

Recent Analyses of Nitromusks in Sewage and River water in the UK

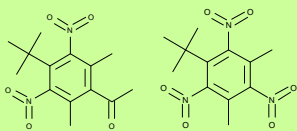
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ABSTRACT

The concentrations of Musk Ketone (MK) and Musk Xylene (MX) were determined in influents and effluents from trickling filter (TF) and activated sludge (AS) wastewater treatment plants (WWTPs) in the Aire Basin (Yorkshire, UK) in September 2000. Concentrations were also determined in the river receiving the effluent from the TF plant. MK influent concentrations were 0.37 µg/l for the TF plant and 0.75 µg/l for the AS plant. MX influent concentrations were 0.34 µg/l for the TF plant and 0.22 µg/l for the AS plant. After passage through the WWTPs, effluent concentrations were 0.04 - 0.06 µg/l for MK and 0.01 - 0.02 µg/l for MX. Removal rates for MK & MX respectively were 90% and 95% in the TF plant and 92% and 98% in the AS plant. River concentrations ranged from 0.002 µg/l for both MK and MX upstream of the effluent discharge to 0.024 µg/l MK and 0.007 µg/l MX immediately downstream of the discharge (dilution factor 2). Concentrations declined to 0.017 µg/l MK and 0.003 µg/l MX at 3.5 km downstream. A preliminary estimation of in-stream removal rate (via biotransformation, sorption and/or volatilization) in this river was 0.071 h⁻¹ for MK and 0.193 h⁻¹ for MX. The concentrations reported here are low relative to historical levels. This reflects changing usage patterns of nitromusks in detergents within the EU. As the study was conducted in the area covered by GREAT-ER (Geography-referenced regional exposure assessment tool for European rivers), the measured concentrations and WWTP and in-stream removal rates were used in the model to predict site-specific distribution of nitromusk concentrations in the Aire Basin.

INTRODUCTION

Musk Xylene (CAS 81-14-2) and Musk Ketone (CAS 81-14-1) are perfume compounds employed in fragranced products such as cosmetics and household products (e.g. detergents). Both materials are currently subject to risk assessment under the EU 3rd priority list. Use of these materials has declined in recent years as a result of voluntary industry initiatives. Use in Europe (1998) is reported at 88 & 40 tonnes/annum for Musk Xylene and Musk Ketone respectively. One of the main routes these chemicals enter the environment is via down-the-drain disposal of consumer products. The concentration and distribution of nitromusks in the aquatic environment are governed by removal rates during wastewater treatment and subsequent partitioning, chemical and biological degradation in surface waters.



Musk Ketone

Musk Xylene

STUDY OBJECTIVES

The current study was undertaken in order to better understand the fate of nitromusks in the aquatic environment, including their removal during wastewater treatment and in-stream dissipation rate. The data from the study were used to model the concentration distribution of nitromusks in a real river basin using GREAT-ER, a GIS-based exposure assessment model.

RIVER AIRE BASIN

The Rivers Aire and Calder Basin is situated in Yorkshire, north of England. The River Aire drains the central Pennines and flows south-eastward through West Yorkshire metropolitan area and the Yorkshire coalfield, where it is joined by Calder, its major tributary. These areas are characterized by a high density of population, large number of small tributaries and medium to small size wastewater treatment plants with dilutions factors as low as 2.

GREAT-ER

River Aire and three related river basins (Calder, Went and Rother) are modelled in GREAT-ER, the Geography-Referenced Regional Exposure Assessment Tool for European Rivers. GREAT-ER is an environmental model developed by ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals) and others on behalf of ERASM. GREAT-ER combines environmental models and GIS techniques to predict and visualize the concentration of down-the-drain chemicals in European river basins (Schwanek *et al.*, 2001).

