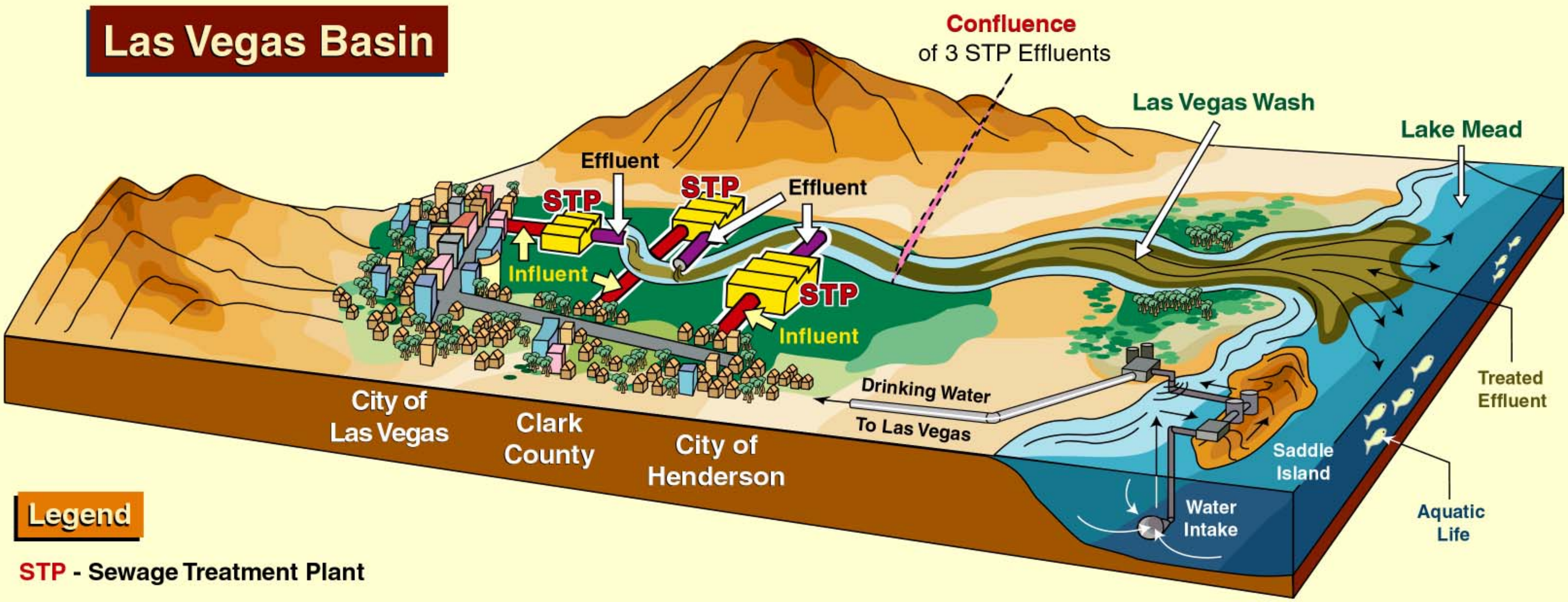
Ubiquitous and Harmful Effects in the Environment?

- Industrial mass production. (Herren and Berset 2000)
- Persistent and bioconcentrate in fish tissues (G.G Rimkus, 1997)
- Musk ambrette is known to cause testicular atrophy in laboratory rats (Davis, 1967)
- Versalide is known to cause the paralysis of the hindlimbs in laboratory rats (Opdyke, 1979; Spencer et al., 1980)
- Discoloration of internal organs in rats. (Opdyke 1979)
- MK negatively affects reproduction in zebrafish (Carlsson et al., 2000)

Origin, Transport & Fate of Synthetic Musk Compounds in the Las Vegas Basin



Legend

STP - Sewage Treatment Plant

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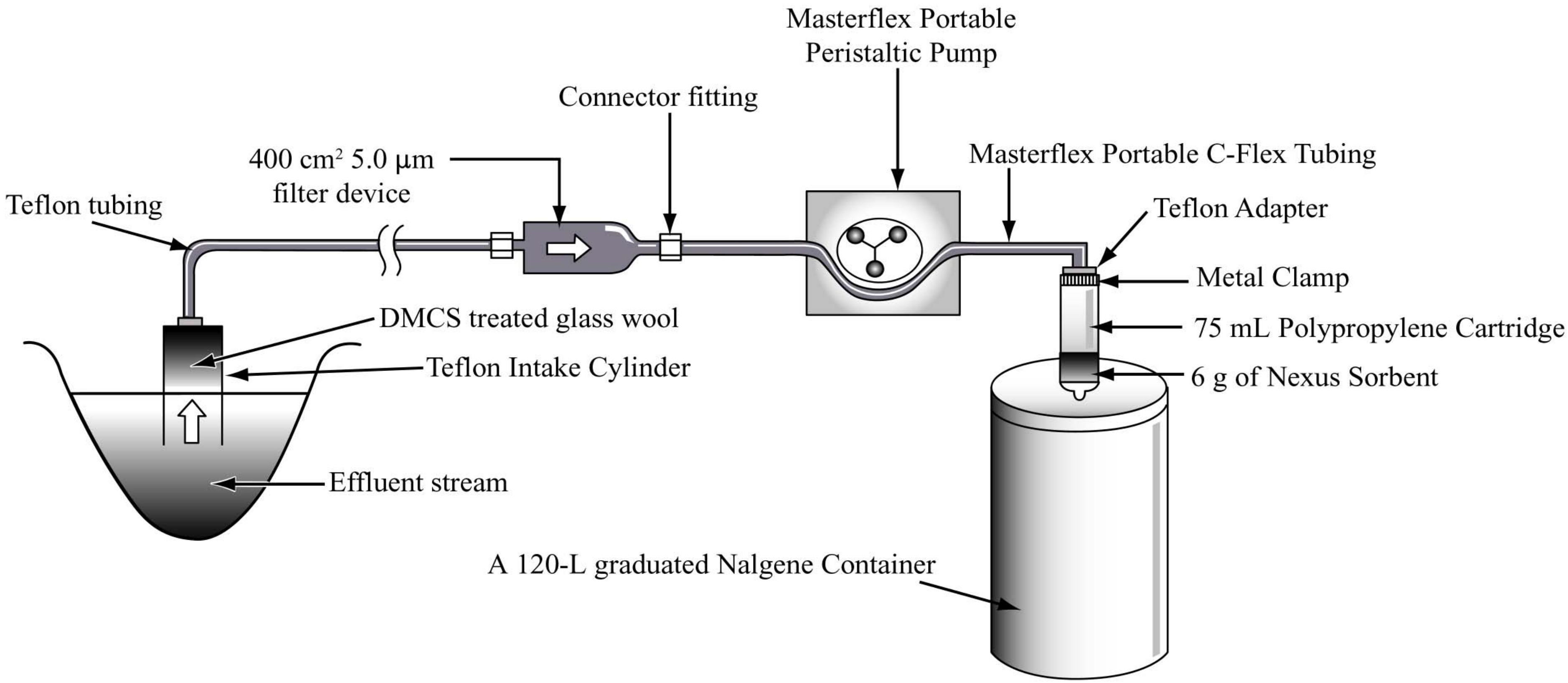
On-site Solid-phase Extraction Assembly



