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LONG LASTING PERFUME - A REVIEW OF SYNTHETIC MUSKS IN WWTPs

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Abstract

Synthetic musks have been used for a long time in personal care and household products. In recent years, this continuous input has increased considerably, to the point that they were recognized as emerging pollutants by the scientific community, due to their persistence in the environment, and hazardous potential to ecosystems even at low concentrations. The number of studies in literature describing their worldwide presence in several environmental matrices is growing, and many of them indicate that the techniques employed for their safe removal tend to be ineffective. This is the case of conventional activated sludge treatment plants (WWTPs), where considerable loads of synthetic musks enter mainly through domestic sewage.

This review paper compiles and discusses the occurrence of these compounds in the sewage, effluents and sludge, main concentration levels and phase distributions, as well as the efficiency of the different methodologies of removal applied in these treatment facilities.

To the present day, it has been demonstrated that WWTPs lack the ability to remove musks completely. This shows a clear need to develop new effective and cost-efficient remediation approaches and foresees potential for further improvements in this field.

Keywords: synthetic musks, wastewater treatment plants, removal efficiency

Abbreviations

2-AMK - 2-amino musk ketone; 2-AMX - 2-amino musk xylene; 4-AMX - 4-amino musk xylene; ADBI – celestolide; AETT – versalide; AHMI – phantolide; AHTN – tonalide; ATII – traseolide; DPMI – cashmeran; HHCB – galaxolide; HHCB-lactone - galaxolidone; HRT - hydraulic retention time; K_{OW} - octanol-water partition coefficient; MA - musk ambrette; MC4 - muskonate; MK - musk ketone; MM - musk moskene; MT - musk tibetene; Musk-NN - ethylene brassylate ; MX - musk xylene; OTNE - orbitone; PAHs - polycyclic aromatic hydrocarbons; PCBs - polychlorinated biphenyls; PCPs - personal care products; REACH - Registration, Evaluation, Authorisation and Restriction of Chemicals; SRT - solids retention time; STRB - sludge treatment reed bed; UV - ultraviolet; vPvB - very persistent and very bioaccumulative; WWTP - wastewater treatment plant

Abbreviations

2-AMK - 2-amino musk ketone; 2-AMX - 2-amino musk xylene; 4-AMX - 4-amino musk xylene; ADBI – celestolide; AETT – versalide; AHMI – phantolide; AHTN – tonalide; ATII – traseolide; DPMI – cashmeran; HHCB – galaxolide; HHCB-lactone - galaxolidone; HRT -

1. Introduction

The expansion of industrial activities has promoted an increase of environmental pollution, mainly due to the generation of considerable amounts of waste. Therefore, quality control became an extremely important issue for the scientific community, particularly directed to the safety of our surrounding environment. In the last years, however, the focus of environmental research has been broadened from conventional priority pollutants such as polycyclic aromatic hydrocarbons (PAHs), pesticides or polychlorinated biphenyls (PCBs) to a continuous surge of emerging micropollutants (Bu et al. 2013). Among these compounds, personal care products (PCPs) are one of the most important groups (Liu et al. 2010, Polo et al. 2007), which includes antimicrobial agents, insect repellents, preservatives, UV filters and fragrances (Liu and Wong 2013, Richardson et al. 2005).

Synthetic musk fragrances are PCPs with widespread use, incorporated in several personal care and household products (e.g. lotions, perfumes, shampoos, washing powders, softeners, air fresheners) as fragrance additives and fixative elements (Ramírez et al. 2011, Zhang et al. 2008). They are usually divided into 4 main groups according to their chemical structure: nitro, polycyclic, macrocyclic and alicyclic musks. Due to their potential toxicity, namely phototoxic, neurotoxic, carcinogenic and estrogenic activity (Hu et al. 2011b, Polo et al. 2007), most nitromusks were phased out from the market. In fact, in Europe, musk ambrette (MA), musk moskene (MM) and musk tibetene (MT) were banned from cosmetic products, while the use of musk xylene (MX) and musk ketone (MK) is restricted (European Parliament 2009) due to suspected carcinogenic effects at high concentration levels (Polo et al. 2007). Recently, the European Commission under the new chemical regulation REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals), considered MX a very persistent and very bioaccumulative (vPvB) substance and therefore decided to ban it as well (European Commission 2011).

With the decreasing use of nitromusks, polycyclic musks became the most important commercial synthetic musks and currently dominate the global market. The most representative compounds of this class are galaxolide (HHCB), tonalide (AHTN), celestolide (ADBI),

phantolide (AHMI), traseolide (ATTI) and cashmeran (DPMI). Nevertheless, recent studies reported their potential estrogenic and anti-estrogenic effects (Hu et al. 2011b, Toivanen et al. 2008, Yamauchi et al. 2008) and presence in different environmental compartments. For this reason, their use in cosmetic products is currently under discussion. In contrast, macrocyclic musks (e.g. ethylene brassylate, exaltolide) represent only a small fraction of the market (3-4%) and are almost exclusively used in perfumes, given their relatively high production costs. Moreover, having a more intense odour, smaller quantities are needed to obtain the same performances as other synthetic musks. These compounds show a similar chemical structure to the musks of natural origin, and hence seem to be more environmental-friendly, with greater degradability in the environment than the previous classes (Vallecillos et al. 2012a). Alicyclic musks are the 4th generation of musk odourants and are known as the linear musks (e.g. cyclomusk, helvetolide; Arbulu et al. 2011). Their use in personal care products is still very limited. As mentioned previously, synthetic musks are incorporated in products used in our everyday life (Correia et al. 2013, Homem et al. 2013). Following their application, most of these compounds are released via household effluents, reaching the WWTPs (García-Jares et al. 2002). Due to their physicochemical properties, they are considered bio-accumulative, lipophilic and only partially biodegradable. For this reason, some of them, namely polycyclic musks, are not completely removed during wastewater treatment (Lv et al. 2010, Posada-Ureta et al. 2012, Zeng et al. 2005, Zhang et al. 2008) and are therefore frequently found in surface waters (e.g. Lv et al. 2009, Posada-Ureta et al. 2012, Yang and Ding 2012). In fact, the application of sludge and/or biosolids to agricultural fields is a direct input of musks into the soil (e.g. Chase et al. 2012), and thus into the food chain (Hu et al. 2011b), whereas the discharges of effluents are the major route for water and aquatic biota contamination (e.g. Duedahl-Olesen et al. 2005, Nakata et al. 2012, Reiner and Kannan 2010). Apart from persistent or pseudo-persistent (due to continuous emission), musks are also semi-volatile, which may explain their detection in remote areas (long-range atmospheric transport; Arbulu et al. 2011, Ramírez et al. 2011). Therefore, this phenomenon also plays a role in the dispersion ofmusks in the environment.

