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Environmental Sources, Occurrence, and Effects of Synthetic Musk Fragrances

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Aquatic Processes and Systems in Perspective

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Introduction

The following *Perspective on Aquatic Processes* provides an excellent review of the latest information on musk fragrances in the environment. The importance of the presence of these common yet little studied compounds in the environment cannot be underestimated. Concentrations of these compounds, currently increasing over time and showing evidence of persistence, are in the range of 1–50 ng g^{-1} ww in aquatic organisms and wildlife, and are comparable to other POPs of concern. The authors highlight the need to continue to understand the processes and impacts of these emerging contaminants.

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Environmental sources, occurrence, and effects of synthetic musk fragrances†

Synthetic musk fragrance usage and trends

Synthetic musk fragrances are a class of semivolatile, organic compounds used to give soaps, detergents, and other household and personal care products pleasing scents. Use of musk xylene, musk ketone, and other nitro musks began around the turn of the century. These compounds were used as inexpensive, synthetic alternatives to the natural product, a macrocyclic compound, obtained from the musk deer. Musk xylene and musk ketone were first detected in the environment in fish collected from Japanese coastal waters in 1980.[1] These compounds were measured in waste and surface water from this same area at concentrations ranging from 1.7 ng L^{-1} to 410 ng L^{-1} in 1981.[2] Today, another group of compounds, the polycyclic musks, dominate the global musk fragrance market (Table 1). From 1987 to 2000 the global use of the polycyclic musks has more than doubled, from 4300 metric tons[3] to 10 000 metric tons.[4] The global use of nitro musks in 2000 (800 metric tons[4]) was less than one-third of their use in 1987 (2450 metric tons[5]). The occurrence and increasing concentrations reported in a variety of environmental compartments over the past decade reveal this shift in use and have accelerated concern about the potential environmental impacts of these contaminants.[6–9] Overall, production data suggest that fragrance use is rapidly increasing (see Fig. 1).

Table 1 Annual global use of nitro and polycyclic musk fragrances (metric tons)

Year	Nitro musk fragrances	Polycyclic musk fragrances
1987	2450[5]	4300[3]
1996	2000[5]	5600[4]
2000	800[4]	10 000[4]

Previous papers have reviewed the environmental occurrence, effects, and risk assessment based primarily on work through 2000.[3,5,10–14] This review focuses on work on the sources, occurrence, and effects of synthetic musk fragrances, particularly the polycyclic musks and their metabolites, from 1999 through 2005. Metabolites of HHCB (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyran) and the nitro musks have also been reported in the literature. Undoubtedly, there are many other fragrances produced and released to the environment; however, it is difficult to create a complete list of current-use fragrances and the analytical method development has so far been limited to the compounds mentioned.

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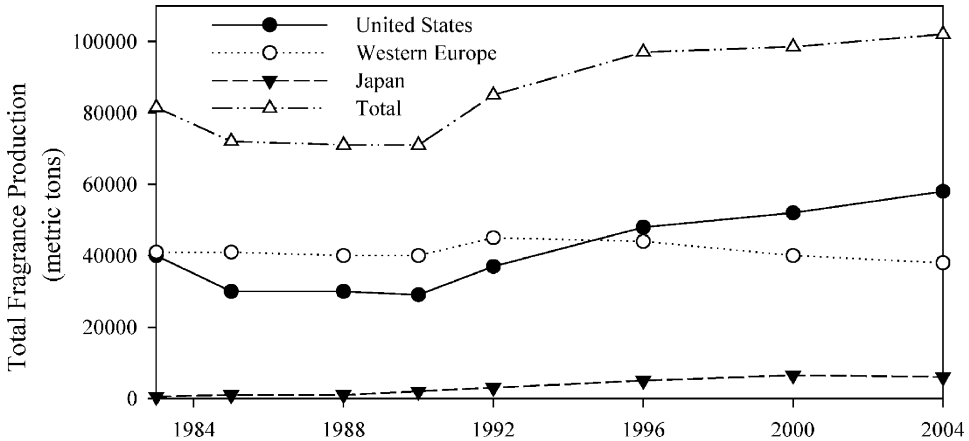

Fig. 1 Total fragrance production in the United States, Western Europe, and Japan from 1983 to 2004. This includes synthetic musk fragrances and other types of fragrance materials. Production data from Somogyi and Kishi.[4]