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On-site Solid-phase Extraction of 65 L of STP Effluent

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In-situ Extraction of Synthetic Musk Compounds

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Monthly Collection of Eight Carp

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EPA's QA/QC manager monitored fish sampling

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-80 ºC Storage Facility

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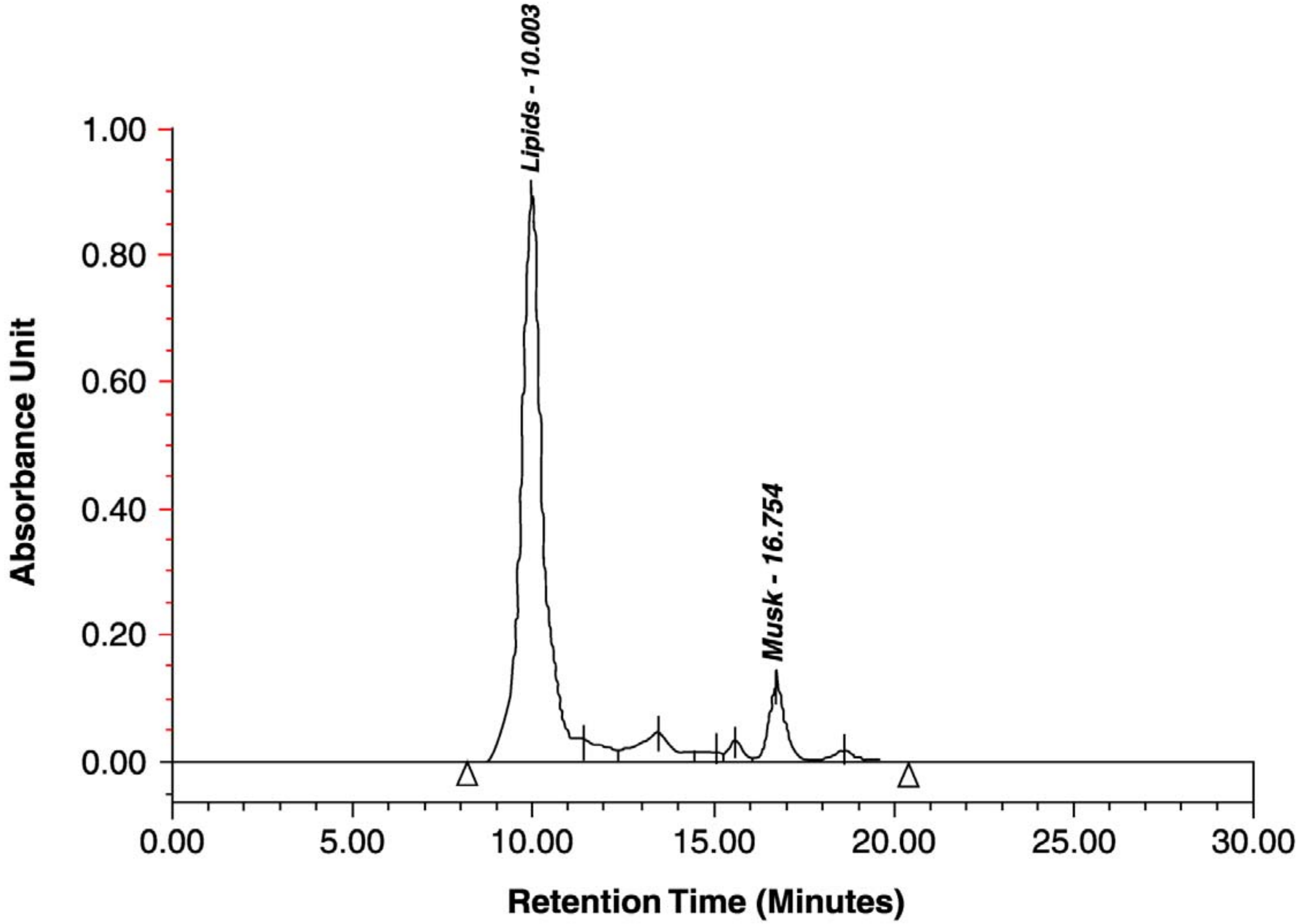
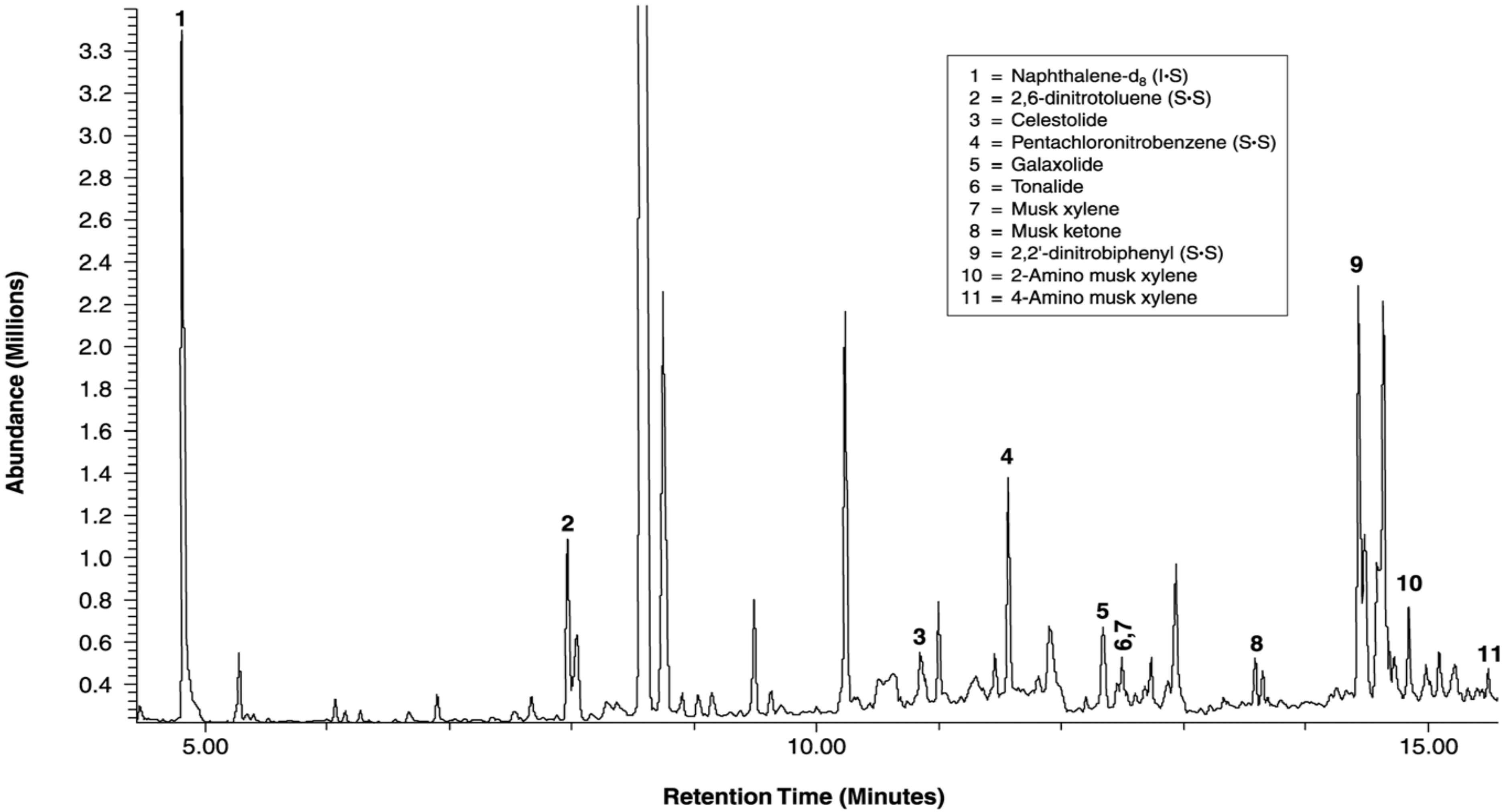
Gel permeation chromatography showing residual lipids after selective PLE system