With the increase of material published on these subjects, there is a lack of systematic investigation that can provide a good overview of the incidence and behaviour of musks in their main contamination route, the WWTPs. Bearing in mind the aforementioned information, the aim of this work is to present levels, describe the fate and trends of musks detected in the WWTPs, as well as to discuss the efficiency of the removal methodologies applied in these treatment facilities.

2. Methodology

Scientific publications regarding the occurrence and fate of musks in WWTPs between 1996 and 2014 were searched and presented in this work. This literature review was done using several available electronic databases:Scopus®, Elsevier®, Taylor & Francis®, ACS Publications®, Springer® and Google® Scholar.

3. Discussion

The WWTPs represent the main potential source of environmental contamination for musks, but at the same time the crucial point for remediation actions through the development and application of removal processes. For that reason, an increasing number of studies about musks in WWTPs have emerged in recent years (**Fig. 1**). These studies focused on the assessment of diverse procedural steps of WWTPs, with sampling strategies covering different matrices (sludge, wastewater and even the surrounding air). The analysis of these matrices can be challenging given their complexity and, for that reason, several analytical approaches have been developed.

3.1. Overview of WWTPs

Wastewater treatment plants were initially designed in the 20th century to remove pathogens, organic matter and nutrients from the final effluents (Amy et al. 2008), which should not be a new source of contamination. However, the demands on wastewater treatment systems have since increased dramatically, and nowadays the attention is focused on emergent pollutants (i.e.

pharmaceuticals, personal care products, perfluorinated compounds, etc). These compounds have been detected in ng L^{-1} to mg L^{-1} concentration levels in WWTPs and to ensure that they will not affect the environment or pose a threat to human health, the implementation of new technologies and control measures is required (Amy et al. 2008, Weiner and Matthews 2003). Conventional wastewater treatment generally involves four main stages: preliminary, primary, secondary and tertiary treatment.

In the preliminary treatment, elements on the influent flow prone to cause maintenance and operational problems in the system are removed. Afterwards, wastewater is conducted to a primary treatment that usually involves a physical process (Tchobanoglous et al. 2003, Weiner and Matthews 2003), but chemicals (flocculants and coagulants) are sometimes added to enhance the removal of suspended solids and, to a lesser extent, dissolved solids. In the secondary treatment, biological processes are used to remove most of the biodegradable organic matter. At this stage, different methods can be employed, but trickling filters (percolated fixed beds) and activated sludge systems are the most common. In some WWTPs, this is the final stage of the process and the effluent is ready to be released into the environment. There are, however, cases where additional processes are applied - tertiary treatment – to further improve its quality. The objective is to remove residual suspended solids and some specific contaminants, such as nutrients and toxic substances (e.g. nitrogen, phosphorous, heavy metals), by filtration over activated carbon or reverse osmosis, chlorination, ozonation, degradation with UV-light and biological nutrient removal (Tchobanoglous et al. 2003, Weiner and Matthews 2003).

Within the whole WWTP processes, sludge is produced from nearly all treatment phases, and must be treated before disposal. In order to reduce their volume, a thickening and/or dewatering treatment is applied, and a stabilization process to reduce problems related with odour or putrescence and to lower the pathogenic load can also be employed (Sanin et al., 2011). After biological and/or chemical treatment (e.g. composting) sludge is transformed into biosolids, which can be used as fertilizers for agricultural purposes.

3.2. Occurrence and fate of musks in WWTPs

The conventional processes mentioned above are not always capable of removing micropollutants such as synthetic musks. In fact, this is a group of compounds with a chemical structure that is not readily biodegradable (Gatermann et al. 1998, Osemwengie and Steinberg 2001). For that reason, their removal in WWTPs occurs mainly due to a transfer from the liquid to the solid phase - sorption onto sludge particles (Simonich 2005), and this is why WWTPs are considered the largest contributing source of environmental contamination for musks (García-Jares et al. 2002). Table 1 shows an overview of the works published in international journals regarding the presence of these compounds in WWTPs.

The removal of synthetic musks depends highly on the size of the WWTP, type of methodologies applied, origin of waste to be treated (domestic, industrial and/or agricultural effluents), population density and type (rural or urban) and industries (Horii et al. 2007, Lee et al. 2010, Chase et al. 2012). Therefore, the discussion of typical concentrations in wastewater or sludge is not always easy because their levels can change dramatically with the mentioned parameters. Moreover, most published studies do not specify the type of waste or treatment applied, making the analysis and comparison of results a complex task.

To the authors' best knowledge, the first case of musks reported in residual waters was in Japan more than three decades ago, when Yamagishi et al. (1983) detected musk xylene and musk ketone in an effluent of a WWTP at 25 to 410 ng L^{-1}. The number of studies increased ever since, particularly in the past two decades (**Fig. 1**).

Most papers focus on the presence of musks in urban areas, probably because being usually highly populated and propitious for the establishment of industrial clusters, the frequency of wastewater production (and consequently the existence of WWTPs) is increased. Differences between urban and rural areas are difficult to discuss, since there are only a small number of studies in the latter regions. Horii et al. (2007) studied two domestic WWTPs (urban and rural) that employ an activated sludge treatment process. As expected, the highest concentrations were detected in the influents (3-60 times higher than those in effluent) and the mean concentrations of HHCB and AHTN in the influent of the rural plant were 5 times higher than those obtained in

the urban plant. Furthermore, the authors report that the daily inflow of wastewater into the urban plant was 4-fold greater than in rural plant. Therefore, the mass flow of musks in both plants was similar. However, these results are not entirely expected, as a lower incidence of synthetic musks is common in rural areas. The authors also concluded that no significant differences were found in both plant effluents (rural plant: 44 ng L^{-1} HHCB, 130 ng L^{-1} AHTN, 229 ng L^{-1} HHCB-lactone; urban plant: 55 ng L^{-1} HHCB, 139 ng L^{-1} AHTN, 378 ng L^{-1} HHCB-lactone). To better understand this behaviour, more studies should be made in these areas. Still, some assumptions can be drawn about the origin of the waste to be treated. As can be seen in **Table 1**, domestic effluents are commonly the main source of musk compounds, since they are directly released from human activities like showering, bathing or household cleaning. Nevertheless, industrial effluents may have a strong contribution, depending on the type of the facilities. Companies related to the manufacture of toiletries, cosmetics, perfumes and even pharmaceutical compounds are found to release high amounts of musks (up to mg L^{-1}) in their effluents (Chen et al. 2007, Guo et al. 2010, Zeng et al. 2005). As expected, the wastewaters from agricultural activities (livestock, poultry, etc) show the lowest levels of contamination - concentration levels between 10 and 4000 ng L^{-1} in effluents and 3 to 1000 ng g^{-1} in sludge (Gómez et al. 2009, Guo et al. 2010). Still, most studies focus on WWTPs that receive a mixture of effluents, namely domestic and industrial. In most cases, the discharging industries do not operate with this type of compounds and, therefore, the concentrations detected in mixed wastewater are lower than in domestic effluents (about ten times), due to an important dilution effect (Herren and Berset 2000, Zeng et al. 2005).