Major environmental source: wastewater treatment plant effluent and digested sludge

Wastewater treatment plant (WWTP) effluent is a major source of synthetic musk fragrances to the environment.[15] There have been several reports of synthetic musk fragrances in WWTP effluent worldwide.[16–28] HHCB and AHTN are normally found in the highest concentrations (typically on the order of 1000 ng L^{-1} to 5000 ng L^{-1}), with the concentrations of the other polycyclic musks one to two orders of magnitude lower and the nitro musks and their amino metabolites two to three orders of magnitude lower. This is not to suggest that wastewater treatment is not effective. Typically, the synthetic musk fragrance concentrations in effluent leaving a WWTP are less than 30% of the concentration in the influent, regardless of the treatment plant design.[19–21,28,29] For example, Kupper *et al.*[29] reported that concentrations of polycyclic musks were not affected by the type of treatment utilized at wastewater treatment plants in Switzerland. In all wastewater treatment plants, the removal of HHCB and AHTN from wastewater is primarily to sludge.[30] There is little evidence that synthetic musk fragrances are actually degraded, either by chemical or biological processes during wastewater treatment. The fragrances simply move from water to solids. This is caused by the relatively high affinity of the fragrances for solids. This affinity is quantified by large solid concentration to water concentration ratios, called partition coefficients. Ternes *et al.*[31] reported sorption coefficients (K_d) for HHCB and AHTN to primary sludge from an activated sludge wastewater treatment of 4920 L kg^{-1} and 5300 L kg^{-1}, respectively. The K_d values for HHCB and AHTN in secondary sludge from this plant were somewhat lower (1810 L kg^{-1} and 2400 L kg^{-1}, respectively). Because of this partitioning, digested sludge applied as fertilizer to soils may be an important source of these compounds to terrestrial ecosystems. Synthetic musk fragrances have been measured in primary,[31–34] secondary,[31,34] and digested sludge.[21,23,24,29,35–37]

Concentrations of HHCB and AHTN (7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene) are similar to that of other fragrance materials in digested sludge from the United States.[38] The fragrances OTNE (7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene), diphenyl ether, and acetyl cedrene were measured at concentrations of 7.3 ng g^{-1}, 99.6 ng g^{-1}, and 9.0 ng g^{-1}, respectively in sludge from Wilmington, DE. HHCB and AHTN were 21.8 ng g^{-1} and 8.1 ng g^{-1}, respectively in that sludge. OTNE and acetyl cedrene were measured at concentrations of 31.3 ng g^{-1} and 30.7 ng g^{-1}, respectively in sludge from Georgetown, DE. HHCB and AHTN were 37.6 ng g^{-1} and 17.7 ng g^{-1}, respectively in that sludge.

Although fragrances are captured by solids during wastewater treatment, they are not strongly bound. Under the right conditions, fragrances desorb or otherwise are removed from the solids. Difrancesco *et al.*[38] found that the concentration of HHCB in sludge-amended soils dropped to below measurable levels in one year. AHTN was lost more slowly in these experiments; the concentrations of AHTN were above detection limits at the end of one year. Less than 1% of the HHCB and AHTN loss from these soils was measured in leachate from these experiments. Their fate was more likely a result of volatilization and, to a lesser extent, transformation. In a related field study, Yang and Metcalfe[23] examined sludge (biosolids) applied to an agricultural field at a rate of 91 m^3 per hectare and ploughed under after 24 h. The HHCB and AHTN concentrations in the soil following application were 2.0 ng g^{-1} and 2.6 ng g^{-1}, respectively. After four weeks both compounds were detected with concentrations below the quantification limit. The fate of the compounds is not clear. They may have volatilized, been degraded by microbial or chemical processes, or leached into water.