PLE Extracted Fish Sample



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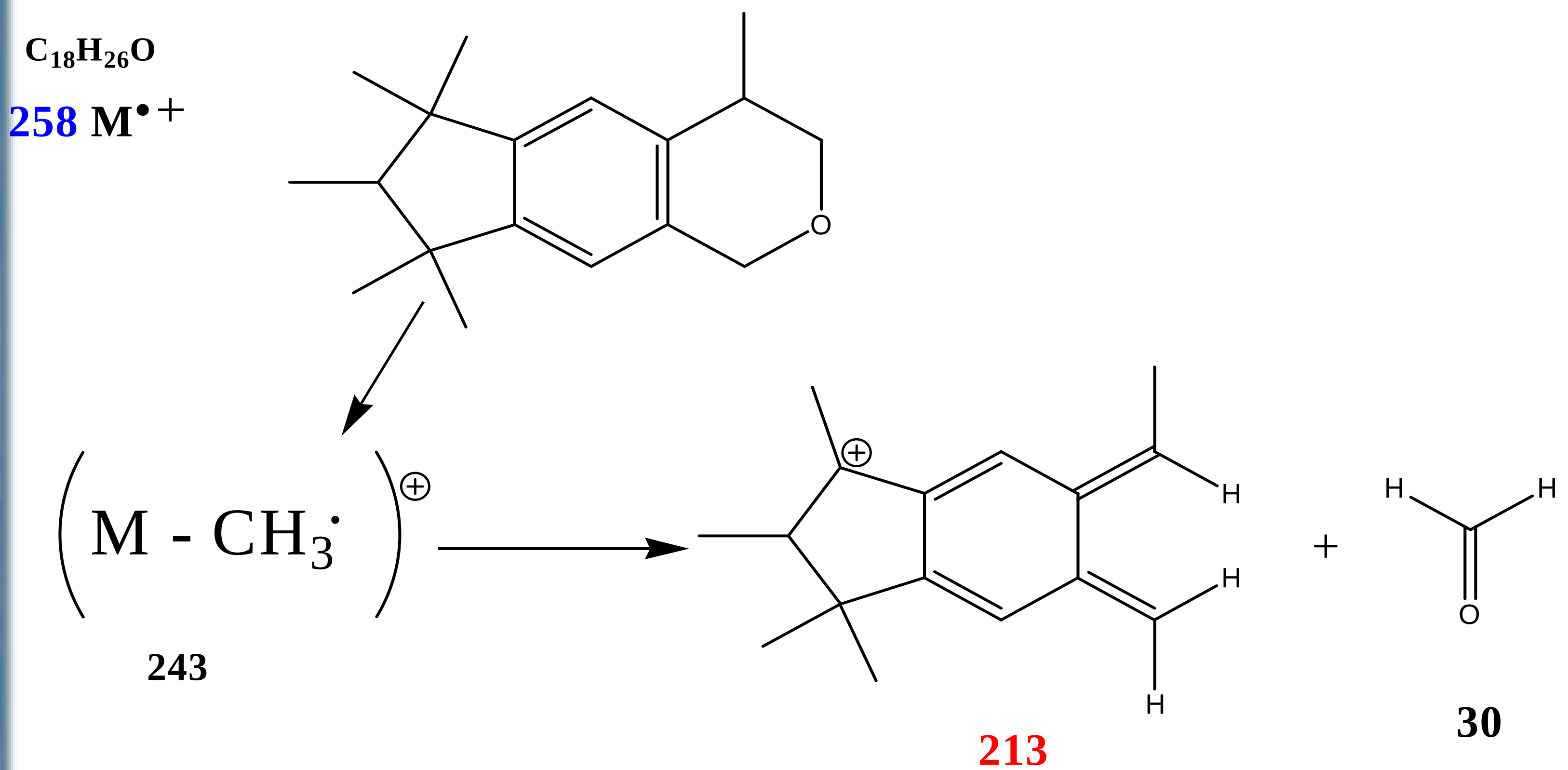
Galaxolide Fragmentation



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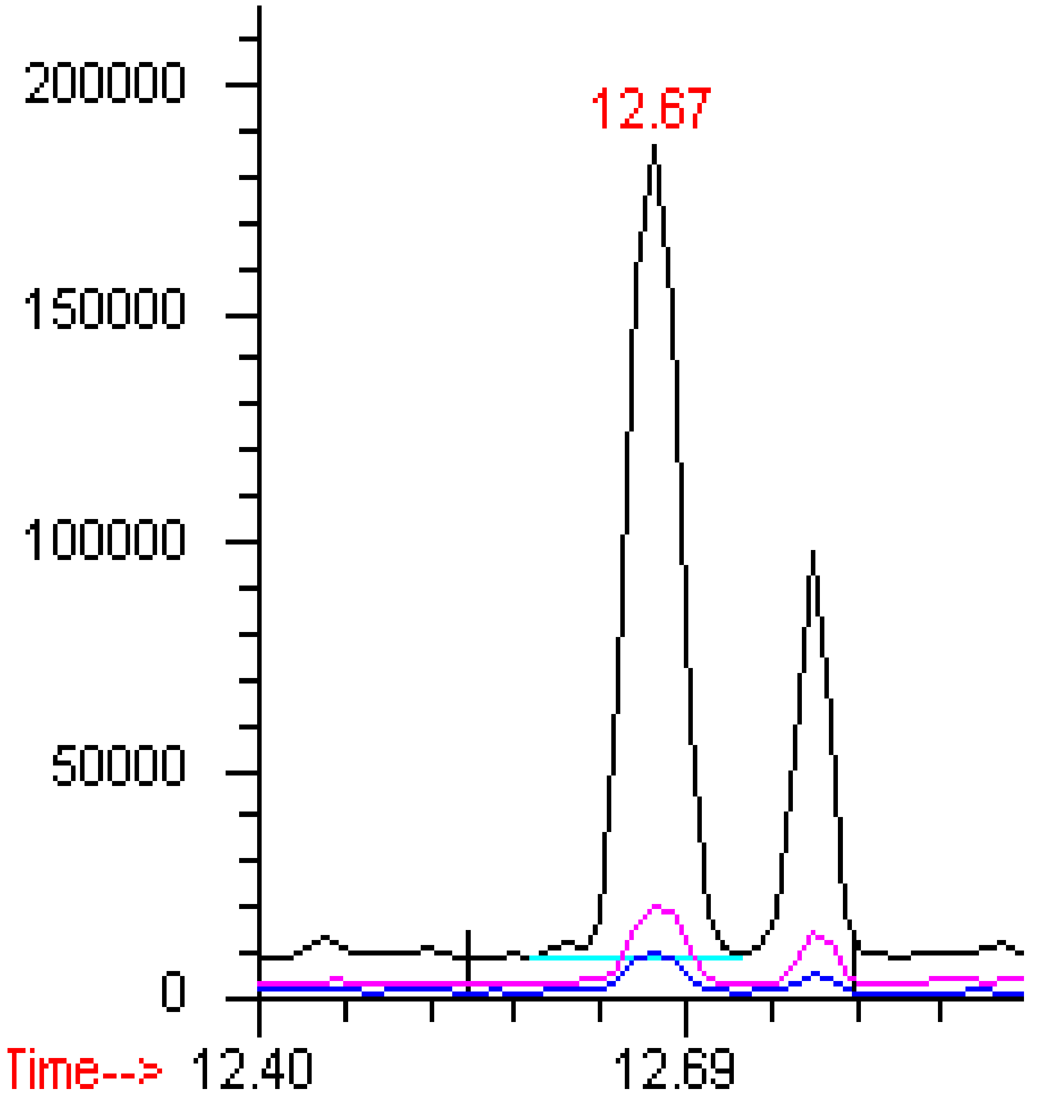
Ion Chromatogram of Galaxolide present in fish tissues