The two older classes of synthetic musks (nitro and polycyclic) have been the target of most studies in WWTPs. In general, polycyclic musks were detected in higher concentrations and more often than the other musk classes (>98% samples). For the reasons mentioned above, the ranges of total concentration were usually lower for agricultural wastes (11-8697 ng L^{-1} in effluents and 3-1175 ng g^{-1} in sludge; Gómez et al. 2009, Guo et al. 2010), and higher for cosmetic industries (3730-595480 ng L^{-1} in influents, 500-33540 ng L^{-1} in effluents, 302-703681

ng g^{-1} in sludge; Zeng et al. 2005, Chen et al. 2007).Individually, HHCB, AHTN and DPMI were the predominant compounds.

As stated before, nitromusks have been phased out from the market and their use is prohibited or restricted in Europe (European Parliament 2009), and this is probably the reason they were not reported in these studies. Only MX and MK were detected and their concentrations ranged from 6.2 to 1550 ng L^{-1} in influents, 0.3 to 5000 ng L^{-1} in effluents and 1.1 to 1920 ng g^{-1} in sludge. A total of merely six studies were found about macrocyclic musks (Arbulu et al. 2011, García-Jares et al. 2002, Matamoros et al. 2012, Sumner et al. 2010, Vallecillos et al. 2012a, 2013), with levels between 10 and 9300 ng L^{-1} in residual waters and 0.025 and 150 ng g^{-1} in sludge. Ambrettolide and exaltone were the most detected (Matamoros et al. 2012, Vallecillos et al. 2012a, 2013), ranging from 1500 to 9300 in influents, 10 to 2500 in effluents and 0.03 to 150 ng g^{-1} in sludge.

Individual musk compounds have analogous physicochemical behaviour and, therefore, their mechanisms and locations for removal in a WWTP are bound to be similar. Generally, biological or chemical transformation and volatilization are their possible removal mechanisms from WWTPs. As these compounds have a relatively high octanol-water partition coefficients (log K_{OW} > 5.0; Jones-Lepp and Stevens 2007) and low water solubility, a tendency to accumulate in the sludget is expected for most of them. This is confirmed by several authors (e.g. Bester 2004, Reiner et al. 2007, Lv et al. 2010). For instance, Lv et al. (2010) verified that 11-35% of the polycyclic musks in the influent loadings were partitioned to the sludge after the primary treatment. Moreover, 17-58% of those were ultimately adsorbed to the treated sludge (after conditioning and dewatering). However, they also concluded that less than 10% of the incoming nitromusks were detected in biosolids, suggesting that biodegradation or photolysis may play a more important role. The biological processes studied (anaerobic/anoxic/oxic bioreactor) proved their efficiency mainly on the degradation of nitromusks. This is expected as only substances freely dissolved in the aqueous phase are directly available for microbial degradation. The overall removal of the whole process (primary + biological treatment) ranged

from 35.5 to 62.5% and 33.9 to 75.6% for HHCB and AHTN, respectively, >60% for MK and about 99% for MX.

Bester (2004) investigated the behaviour of two polycyclic musks in a conventional activated sludge plant (HRT = 8 h; SRT = 8-10 days; sludge retention in digester = 20 days) and found that removal occurs mainly by sorption to sludge, with an efficiency ranging between 50 and 80%. Carballa et al. (2004) also studied the same type of WWTP configuration. They reported that in the primary treatment 30-40% of musks were removed by sorption processes, and 30-50% in biological treatment. Therefore, the overall removal from the water phase (HRT = 24 h) ranged from 60 to 90%. Zeng et al. (2007) studied the distribution of polycyclic musks in a conventional activated sludge plant. After gravitational settling in the primary clarifier, about 21-75% of synthetic musks were removed with the sedimentation of particles. In the end of the treatment, 61 to 97% of compounds were removed. Once more, this mainly occurred by transfer to sludge due to sorption on the particulate phase. The same type of biological system configuration was investigated by Horii et al. (2007), which found similar removal rates (72-98%). Reiner et al. (2007) studied the distribution of polycyclic musks in two conventional activated sludge plants (HRT = 16 h, SRT = 12-14 days) and obtained similar results for both (total removal of 46-63% with higher adsorption onto sludge particles).

Simonich et al. (2000) compared two WWTPs with different biological treatments (activated sludge and trickling filter) and the removal profiles found were 35 to 43% by sorption onto solids in the primary system of the activated sludge WWTP, and 14 to 51% in the clarifier of the trickling filter WWTP. This lower reduction in the latter plant is due to a shorter hydraulic residence time in the primary clarifiers. The overall removal (primary + secondary treatment) of both approaches is similar (83-99% in activated sludge and 80-91% in trickling filter). Simonich et al. (2002) also compared different secondary wastewater treatment processes (activated sludge, carousel, oxidation ditch, trickling filter, rotating biological contactor and lagoons processes) and concluded that 37-41% of synthteic musks were removed during the primary phase. The overall removal (primary + secondary treatment) ranged from 88-98% for activated sludge, 59-89% for carousel, 90-97% for oxidation ditch, 78-88% for trickling, 81-89% for

rotating biological contactor and 97-99.7% for lagoons. Although the last process is considered the simplest form of treatment, higher removals are achieved. This kind of treatment presents the longest retention times (90-120 days), enabling the biodegradation, photodegradation, sorption and/or volatilization of the compounds. These authors also investigated the relationship between the plant design and operating parameters and the overall removal of synthetic musks. They acknowledge a positive trend between the removals of musks and total suspended solids, consistent with the high removals found in the primary treatment. Lishman et al. (2006) studied different types of biological treatments - lagoon, activated sludge (HRT = 10-23 h) and activated sludge with filtration (HRT = 22-43 h). Average musk reductions of 98-99% in lagoons, 37-65% in the activated sludge systems and 12-56% in activated sludge with filtration were seen. This last result was uncommon, since musks tend to adhere on solids due to their lipophilic behaviour (Lv et al. 2010). So, the additional filtration step would normally result in a higher reduction. Furthermore, the overall removal rates in activated treatment sludge were much lower than those reported for Simonich et al. (2000 and 2002). The differences found might be related to the organic carbon content of the sewage and/or differences in the HRTs.