Ubiquitous environmental occurrence

Synthetic musk fragrances are everywhere. They have been measured in air, fish, birds, mammals, sediments, rivers, and lakes. A comparison of HHCB and AHTN concentrations from ambient air in North America[15,39] and Norway[40] and indoor air from kindergartens in Berlin[26] are shown in Fig. 2. Typical urban air concentrations of HHCB and AHTN are

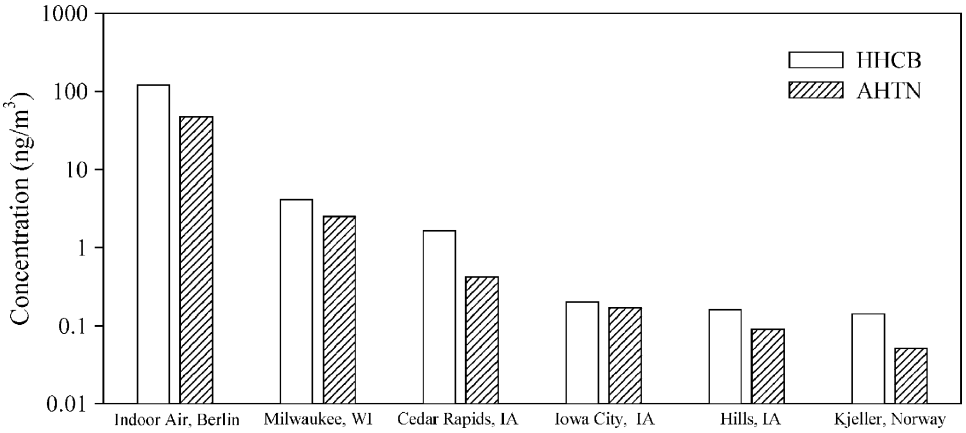

Fig. 2 HHCB and AHTN air concentrations in urban, suburban and rural locations. The sample from Berlin was collected from 74 kindergartens.[26] The other locations are arranged left to right from urban to rural (urban: Milwaukee[15] and Cedar Rapids;[39] suburban: Iowa City;[39] rural: Hills[39] and Kjeller[40]).

on the order of 1 ng m^{-3} to 5 ng m^{-3} with indoor air about one to two orders of magnitude higher and background terrestrial concentrations about an order of magnitude lower.

In recent years several synthetic musk fragrances have been measured in a variety of fish, birds, and mammals. HHCB and AHTN concentrations from several studies are summarized in Table 2. Kannan *et al.*[41] reported HHCB concentrations in marine mammals from the California and Florida coasts up to 25 ng g^{-1} wet mass. HHCB concentrations were similar in fish (1.9 ng g^{-1} wet mass to 4.2 ng g^{-1} wet mass) and birds (<1 ng g^{-1} wet mass to 5.4 ng g^{-1} wet mass) collected in New York. The AHTN concentrations were typically half that of HHCB in these animals. Nakata[42] reported HHCB concentrations in finless

Table 2 Recent HHCB and AHTN concentrations in wildlife (ng g^{-1} wet mass)