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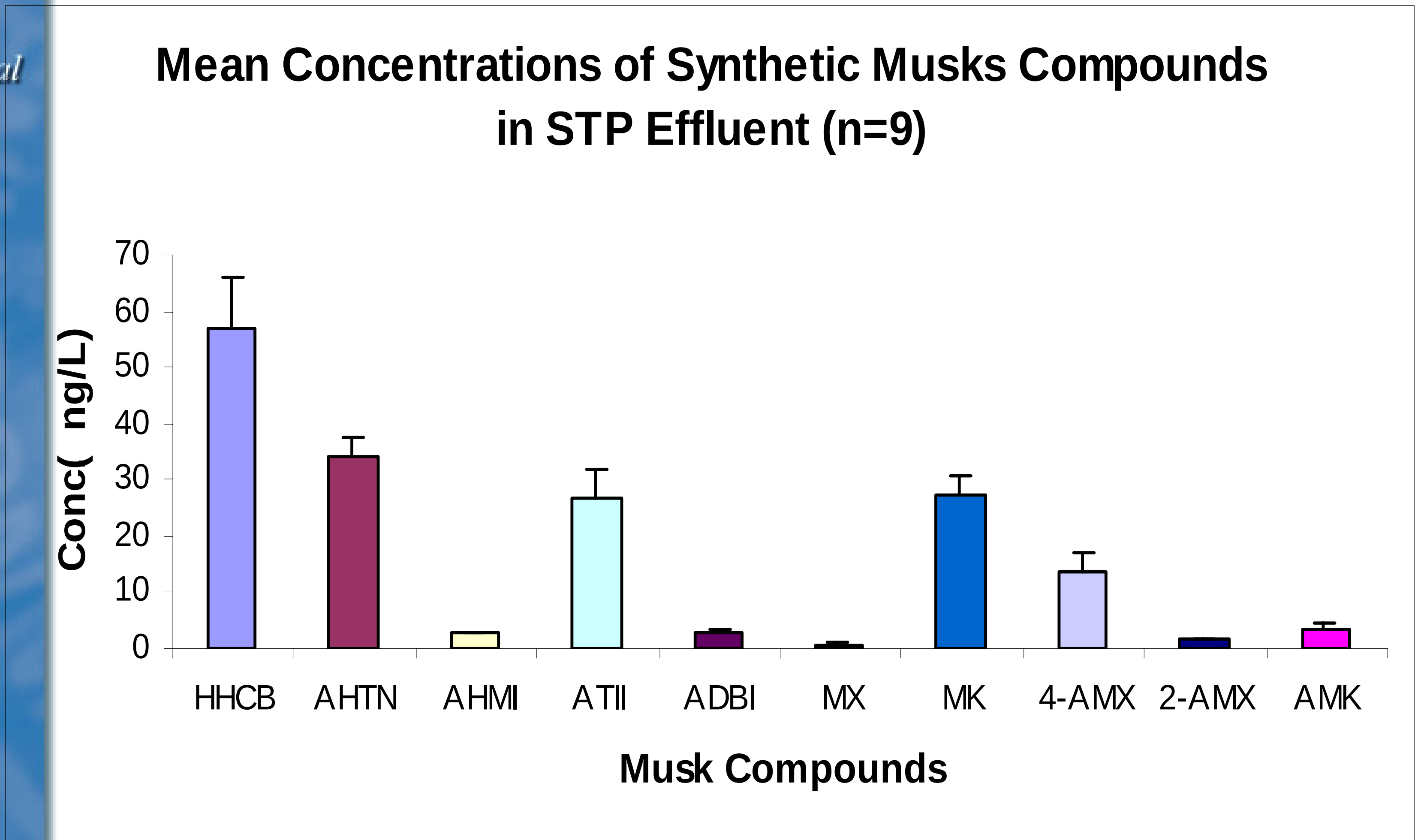