Two different biological treatment systems (activated sludge and membrane bioreactor) were investigated by Clara et al. (2005), involving three different conventional activated sludge WWTPs (WWTP$_1$: HRT = 13-14 days, SRT = 52-237 days; WWTP$_2$: HRT = 0.08 days, SRT = 2 days; WWTP$_3$: HRT = 1.2 days, SRT = 46 days). The authors reported higher removal rates in WWTP$_1$ (about 95%), followed by WWTP$_2$ (70-85%). The lower removal rates are attributed to the low HRT and SRT installed in the second plant. In WWTP$_3$ even lower removal were achieved (50-60%), perhaps due to the low rate of sewage discharges. In the membrane bioreactor about 90-95% removal occurred (HRT = 0.5-4 days, SRT = 10-55 days), similar to the values observed in the conventional WWTP$_1$.

The removal of synthetic musks along a wastewater treatment facility was also studied by Yang and Metcalfe (2006). In the primary treatment, about 17.9 to 26.3% of the musks have been removed by sorption on solids, while in primary + activated sludge secondary treatment the reduction was from 43.3 to 56.9%. The authors also tried a tertiary treatment (UV

disinfection), but its application did not seem to affect the results. These results were similar to those obtained by Lishman et al. (2006). In short, Yang and Metcalfe (2006) concluded that about 3% of the musks were removed by discharge *via* suspended solids in the final effluent; 73% by sorption on biosolids and 24% remained in the aqueous phase of the final effluent.

The removal of HHCB and AHTN in different sewage treatment plants (anaerobic/anoxic/oxic - HRT = 6.8 h, anoxic/oxic - HRT = 10.2 h or extended aeration oxidized ditch biological treatment - HRT = 14 h) was mentioned by Zhou et al. (2009), which reported an enhanced removal rate from the primary treatment to the secondary treatment (2.4-24.6% and 23.1-47.5%, respectively). Therefore, the authors assumed that the removal was mostly achieved in the biological treatment step (over 75% of the overall removal). Lee et al. (2010), comparing four different biological treatment processes (activated sludge; modified Ludzack-Ettinger, sequential batch reactor and anaerobic/anoxic/oxic processes - modified versions of the conventional activated sludge process) found average musks removal of 53% in the conventional activated sludge process (HRT = 12-17 h) and slightly higher in other modified versions: modified Ludzack-Ettinger (HRT = 12 h) and anaerobic/anoxic/oxic (HRT = 21 h) process - 65%, sequential batch reactor (18 h) - 70%. These authors also analysed the application of tertiary treatments as filtration, flocculation/coagulation and disinfection by chlorination and UV light, reporting that a chemical flocculation/coagulation treatment had lower removal rates (about 35%), as well as physical filtration and disinfection (3-35%). The general conclusion was that all biological treatments produce similar results and are much more efficient than physical and chemical treatments.

Activated sludge, anaerobic/anoxic/oxic and anoxic/anaerobic/oxic processes were investigated by Ren et al. (2013) and in the first WWTP (HRT = 12-13 h; SRT = 6.5 days) about 65-73% removal was reached, while in anaerobic/anoxic/oxic WWTP (HRT = 20-21 h and SRT = 15.3 day) and in anoxic/anaerobic/oxic WWTP (HRT = 16 h and SRT = 14.0 day) 43 to 54% and 70-84% was respectively found. Hence, advanced processes did not show a significant improvement compared to the conventional ones. However, these results indicate

that the order of anoxic and anaerobic basins affected the removal of synthetic musks in the aqueous phase, which resulted mainly from adsorption onto sludge particles.

The chemical treatments have been poorly explored in this area, but for instance UV disinfection seems to be inefficient, as mentioned previously (Ternes et al. 2003, Yang and Metcalfe 2006, Lishman et al. 2006, Lee et al. 2010). Ternes et al. (2003) also studied the application of ozonation in a pilot plant, finding that applying 10-15 mg L^{-1} of ozone during 18 min would be enough to degrade HHCB and AHTN completely. The same kind of study was performed at lab scale by Rosal et al. (2010). The authors reported that MX was completely refractory to ozone, while MK (38%), AHTN (72%) and HHCB (83%) were partially removed with an ozone dose of 340 μM. These studies indicate that polycyclic musks seem to be more readily degradable than nitromusks by ozonation. Ramírez et al. (2011 and 2012) analysed a filtration process -reverse osmosis- and concluded that this kind of treatment increased the removal rates in WWTPs. The use of treatments such as advanced oxidation technologies (e.g. ozonation, photo-Fenton) and membrane filtration should be investigated in more detail, being aware of the possible formation of toxic degradation products. Consequently, the monitoring and study of these products is extremely important, namely in the toxicological aspect.

As can be seen from the results presented above, the discussion on the removal efficiencies can be further complicated considering that they depend on factors such as mixtures effects, hydraulic and temperature variations and combinations of different treatment approaches. However, analysing the available literature, biological treatment seems to be the most appropriate method to eradicate both polycyclic and nitromusks. The removal occurs mainly through sorption onto sludge particles, since synthetic musks are poorly biodegraded or susceptible to chemical degradation. In fact, nitromusks are apparently more prone to photolysis and biodegradation (Herren and Berset, 2000). Furthermore, removal efficiencies usually increase with higher hydraulic and solid retention times (Clara et al. 2005, Ren et al. 2013).

Although some WWTPs have a specific line dedicated to sludge treatment, the removal of musks in these steps is usually poorly discussed in literature. Ternes et al. (2005) studied the

influence of the anaerobic digestion of sludge. Regarding concentration, they concluded that AHTN and HHCB were detected in 2.3-8.5 μg g^{-1} before treatment and 6.6-15 μg g^{-1} after digestion. This increase may be related to the simultaneous drastic solid mass reduction (between 50-70%) and low degradation. Horii et al. (2007) investigated thickening and dewatering treatments and also obtained increasing levels of musks in the final effluent. Yang and Metcalfe (2006) studied the distribution of synthtetic musks in sludge/biosolids at different stages of sewage treatment. They observed that dry weight concentrations of synthetic musks increased from the combined raw sludge (primary + secondary sludge) to the activated return sludge (secondary sludge that goes back to the primary clarifier) and to the digested biosolids (anaerobic sludge digestor). This should be related to the reduction of volatile solids during anaerobic digestion (35-45%) and therefore there is no appreciable degradation of synthetic musks adsorbed onto the sludge/biosolids in the solid treatment line. Analogous results were reported by Lv et al. (2010). Matamoros et al. (2012) studied the efficiency of a sludge treatment reed bed (STRB) to dewater and mineralize sludge contaminated with synthetic musks. In this approach, primary and secondary liquid sludge is loaded onto the surface of a bed over several years, where it is dewatered, mineralized and turned onto a biosolid with high dry matter content for use as an organic fertilizer. The authors assessed the degradation and fate of four musks (HHCB, AHTN, DPMI and ambrettolide) in the accumulated sludge in a 20-year old STRB. Results showed that deposited sludge reaches a dry matter content of approximately 29% in the dewatering process and up to a third of its organic content is mineralised. The concentrations decreased with depth in the vertical profile and ranged from 10 to 5000 ng g^{-1}. Musk fragrances are generally degraded during storage in the STRB, with attenuations between 40 and 98%. Chen et al. (2009) also studied an STRB system, but on the contrary, they reported no degradation in the 13 months of experimental work and suggest half-lives from 2 to more than 3 years, a very long time for these compounds. Still, this process seems to be cost-effective and environmental-friendly.