STUDY SITES

Two wastewater treatment plants (WWTPs) were selected for the study. Crofton activated sludge (AS) plant southeast of Wakefield serves the population of about 9,000 people with the wastewater flow of approx. 1,400 m³/day, and Meltham trickling filter (TF) plant south of Huddersfield serves the population of 8,000 people with the wastewater flow of approx. 4,100 m³/day. The latter plant operates two consecutive series of trickling filters, i.e. the level of water treatment is equivalent to tertiary treatment. Both plants receive municipal wastewater only. The Meltham plant discharges into Mag Brook, the 3.5-km section of which below the discharge point was used for river water die-away study.

SAMPLING

One-day (24 h) hourly composite samples of influent, primary effluent and final effluent were collected at each wastewater treatment plant. The river water die-away study was carried out by following a water plug using the Rhodamine WT dye with fluorescent detection. Triplicate grab river water samples were taken at distances 20 m, 0.5 km, 1.5 km and 3.5 km downstream from the effluent discharge point at the time of the peak fluorescent dye concentration. Another set of water samples was taken about 50 m upstream from the wastewater plant discharge point.

SAMPLE PROCESSING AND ANALYTICAL

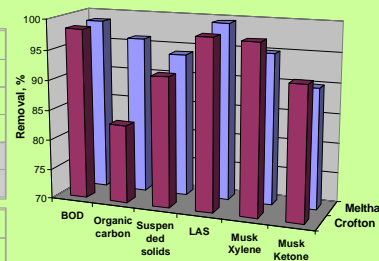
Wastewater and river water samples were preserved with 3% (v/v) formalin, extracted and analysed with GC/MS as described in Simonich *et al.* (2001). Limits of quantification were 2 ng/l for MX and 1 ng/l for MK in influent and 1 ng/l and 0.7 ng/l respectively in effluent.

RESULTS

Wastewater treatment removal

Meltham TF	BOD (mg/l)	Organic carbon (mg/l)	Suspended solids (mg/l)	LAS (mg/l)	NM (mg/l)
Influent	204	151	228	3.18	MX 0.34 MK 0.37
Primary effluent	55.3	33.2	56	2.88	MX 0.18 MK 0.26
Final effluent	2.7	5.88	14	0.016	MX 0.02 MK 0.04
Primary removal (%)	72.9	78	75.4	9.4	MX 47 MK 30
Total removal (%)	98.7	96.1	93.9	99.5	MX 95 MK 90

Crofton AS	BOD (mg/l)	Organic carbon (mg/l)	Suspended solids (mg/l)	LAS (mg/l)	NM (mg/l)
Influent	262	126	166	1.71	MX 0.22 MK 0.25
Primary effluent	230	142	120	2.4	MX 0.09 MK 0.42
Final effluent	4.1	21.4	14	0.029	MX 0.01 MK 0.06
Primary removal (%)	12.2	0	27.7	0	MX 59 MK 44
Total removal (%)	98.4	83	91.6	98.3	MX 98 MK 92

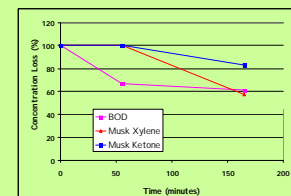


Graphic representation of BOD, organic carbon, suspended solids, LAS, Musk Xylene and Musk Ketone removal rates.

In-stream removal

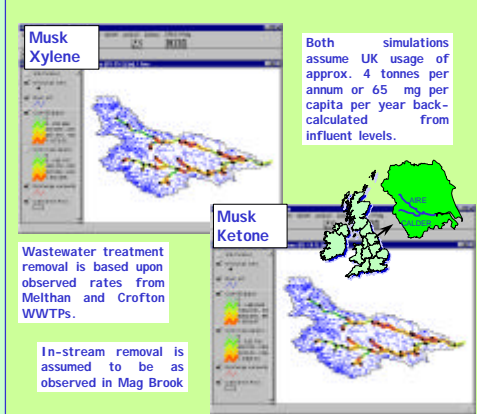
	Conductivity		Suspended solids (mg/l)	BOD (mg/l)	Organic carbon (mg/l)	NM	
	µS/cm	Dilution				MX (ng/l)	MK (ng/l)
Site A (50 m)	175	-	10	3.9	6.36	2	2
Site B (20 m)	352	Start ¹	9	3.6	9.28	7	24
Site C (0.75 km)	282	1.25	7	2.4	7.53	7	24
Site D (1.5 km)	293	1	6	2.2	7.07	4	20
Site E (3.5 km) ²	316	1	51	3.1	5.95	3	17
Die away rate B-D (h ⁻¹)	N/A		0.14	0.16	0.09	0.193	0.071