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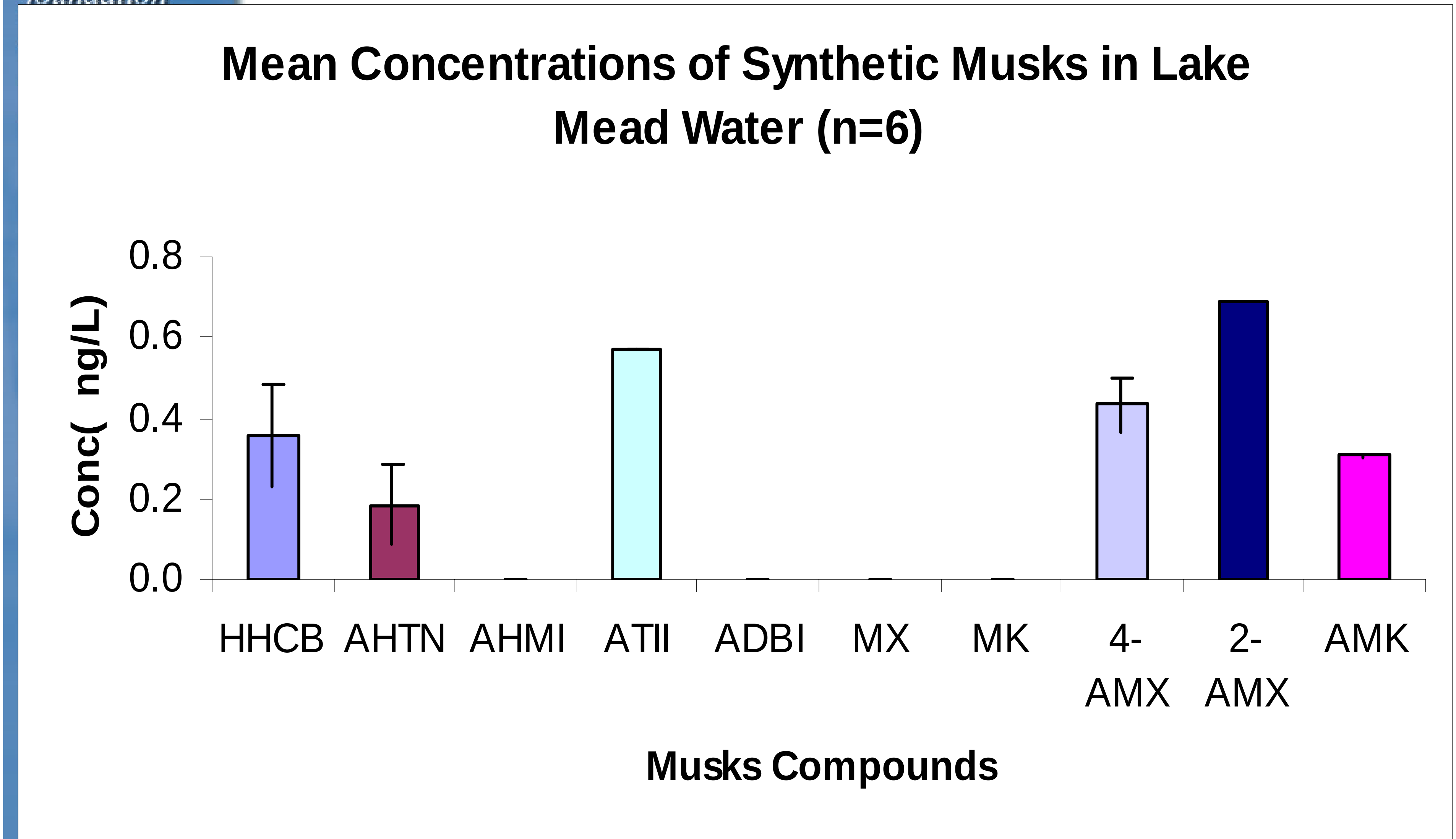

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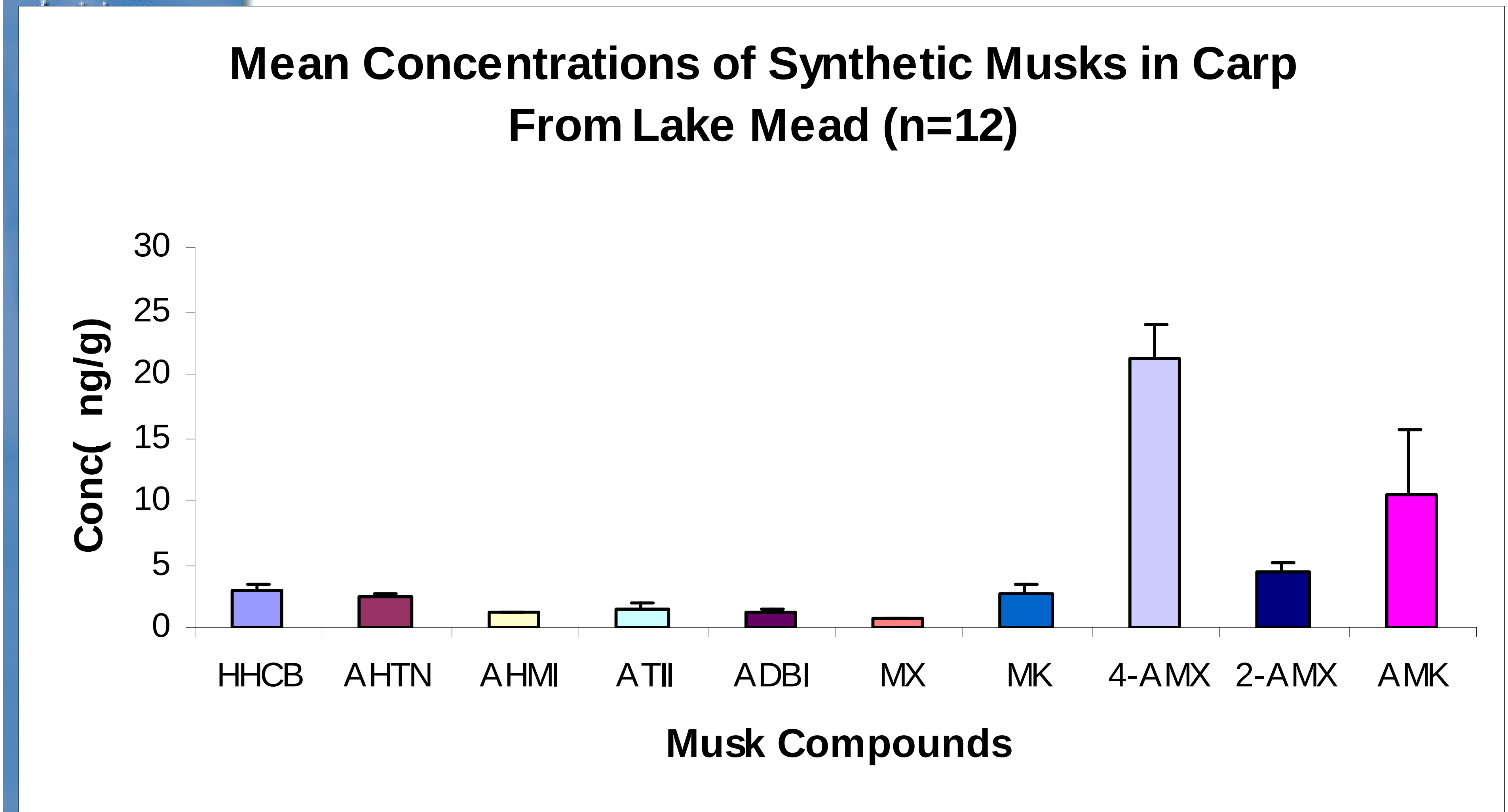