Another very important subject in this field is the study of degradation products. In a WWTP, they can result from biotic (biological treatment) or abiotic degradation (e.g. UV

radiation, hydroxyl radicals formed during advanced oxidation processes; (OSPAR Commision 2000, SWECO Environment 2010). The degradation products/metabolites are usually more polar than parent compounds and approximately one order of magnitude less lipophilic (Chou and Dietrich 1999), therefore more water-soluble and more available to aquatic organisms. Nitromusks showed propensity to be transformed via reduction of the 4 or 2-nitro group, producing aniline derivatives (2 or 4-amino compounds) like 2-AMK, 4-AMX and 2-AMX (Herren and Berset 2000, Peck 2006). They can also suffer hydroxylation of the methyl groups (SWECO Environment 2010). These degradation compounds have been detected during the wastewater treatment, namely in the final effluent, in levels between 1.6 and 250 ng L^{-1}. In polycyclic musks, the degradation products are typically formed by hydroxylation of the parent compounds at different carbon positions (Martin et al. 2007). The most detected and investigated is HHCB-lactone. This compound, unlike the ones mentioned before, was found in the influents at relatively high concentrations: 107 to 1150 ng L^{-1} (Berset et al. 2004, Bester 2004, Horii et al. 2007, Ramírez et al. 2012, Reiner et al. 2007, Vallecillos et al. 2012b). This may indicate that HHCB already undergoes a degradation process in the sewer system, since HHCB-lactone has not been often detected in sanitation and personal care products. In the WWTP effluents, HHCB-lactone was found at concentrations of 20-4000 ng L^{-1} (Berset 2004 and 2005, Reiner et al. 2007, Horii et al., 2007, Ramírez et al. 2012), demonstrating that, in most cases, its incidence in the final effluent is greater than in the influent, again suggesting that HHCB suffers degradation along the WWTP treatment. Due to their higher hydrophilicity, these chemicals tend to accumulate in water matrices instead of sludge. Therefore, they are present in sewage effluents and, consequently, will reach the ecosystems through surface waters. Due to the relatively low number of studies on their occurrence and real impact on the environment, this subject becomes an emergent issue for environmental scientists and should be an object of intensive research in the future.

4. Conclusions

This review provided comprehensive information about the occurrence and fate of synthetic musk compounds in WWTPs. Although synthetic musks have been used in large scale in the last decades, it was only in recent years that their occurrence in the environment, namely in WWTPs, became a subject of scientific and public relevance and concern. In the past, analytical methodologies were not powerful enough to achieve low detection limits (ng L^{-1} levels) and the knowledge about the behaviour of these compounds (biodegradability, toxicity, etc) was scarce, contributing to the unawareness of the impacts caused. As this study reflects, synthetic musks are frequently found as important residues in WWTPs, both in the water and in the solid lines. Due to their lipophilicity and low biodegradation, they tend to be removed from wastewaters by sorption on sludge. HHCB and AHTN, two polycyclic musks, have been identified as the two most important synthetic musks due to their predominant detection frequencies and levels.

Bearing in mind the compiled occurrence of musks and the inefficiency of the current WWTPs layouts to cope with this new class of compounds, new approaches should be developed in order to reduce discharges into the environment. This can either be achieved by novel treatment processes, or through a combination of existing conventional ones, leading to effective but also cost-efficient approaches, able to allow a generalised implementation of these contamination reduction strategies.

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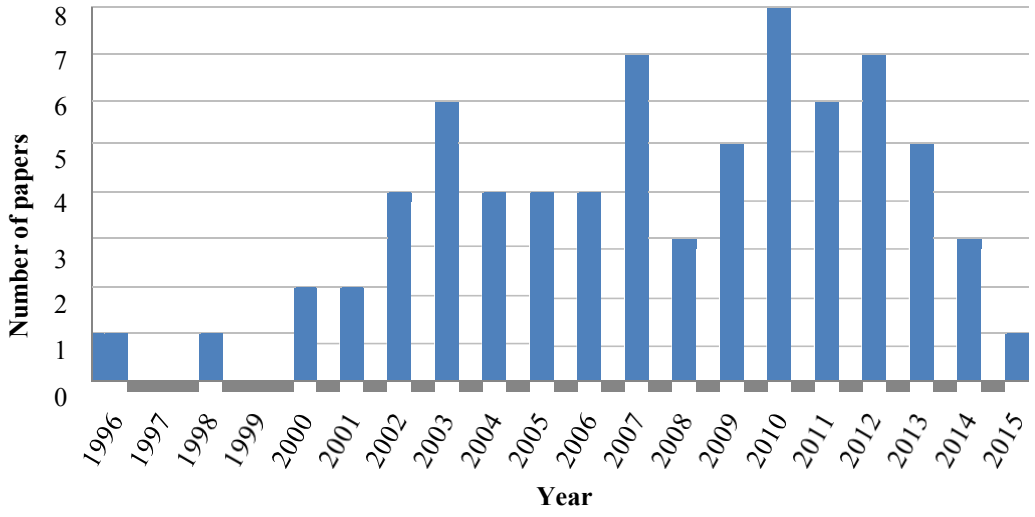

Fig.1. Number of publications per year studying synthetic musks in WWTPs.