Species	Tissue	Location	Year	*N*	HHCB	AHTN	Ref.
Fish							
Atlantic salmon	Skin-on filet	New York	2003	6	<1–3.2	<1–1.6	Kannan *et al.*[41]
Smallmouth bass	Liver	New York	2003	3	4.3–5.4	1.6–1.9	Kannan *et al.*[41]
Hammerhead shark	Blubber	Japan	2004	5	16–48	<9.1	Nakata[42]
Eel	Filet	Germany	1996–1997	165	<30–4800	<20–2300	Fromme *et al.*[59]
Carp	Whole	Nevada	2000–2001	12[a]	1.4–4.5	1.4–3.6	Osemwengie and Gerstenberger[43]
Thornback ray	Filet	Norway	1999	1	8.3	0.77	Kallenborn *et al.*[45]
Thornback ray	Liver	Norway	1999	1	0.63	1.2	Kallenborn *et al.*[45]
Haddock	Filet	Norway	1999	2	1.5–1.7	1.1–1.8	Kallenborn *et al.*[45]
Haddock	Liver	Norway	1999	3	47–250	10–23	Kallenborn *et al.*[45]
Atlantic cod	Filet	Norway	1999	3	0.14–0.51	0.073–0.24	Kallenborn *et al.*[45]
Atlantic cod	Liver	Norway	1997–1999	13	2.4–530	0.92–760	Kallenborn *et al.*[45]
Saithe	Filet	Norway	1999	1[b]	5.2	2.1	Kallenborn *et al.*[45]
Saithe	Liver	Norway	1999	1	2.6	0.37	Kallenborn *et al.*[45]
Farmed trout	Filet	Denmark	1999	50	<0.52–53	0.44–16	Duedahl-Olesen *et al.*[71]
Farmed trout	Filet	Denmark	2003–2004	87	<0.52–28	<0.61–7.5	Duedahl-Olesen *et al.*[71]
Birds							
Common merganser	Liver	New York	1999	2	3.7–4.2	1.6–1.7	Kannan *et al.*[41]
Greater and lesser scaup	Liver	New York	1995–1999	2	1.9–2.7	1.0–1.1	Kannan *et al.*[41]
Mallard	Liver	New York	1995	1	2.7	1.1	Kannan *et al.*[41]
Mammals							
Finless porpoise	Blubber	Japan	1999–2002	9	13–150	<9.1–9.6	Nakata[42]
Polar bear	Liver	Alaska	1997–2000	5	<1	<1	Kannan *et al.*[41]
Sea otter	Liver	California	1993–1999	8	<1–3.2	<1	Kannan *et al.*[41]
Harbor seal	Liver	California	1996–1997	3	4.4–5.5	<1–2.3	Kannan *et al.*[41]
California sea lion	Liver	California	1993–1996	3	1.5–4.4	<1–2	Kannan *et al.*[41]
River otter	Liver	Michigan	1997	3	2.4–3.0	<1–1.2	Kannan *et al.*[41]
Bottlenose dolphin	Blubber	Florida	1994–2000	4	4.2–21	NA	Kannan *et al.*[41]
Striped dolphin	Blubber	Florida	1995–1997	3	8.1–25	NA	Kannan *et al.*[41]
Pygmy sperm whale	Blubber	Florida	2000	1	6.6	<1	Kannan *et al.*[41]
Atlantic sharpnose dolphin	Liver	Florida	2004	3	4.6–5.2	1.4–1.7	Kannan *et al.*[41]
Mink	Liver	Illinois	1997	4	2.2–5.3	1.1–2.7	Kannan *et al.*[41]

[a] Each of the 12 values listed were the average of 7 replicates. [b] A composite sample from 5 fish.

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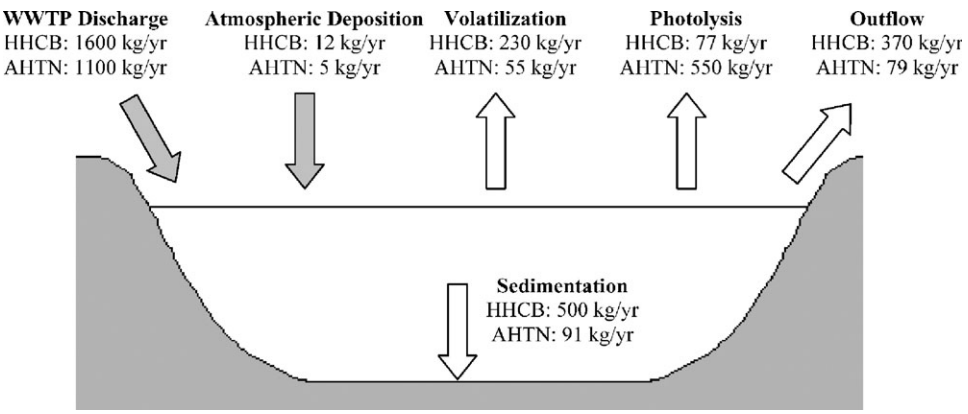

Fig. 3 Fate processes controlling HHCB and AHTN concentrations in Lake Michigan water. Flux estimates for WWTP discharge, atmospheric deposition, volatilization, and outflow were published previously.[15] The losses due to sedimentation and photolysis were estimated using the methods of Buerge *et al.*[48]

porpoise blubber ranging from 13 ng g^{-1} wet mass to 149 ng g^{-1} wet mass. AHTN was detected in one of nine animals at a concentration of 9.6 ng g^{-1} wet mass. Musk xylene, musk ketone, and musk ambrette were not found in finless porpoise blubber. Similar observations were made for these compounds in the livers of five hammerhead sharks. HHCB concentrations ranged from 16 ng g^{-1} wet mass to 48 ng g^{-1} wet mass while AHTN, musk xylene, musk ketone, and musk ambrette were not detected.