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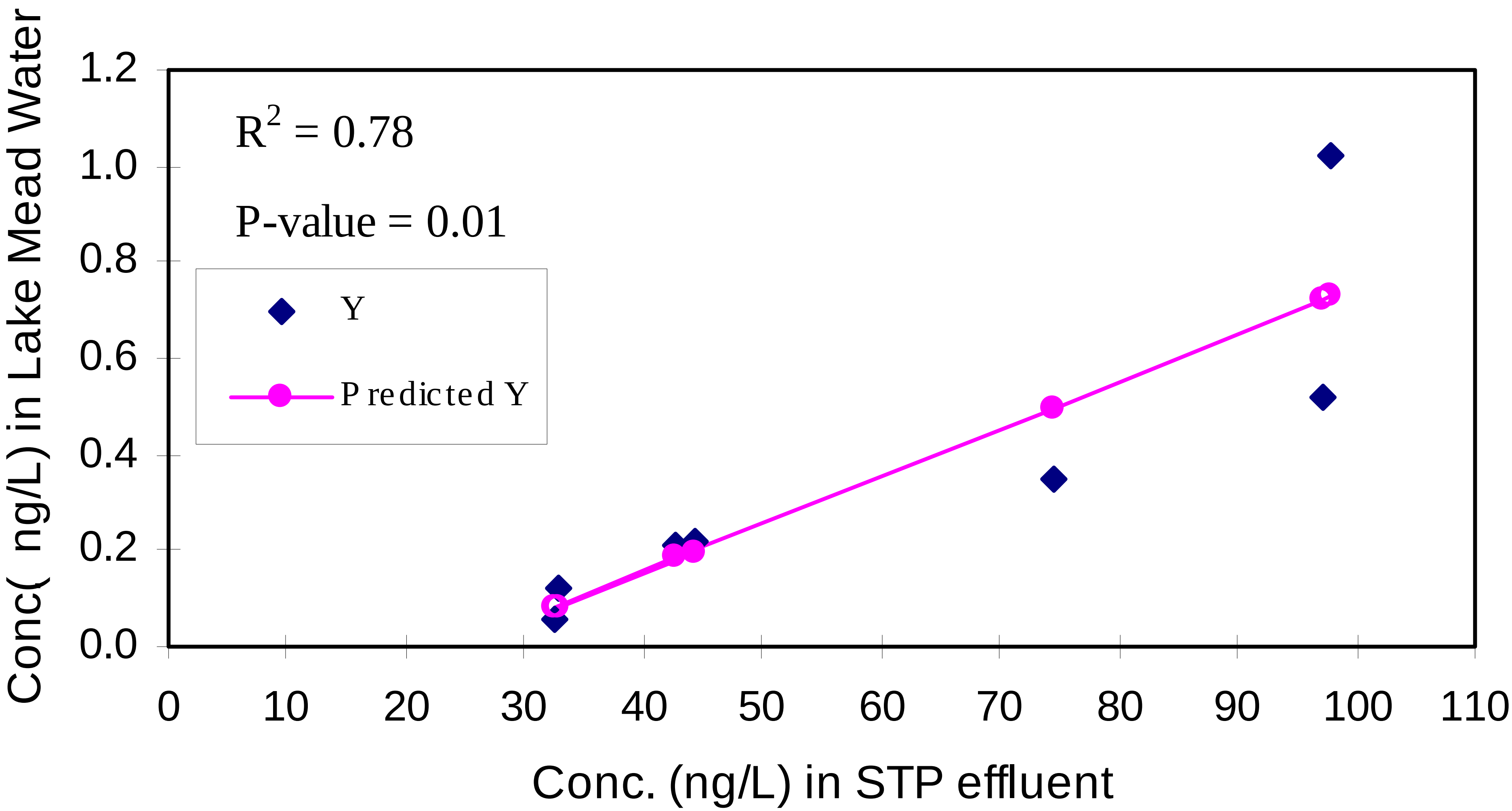
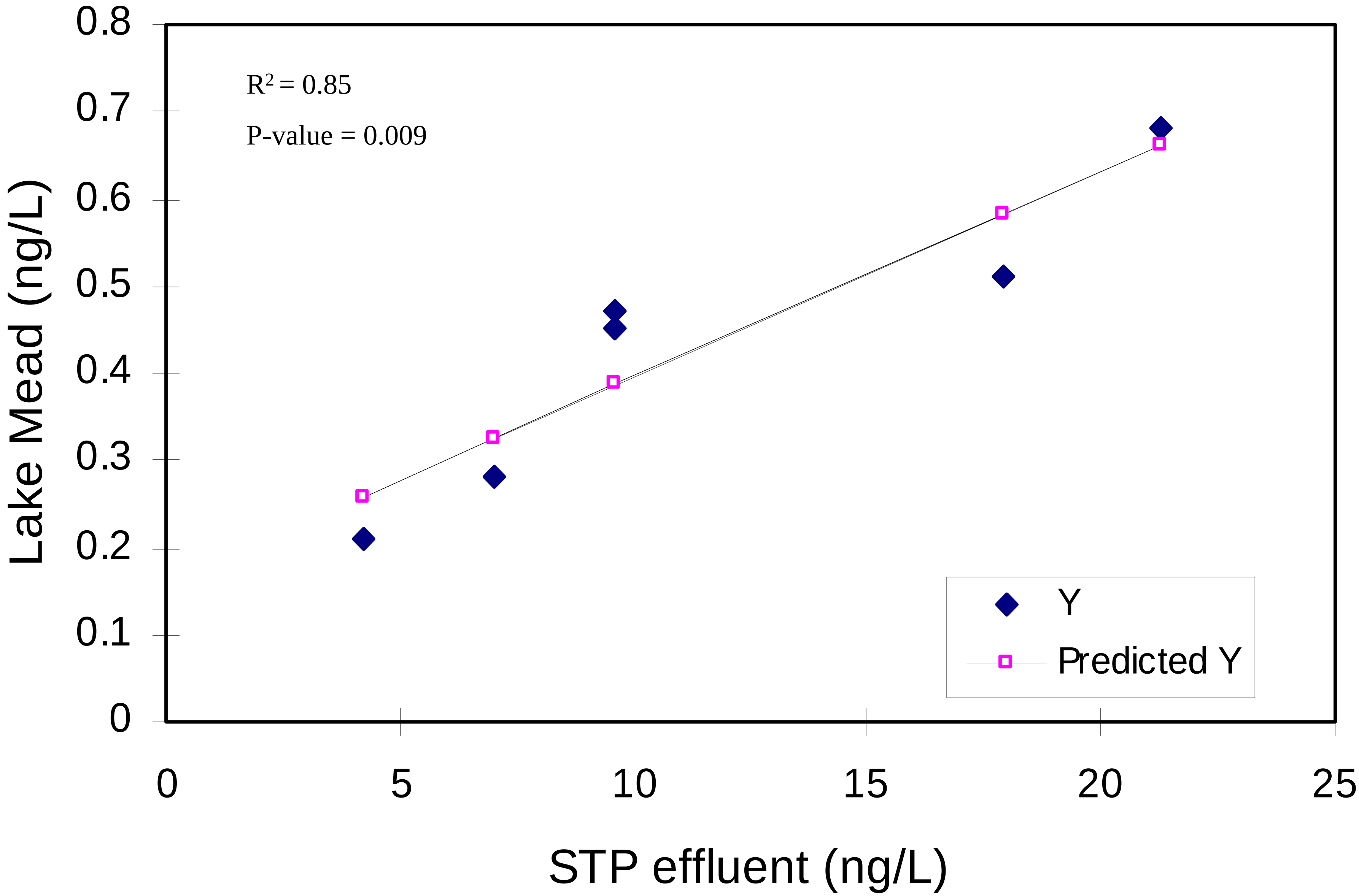
Regression Analysis