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
HHCB, AHTN	Spain	Urban A: Primary + Secondary (activated sludge) + Tertiary treatment (UV+chlorination) B: Primary + Secondary (activated sludge) treatment	---	WWTP A Primary effluent HHCB: 2310 - 3490 (2920) AHTN: nd - 360 (190) Secondary effluent HHCB: 2870 - 5210 (3940) AHTN: nd - 940 (480) Tertiary effluent HHCB: 2670 - 4580 (3560) AHTN: nd - 910 (290) WWTP B Primary effluent HHCB: 1900 - 3430 (2500) AHTN: nd - 480 (140) Secondary effluent HHCB: 2500 - 4230 (3360) AHTN: nd - 1240 (370)	---	---	(Godayol et al. 2015)
MK, MX, HHCB, AHTN, ADBI, AHMI, ATII	China	Urban (domestic, domestic + industrial, industrial) - Primary treatment - Secondary treatment	---	---	HHCB: <2.2 - 41400 (3520) AHTN: <1.5 - 22000 (1750) MX: ? - 382 (362) MK: ? - 2540 (359) ∑Musks: 47.3 - 68200 (5520)	- The detection frequencies were: HHCB (95%), AHTN (98%), ATII (38%), ADBI (29%), AHMI (19%), MK (29%) and MX (14%). - The two main components (HHCB and AHTN) accounted for 95.5% of total synthetic musks. - Similar composition profiles were found in all sludge samples.	(Liu et al. 2014)
AHTN, HHCB	USA	? - Primary treatment - Secondary treatment		AHTN: 50 - 444 HHCB: 453 - 4793	AHTN: 649 - 14971 ---		(Sun et al.

HHCB: 4079 - 91018 --- 2014)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
DPMI, ADBI, AHMI, ATII, HHCB, AHTN, HHCB-lactone, MX, MM, MK, Exaltone, Exaltolide, Muscone, Ambrettolide, MC4, Civetone, musk NN	Spain	Urban (domestic + industrial) A: Primary treatment + secondary treatment (activated sludge) B: Primary treatment + secondary treatment (activated sludge) + tertiary treatment (reverse osmosis)	WWTP A DPMI: nd - 32933 ADBI: nd - 44319 AHMI: 238 - 733 Exaltone: 338 - 1579 Exaltolide: 515 - 1249 Muscone: 69 - 2865 ATII: 214 - 963 HHCB: 818 - 45091 AHTN: 852 - 49904 MX: nd - 632 MM: nd - 1182 Ambrettolide: 507 - 9744 Musk NN: nd - 11758 MK: nd - 4110 HHCB-lactone: 1188 - 4119 MC4, Civetone: nd WWTP B DPMI: 409 - 4342 ADBI: <1 - 10 AHMI: 3 - 54 Exaltone: 95 - 199 Exaltolide: 520 - 10797 Muscone: nd - 258 HHCB: 1820 - 22524 AHTN: 2212 - 14300 Ambrettolide: 3634 - 21528 Musk NN: 1322 - 4932 MK: 348 - 500 HHCB-lactone: 1315 - 4178 ATII, MX, MM, MC4, Civetone: nd	WWTP A DPMI: nd - 9437 ADBI: nd - 9930 AHMI: nd - 3738 Exaltone: nd - 480 Exaltolide: nd - 1276 Muscone: nd - 1748 ATII: nd - 4210 HHCB: 1.5 - 900 AHTN: 2 - 7555 MX, MM, MC4, Civetone: nd Ambrettolide: nd - 4021 Musk NN: nd - 8939 MK: nd - 465 HHCB-lactone: 5.95 - 11007 WWTP B ADBI: <1 AHMI: <1 ATII: 214 - 963 HHCB: 12 - 42 AHTN: 42 - 138 Ambrettolide: nd - 86 Musk NN: 99-194 MK: 104 - 689 HHCB-lactone: 21 - 161 DPMI, Exaltone, Exaltolide, Muscone, ATII, MX, MM, MC4, Civetone: nd	---	---	(Vallecillos et al. 2014)
DPMI, ADBI, AHMI, MA, ATII, HHCB, AHTN, MM, MK	Spain	Urban	ATII: 17 HHCB: 62 DPMI, ADBI, AHMI, MA, AHTN, MM, MK: nd DPMI: 231 - 267 ADBI: nd - 24	ATII: 22 HHCB: 43 DPMI, ADBI, AHMI, MA, AHTN, MM, MK: nd DPMI: 79 - 112	---	---	(Cavalheiro et al. 2013)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

DPMI, ADBI, AHMI, MA, ATII, HHCB, AHTN, MM, MK	France	Urban	HHCB: 1661 - 2347 AHTN: 134 - 261 AHMI, MA, ATII, MM, MK: nd	HHCB: 1146 - 1512 AHTN: 76 - 90 ADBI , AHMI, MA, ATII, MM, MK: nd	---	---	(Cavalheiro et al. 2013)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
						- The daily loads per inhabitant in the influents were 588 and 3617 µg day^{-1} for HHCB and OHTN, respectively.	
OTNE, HHCB	Germany	Urban - Primary treatment - Secondary treatment (activated sludge) - Tertiary treatment	OTNE: 21480 HHCB: 3500	OTNE: 1930 - 6800 HHCB: 1160 - 1750	---	- On average, each inhabitant emits around 179 µg day^{-1} of HHCB and 574 µg day^{-1} of OHTN (removal 63-83%) - Sorption to sludge seems to be the predominant removal process.	(Klaschka et al. 2013)
HHCB, MX	Spain	Urban - Primary treatment - Secondary treatment	HHCB: 2100 MX: nd	HHCB: 1100 MX: nd	---	---	(Pintado-Herrera et al. 2013)
AHTN, HHCB	China	Urban (domestic + industrial) A: anoxic / anaerobic /oxic biological treatment B: Activated sludge treatment + anaerobic /anoxic / oxic	WWTP A: AHTN: 25 HHCB: 125 WWTP B: AHTN: 25 HHCB: 200	WWTP A: AHTN: 10 HHCB: 40 WWTP B: AHTN: 2 HHCB: 100	---	- Musks concentrations increased slightly along the primary process - desorption from inorganic sediments in aerated grit chamber tanks. - Levels decreased in the biological treatment due to sorption into sludge. - Removal efficiencies vary between 60.5% for HHCB and 72.8% for AHTN.	(Ren et al. 2013)
Exaltone, Exaltolide, Muscone, Habanolide, Ambrettolide, Musk MC4, Civetone, Musk-NN	Spain	Urban (domestic + industrial) - Primary treatment - Secondary treatment (activated sludge)	---	---	Mixture of primary and secondary sludge, anaerobically digested and dehydrated: Exaltone: 0.05 – 0.08 Exaltolide: nd – 0.13 Muscone: nd – 2.0 Habanolide: nd – 0.50 Ambrettolide: 0.025 – 0.85 Musk MC4: nd – 0.19 Civetone: nd – 0.13 Musk-NN: 0.025 – 1.45	- Ambrettolide, exaltone and musk NN were the most frequently detected compounds.	(Vallecillos et al. 2013)
ADBI, HHCB, MK, MX, AHMI, AHTN, ATII	Spain	Urban - Primary treatment - Secondary treatment (activated sludge) - Tertiary treatment (flocculation/ coagulation, clarification, filtration, UV disinfection)	---	HHCB: 61	---	- Additional treatments (ultrafiltration, reverse osmosis and UV disinfection)	---
CB, AHTN, DPMI, H H		Urban - Primary treatment					