Osemwengie and co-workers[43,44] reported polycyclic musks, nitro musks, and amino musk metabolites in carp from Lake Mead, Nevada. The monthly average 2-amino musk xylene (<2 ng g^{-1} wet mass to 10 ng g^{-1} wet mass) and 4-amino musk xylene (8 ng g^{-1} wet mass to 40 ng g^{-1} wet mass) concentrations in these fish were 10 to 100 times greater than the musk xylene concentrations (0.4 ng g^{-1} wet mass to 0.9 ng g^{-1} wet mass). The concentrations of 4-amino musk xylene were higher than all other nitro musks and polycylic musks. Kallenborn *et al.*[45] reported HHCB-lactone (median: 6.3 ng g^{-1} wet mass) concentrations in Atlantic cod liver comparable to those of HHCB (median: 11 ng g^{-1} wet mass) and AHTN (4.6 ng g^{-1} wet mass). HHCB-lactone in other fish and tissues were generally lower than HHCB and AHTN.

Synthetic musk fragrances have been detected in surface waters from low ng L^{-1} to low μg L^{-1} concentrations.[15,20,46–54] These compounds have also been measured in suspended[47,55] and surficial[56–59] sediments with typical concentrations ranging from ≈0.5 ng g^{-1} dry to ≈500 ng g^{-1} dry mass. Surface water and sediment concentrations are highly correlated with the proximity to wastewater treatment plant discharges.[20,51]

We have previously examined the processes affecting synthetic musk fragrance concentrations in the water of Lake Michigan.[15] The original analysis determined that wastewater treatment plant discharge was the most important source of these compounds to the lake, with atmospheric deposition contributing less than 1% of the total input. Both volatilization and flow out of the lake were found to be important loss processes. Buerge *et al.*[48] did a similar analysis for several lakes in Switzerland. In that study two additional loss processes, sedimentation and photolysis, were included. Fig. 3 illustrates these sources and fate processes in Lake Michigan. Estimated inputs of HHCB and AHTN to Lake Michigan from WWTP discharge and atmospheric deposition and losses due to outflow and volatilization were published previously.[15] Losses due to photolysis were estimated from photolysis rates and methods described by Buerge *et al.*[48] with an adjustment for the depth of Lake Michigan. The loss due to sedimentation was estimated from the water concentrations of HHCB and AHTN in Lake Michigan,[15] the partitioning coefficients describing the equilibrium partitioning of HHCB and AHTN between water and organic carbon ($10^{4.86}$ and $10^{4.80}$, respectively),[12] typical organic carbon content of sediment in Lake Michigan (0.070 g g^{-1}),[60] the average sedimentation rate for Lake Michigan (0.36 kg m^{-2} $year^{-1}$),[60,61] and the surface area of the lake (5.78×10^{10} m^2).[62] All of the loss processes evaluated are important in controlling the concentrations of HHCB and AHTN in Lake Michigan. The estimated concentration of HHCB and AHTN due to these sources and loss processes are 6.4 ng L^{-1} and 1.5 ng L^{-1}, respectively. These estimates fall within the range of measured concentrations in Lake Michigan (HHCB: 0.80 ng L^{-1} to 8.6 ng L^{-1}; AHTN: 0.20 ng L^{-1} to 2.4 ng L^{-1}). Both this analysis and that by Buerge *et al.*[48] show that while the discharges of HHCB and AHTN to the environment are similar, HHCB is frequently found in larger concentrations in air, water, and sediments due, to some extent, to a significantly greater loss of AHTN due to photolysis. The concentrations of both HHCB and AHTN appear to be increasing in Lake Michigan due to greater inputs than losses of these compounds in the lake system.

Environmental trends

There have been no reported long-term environmental monitoring studies for the synthetic musk fragrances, so evaluating trends in environmental concentrations is difficult. Two studies have evaluated these compounds in dated sediment cores.[57,58] Heim *et al.*[57] examined a sediment core from a riparian wetland in Germany that covered dates from 1930 to 1986. HHCB and AHTN first appeared in the sediment around 1965. Peak concentrations of HHCB and AHTN were observed in 1980 (151

ng g^{-1} dry mass and 44 ng g^{-1} dry mass, respectively). These peak concentrations were followed by slight declines and subsequent increases between 1982 and 1986. Peck *et al.*[58] measured HHCB in a sediment core from Lake Erie with dates from 1979 to 2003. The slight decline in HHCB concentration observed in the German core was also seen in the core from Lake Erie. From 1990 to 2003, the HHCB concentration in the Lake Erie core increased with a doubling time of 8 years. On the other hand, Duedahl-Olesen *et al.* have reported a decrease in synthetic musk fragrance concentrations in trout from Danish trout farms between sampling campaigns in 1999 and 2003–2004.[71] For example, the median HHCB concentration appears to have decreased nearly five-fold.