Note: ¹Conductivity-based dilution factor of Meltham WWTP effluent was 2.94.
²Site E was excluded from the die-away rate calculations due to the high suspended solids content indicating that river sediment was potentially disturbed at time of sampling at this site.

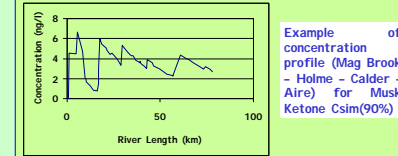


Loss of Musk Ketone, Musk Xylene and BOD from site B to D.

GREAT-ER Simulations: Aire and Calder Basin



GREAT-ER Simulations: concentration profile



Calculated concentrations for the Basin

	Concentration (ng/l)	
	C _{sim} (mean) ± SD	C _{sim} (90%) ± SD
Weighted by volume (loaded stretches only)	MX 0.53 ± 0.41 MK 2.86 ± 2.22	MX 0.76 ± 0.60 MK 4.41 ± 3.44
Weighted by length (loaded stretches only)	MX 1.01 ± 0.10 MK 4.23 ± 0.46	MX 1.50 ± 0.16 MK 6.82 ± 0.73
Weighted by flow increment (all stretches)	MX 0.47 MK 2.62	MX 0.67 MK 4.06
Initial	MX 3.71 MK 9.82	

DISCUSSION

The results demonstrate that both Musk Xylene and Musk Ketone are extensively removed during wastewater treatment with further rapid loss from the water column in surface waters. The WWTP removal rates (>90%) are in line with the results from earlier P & G studies (Simonich *et al.* 2000) where the measured removal of Musk Xylene in Activated Sludge averaged 98.7% and in Tricking Filter averaged 90.9%. Musk Ketone averaged 82.6% and 80.3% respectively. The relative lower removal of Musk Ketone is repeated here.

Measured influent and effluent concentrations are lower than historical European levels (e.g. Eschke *et al.* 1994). This undoubtedly reflects the known decrease in use of these materials (especially in detergents) during the 1990s.

The Musk Xylene in-stream removal rate (0.193 h⁻¹) was comparable to or even higher than the rate of BOD decay (0.16 h⁻¹). The in-stream removal rate for Musk Ketone was lower (0.071 h⁻¹). These rates reflect all potential loss mechanisms (biotransformation, sorption or volatilization). The lower die-away rate for Musk Ketone together with the lower wastewater treatment removal rate accounts for the higher measured and predicted concentrations of this material in surface waters relative to Musk Xylene.

In Mag Brook, the measured concentrations of nitromusks were several-fold higher than those predicted by the GREAT-ER model. This may partially be explained by a low river-flow rate at the time of the study (early September 2000) compared to the year-round distribution of flow rates used in the Monte Carlo simulations of the GREAT-ER.

The GREAT-ER calculated average concentration of Musk Xylene and Musk Ketone in the Aire Basin were in the range of 0.5 - 1 ng/l and 1 - 4 ng/l depending upon the catchment weighing method. For perspective, the PNEC for Musk Xylene is 1.1 µg/l (AF 50 2 chronic NOECs) and 6.3 µg/l for Musk Ketone (AF 10 3 chronic NOECs).

CONCLUSIONS

- Observed nitromusk removal during wastewater treatment corresponds to previously reported rates.
- Influent and effluent concentrations are lower than historical observations in Europe. This reflects known decreases in the use of these materials in cosmetics and especially detergents.
- Instream removal rates are 0.193 h⁻¹ and 0.071 h⁻¹ for Musk Xylene and Musk Ketone respectively.

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