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

HHCB: 4772 – 13399 AHTN: 509 – 2337 DPMI: nd – 427	AHTN: 37.5 ADBI, AHMI, ATII, MK, MX: nd	- HHCB and AHTN were detected in all analysed samples. - HHCB and AHTN were the most commonly found and abundant compounds.					(Cabeza et al. 2012)
HHCB: 2928 – 10525 AHTN: 328 – 1754 DPMI: 77 – 421							
ADBI, AHMI, ATII, MX, MK	USA	- Secondary treatment - Tertiary treatment	ADBI: nd – 45 AHMI: nd – 950 MK: nd – 812 ATII, MX: nd	AHMI: nd – 129 MK: nd – 177 ADBI, ATII, MX: nd	---		(Chase et al. 2012)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
HHCB, AHTN, DPMI, Ambrettolide	Denmark	Urban 20 years sludge treatment reed bed	---	---	HHCB: 250 - 2500 AHTN: 1900 - 5000 DPMI: 10 - 50 Ambrettolide: 10 - 150	- The results showed that deposited sludge suffers a dewatering process, reaching a dry matter content of approximately 29% and in addition up to a third of the organic content of the sludge is mineralized. - The concentrations decreased with depth in the vertical profile and ranged from 10 to 5000 ng g^{-1}. - Musk fragrances are generally degraded during storage in the STRB, with attenuations ranging from 40 to 98%.	(Matamoros et al. 2012)
ADBI, AHMI, AHTN, ATII, DPMI, HHCB, MA, MK, MM, MX	Spain	Urban	HHCB: 295 ± 43 AHTN: 138 ± 12 ADBI: 25 ± 9 MK: 24 ± 7 AHMI, AHTN, ATII, DPMI, MA, MM, MX: nd	HHCB: 259 ± 54 AHTN: 82 ± 6 ADBI, AHMI, AHTN, ATII, DPMI, MA, MK, MM, MX: nd	---	- HHCB and AHTN were the most commonly detected compounds.	(Posada-Ureta et al. 2012)
DPMI, ADBI, AHMI, ATII, HHCB, AHTN, MX, MM, MK, HHCB-lactone	Spain	Urban (domestic) - Primary treatment - Secondary treatment - Additional treatment (reverse osmosis)	DPMI: nd – 112 ADBI: nd – 32 AHMI: nd – 31 ATII: nd – 27 HHCB: 360 – 2219 AHTN: 19 – 264 MX: 45 – 232	Secondary effluent DPMI: nd – 82 ADBI: nd – 25 AHMI: nd – 11 HHCB: 288 – 954 AHTN: 25 – 28 MX: 40 – 96 ATII, MM: nd MK: nd – 20 HHCB-lactone: 120 – 532	---	---	(Ramírez et al. 2012)
DPMI, ADBI, AHMI,		Urban (industrial)					

- Toxic waste disposal - Oil recycling - Synthesis of additives, emulsions and detergents	M M : n d	– 13 ATII: nd – 10 HHCB: nd – 57 AHTN: 14 – 21 MX: nd – 20 MM: nd MK: nd – 19 HHCB-lactone: nd – 153	RO Effluent DPMI: nd – 0.3 ADBI: nd – 1.3 AHMI: nd – 1.0 HHCB: <0.5 – 1.0 AHTN: 0.2- 0.3 MX: 0.3 – 1.1		
	M K : n d – 8 4		ATII, MM, MK, HHCB-lactone: nd	---	---
	HHC B- lacto ne: 142 – 690		DPMI: nd – 137 ADBI: nd – 12	ez et	(Ramír al. 2012)
	D P M I : n d – 1 2 3 2 A D B I : 1 . 7 9 – 2 6 A H M I : n d		HHCB : nd – 64 AHTN : 5.7 – 20 AHMI, ATII, MX, MM, MK: nd HHCB-lactone: nd – 143		

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
Musk MC4, Muscone, Musk-NN, Habanolide, Exaltolide, Ambrettolide, Civetone, Exaltone	Spain	Urban	Exaltone: 1500 – 2900 Exaltolide: nd - 1500 Muscone: nd - 2500 Habanolide: 15 - 1600 Ambrettolide: 2100 - 9300 Musk MC4:10 - 100 Civetone:100 - 2200 Musk-NN: 10 - 500	Exaltone: 400 – 2300 Exaltolide: nd - 500 Muscone: nd - 100 Habanolide: nd - 500 Ambrettolide: 10 - 2500 Musk MC4: 10 - 40 Civetone: 10 - 1800 Musk-NN: 10 - 20	---	---	(Vallecillos et al. 2012a)
DPMI, ADBI, AHMI, ATII, HHCB, AHTN, MX, MM, MK, HHCB-lactone	Spain	Urban	DPMI: <50 ADBI: <50 AHMI: <50 ATII: nd – 650 HHCB: 330 – 2060 AHTN: <70 – 320 MX, MM: nd MK: nd – <100 HHCB-lactone: nd – <100	DPMI: nd – <50 ADBI: nd – <50 AHMI: nd – <50 ATII: nd – <50 HHCB: 90 – 700 AHTN: nd – 140 MX, MM, MK: nd HHCB-lactone: nd – <100	---	- All synthetic musks except HHCB were removed during the WWTP process. - HHCB-lactone remained in the final effluent as a result of the degradation of HHCB during treatment.	(Vallecillos et al. 2012b)
MA, MX, MK, Musk muscone, Globalide, Thibetolide, HHCB, MM, Musk Ambretolide, Ethylene brassilate, AHTN, DPMI, AHMI, ADBI, ATII, MT, Romandolide, Helvetolide	Spain	Urban	HHCB: 900 – 3568 DPMI: 70 – 530 Romandolide: nd – 45 ADBI: nd – 70 MX: nd – 91 AHTN: nd – 79 Helvetolide: nd – 58 MK: 58 – 61 Musk muscone, Ambretolide, MT, MA, Globalide, Thibetolide, MM, Ethylene brassilate, AHMI, ATII: nd	HHCB: 800 – 3021 DPMI: 100 – 400 Romandolide: nd – 56 ADBI: nd – 80 MX: 58 – 61 AHTN: nd – 60 Helvetolide: nd – 70 MK: 32 – 69 Musk muscone, Ambretolide, MT, MA, Globalide, Thibetolide, MM, Ethylene brassilate, AHMI, ATII: nd	---	-HHCB was detected in all samples. - HHCB, ADBI and MK were not effectively removed in the WWTPs. - Some musks showed effluent concentrations higher than the influents, which could be explained by inaccurate sampling or erroneous estimate of hydraulic retention time.	(Arbulu et al. 2011)
AHTN, HHCB, ADBI, AHMI, ATII, MK, MX	China	Urban	HHCB: 30.9 – 3038.97 AHTN: 28.61 – 1486.1 MX: <1.2 – 22.95 MK: 52.25 – 165.8 ADBI, AHMI, ATII: nd	HHCB: 30.4 – 685.62 AHTN: 14.26 – 195.3 MK: 22.77 – 91.6 ADBI, AHMI, ATII, MX: nd	HHCB: 260 – 12590 AHTN:10 – 2560 MK: 130 – 530 ATII: 15 – 300 MX: <3.3 AHMI, ADBI: nd	- The removal efficiencies of HHCB and AHTN were in the range of 14.3-98.0% and 18.5-98.7%, respectively. - The results showed that the outflow for HHCB and AHTN through effluents discharge into environment was 1.8-685.6 and 1.6-195.3 g day^{-1}, respectively.	(Hu et al. 2011b)
MA, MX, MT, MM,				MA: <33 MX: <19			(López-