Impacts and relevance

Synthetic musk fragrances are not regarded as acutely toxic, even to organisms that are highly sensitive. Most LC50s (median lethal concentrations resulting in 50% mortality) for aquatic organisms exposed to synthetic musks are several orders of magnitude higher than environmental concentrations.[63] For example, Gooding *et al.*[64] observed a dose-response relationship between two polycyclic musks and the potentially vulnerable life stages of *L. cardium*, a freshwater mussel. They observed an LC50 for the larval stage of *L. cardium* that ranged from 454 μg AHTN L^{-1} to 850 μg AHTN L^{-1} and from 1000 μg HHCB L^{-1} to the water solubility of HHCB (1750 μg L^{-1}). The concentrations that cause death to half of the exposed organisms are much higher—about 100 or more times higher—than the concentrations reported in natural lakes and rivers. They are within an order of magnitude, however, of some wastewater effluent concentrations.

Sublethal effects may be a more significant concern at environmentally relevant concentrations. For example, synthetic musks can impair estrogenic function in fish by suppressing the effects of 17β-estradiol on estrogen receptors *in vitro* and *in vivo* with transgenic fish.[65] Breitholtz *et al.*[66] observed impairment of larval development in the copepod *Nitocra spinipes* at concentrations as low as 20 μg HHCB L^{-1}. Inhibition of larval development in the copepod *Acartia tonsa* was observed at 26 μg AHTN L^{-1} and 59 μg HHCB L^{-1}.[67] Luckenbach *et al.*[68] demonstrated that four polycyclic musks, including AHTN and HHCB, compromised multixenobiotic defense systems (mxr transporters) in the marine mussel *Mytilus californianus* in the μmol L^{-1} range (200 μg L^{-1} to 2000 μg L^{-1}). A long-term loss of efflux transporter activity can result in continued accumulation of normally excluded toxicants even after direct exposure to the musk has ended, and thus, may increase an organism's susceptibility to other toxicants.[69] Lastly, Gooding *et al.*[64] found that polycyclic musks (particularly AHTN) were associated with significantly lower growth rates and activity in juvenile freshwater mussels.

Two polycyclic musks, HHCB and AHTN, are so clearly linked to wastewater effluent that they have been proposed as tracers of human waste in natural waters. To show this, Standley *et al.*[70] examined a suite of compounds as potential tracers of organic matter sources to surface waters. Their strategy included measuring dozens of compounds in wastewater and rivers, correlating the concentrations of the compounds in watersheds with the watershed uses, and testing the relationship in a separate set of watersheds. They found that the sum of the two fragrance compounds plus caffeine was strongly correlated with the presence of wastewater discharges in drinking water supply watersheds and wastewater discharge volumes. They determined that the combined fragrance plus caffeine parameter was a unique molecular tracer of wastewater effluent. Glassmeyer *et al.*[52] took this several steps further and showed that fragrances were excellent tracers of human fecal contamination, nearly comparable to pharmaceuticals that actually pass through the human body. Several studies have clearly shown that fragrance compounds are significantly higher in rivers downstream of a wastewater effluent discharge than in the river upstream.[20,52–54,59]

Summary

Synthetic musk fragrances are found in virtually every environmental compartment. They are a clear indicator of human impact on natural systems. In air, their concentrations are directly proportional to the human population nearby. In water, the frequency of their detection and the magnitude of their concentrations are a function of inputs of human wastewater. Several of the most widely used fragrances are nonbiodegradable and are accumulating in the environment. This is evident in lake cores that show historical inputs, and in mammals that retain them in their fat stores. Does this widespread exposure cause environmental degradation or harm? It is not clear, although there is strong evidence to suggest that they cause subtle effects in aquatic organisms.

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