- Musks in STP versus Musks in fish
- Using Statistical analysis system (SAS) best fit regression lines were obtained from the 12 months raw data for musk conc. in STP effluent v. in Lake Mead water.
- Slopes and Y-intercepts for the regression lines were obtained for all musk compounds.

Concentration of Galaxolide (HHCB)
in Lake Mead Water v. STP Effluent



Concentration of 4-Amino Musk Xylene in Lake Mead Water v. STP Effluent



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Cross-correlation of Synthetic Musks in Fish Tissue (r-values)

	MX	MK	HHCB	AHMI	ADBI	ATII	AHTN	4-AMX	2-AMX
MX	-----	-----	-----	-----	-----	-----	-----	-----	-----
MK	0.81**	-----	-----	-----	-----	-----	-----	-----	-----
HHCB	0.46	0.75*	-----	-----	-----	-----	-----	-----	-----
AHMI	0.51	0.96***	0.67	-----	-----	-----	-----	-----	-----
ADBI	0.57	0.61	0.41	0.60	-----	-----	-----	-----	-----
ATII	-0.10	-0.29	-0.06	0.77*	0.43	-----	-----	-----	-----
AHTN	0.35	0.78**	0.96***	0.67*	0.37	-0.14	-----	-----	-----
4-AMX	0.68*	0.64	0.53	0.38	0.75	0.49	0.49	-----	-----
2-AMX	0.44	0.43	0.48	0.67*	0.90**	0.50	0.39	0.83**	-----
AMK	0.89*	0.91	0.48	0.69	0.66	0.08	0.32	0.47	0.18

* $p < 0.05$

** $p < 0.01$

*** $p < 0.001$

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Summary

- By understanding the chemistry of synthetic musk compounds, we were able to determine their presence in environmental samples.
- Enrichment factor approaches $10^6 : 1$, we were able to detect low concentrations of synthetic musk compounds in Lake Mead.
- Performed statistical evaluation of raw data.
- Result suggests bioconcentration in carp.
- Unable to provide definitive equation for concentrations in STP v. fish.

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Conclusion

- Developed extraction, clean-up, analysis, and detection method for monitoring synthetic musk compounds in aquatic environment.
- HHCB – can be predicted in the receiving waters, using concentrations from the source.
- Variation in the concentrations of HHCB (polycyclic musk) and MX (nitro musk) in Lake Mead is a function of their levels in the STP effluent.

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Acknowledgement

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