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

MK	Spain	Effluent	MT: <6 MM: <4 MK: <7	---	---	Nogueroles et al. 2011)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
DPMI, ADBI, AHMI, ATII, HHCB, AHTN, MX, MM, MK	Spain	Urban - Primary treatment - Secondary treatment - Additional treatment (reverse osmosis)	DPMI: 15.7 – 87.7 ADBI: 3.6 – 35.4 AHMI: <0.10 – 25.6 ATII: nd – 8.1 HHCB: 476 – 2069 AHTN: 17.7 – 78.7 MX: 22.0 – 29.1 MM: nd MK: <0.15 – 20.3	Secondary effluent DPMI: 29.8 – 43.3 ADBI: <0.20 – 4.56 AHMI: <0.10 – 4.15 ATII: nd HHCB: 233 – 1432 AHTN: 25.4 – 93.6 MX: 13.1 – 126 MM: nd MK: 29.2 – 53.5 RO Effluent DPMI: <0.30 – 0.67 ADBI: nd – 0.24 AHMI: <0.10 – 0.17 HHCB: nd – 1.45 AHTN: nd – 0.35 MX: nd – 0.3 ATII, MM, MK: nd	---	---	(Ramírez et al. 2011)
HHCB, AHTN, DPMI, ADBI, ATII, AHMI	Portugal	Urban (domestic)	HHCB: 50 - 2780 AHTN: 18 - 816 DPMI: 66 - 4040 ADBI: 6 - 1442 ATII: 7 - 676 AHMI: nd	---	---	- HHCB, AHTN, DPMI, ADBI and ATII were detected in the analysed samples. - Hiher concentrations were observed during the dayand lower at night.	(Salgado et al. 2011)
HHCB, MX, MK, AHTN, ADBI	USA	Urban	- Primary	Aeration tank effluent treatment - Secondary treatment - Tertiary treatment	---		

MX, MK, ADBI, AHTN; nd HHCB:
7860 - 25000

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

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Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
HHCB, AHTN, ADBI, AHMI, ATII, DPMI, MA, MX, MM, MT, MK	Korea	Rural (agricultural - livestock) Urban (domestic, industrial – pharmaceutical company)	---	---	Dewatered sludge Rural (agricultural - livestock) ADBI, AHMI, MK: <3 HHCB: <7 - 1175 AHTN: <7 - 308 DPMI, ATII, MA, MX, MM, MT: nd ∑Musks: nd – 1480 Urban (domestic) ADBI: <3 - 250 AHMI: <3 - 235 HHCB: 15900 - 82100 AHTN: 4480 - 28800 MK: <3 - 1900 DPMI, ATII, MA, MX, MM, MT: nd ∑Musks: 20500 - 108000 Urban (industrial - pharmaceutical company) ADBI, AHMI, MK: <3 HHCB: 9090 AHTN: 1370 DPMI, ATII, MA, MX, MM, MT: nd ∑Musks: 10500	- HHCB was the predominant musk, followed by AHTN. - The highest total concentration was detected in the sludge sample from the WWTP located in the biggest city. - Total concentrations of synthetic musks in the sludge of the urban WWTPs were much higher than those of the rural areas and livestock. - Total synthetic musk levels were related with the volume of treated sewage, degree of urbanization and the living habits of the locals.	(Guo et al. 2010)
MK, MX, HHCB, AHTN	34 35 36 37	Urban (domestic, industrial)	Korea	- Primary treatment - Secondary treatment	(biological)	- Household sewage was the main source of contamination. -Average removals of HHCB, AHTN and MK in the conventional activated sludge treatment were between 53 and 91 or chemical) - Additional treatment (filtration, disinfection)	MK: 220 – 1550 MX: nd – 220 HHCB: 2450 – 4450

AHTN: 450 – 1100

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

	MK: 85 – 542 MX: nd HHCB: 500 – 1875 AHTN: 167 – 417	---	56%. - Modified versions of activated sludge treatment (modified Ludzack-Ettinger, sequential batch reactor or anoxic/oxic treatment) conducted to slightly higher removals than the conventional process (64-72%). - Chemical coagulation treatment (Densadeg process) had lower removal efficiencies (35%). - Chlorination and UV disinfection as an additional treatment showed removals below 10%.	(Lee et al. 2010)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent ($ng\ L^{-1}$)	Effluent ($ng\ L^{-1}$)	Sludge ($ng\ g^{-1}$ dw)	Observations	Reference
HHCB, AHTN, MX, MK	China	Urban (domestic + industrial) - Primary treatment - Secondary treatment (biological)	Raw influent HHCB: 1478.3 – 2214.3 AHTN: 553.5 – 1037.7 MX: 63.0 – 164.0 MK: 74.5 – 161.3	Primary effluent HHCB: 765.9 – 954.5 AHTN: 248.1 – 400.5 MX: 14.4 – 80.4 MK: 20.5 – 52.8 Final effluent HHCB: 181.1 – 242.2 AHTN: 46.7 – 88.3 MX: nd – 6.5 MK: 6.7 – 18.5	Primary sludge HHCB: 2605.6 – 3293.3 AHTN: 676.6 – 1188.9 MX: 1.1 – 7.1 MK: 4.4 – 7.1 Treated dewatered sludge HHCB: 3281.3 - 3560.2 AHTN: 793.1 - 1529.2 MX: nd MK: nd – 28.8	- HHCB and AHTN were detected in all the samples. - The highest input loading of total synthetic musks occurred in summer with 1789 µg $inhabitant^{-1}day^{-1}$. The lowest loading was in spring with 980 µg $inhabitant^{-1}day^{-1}$. - Removal rates of total synthetic musks ranged from 86.9-94.5% in the water line. - Nitromusks showed better average removal in the bioreactor (88.5% for MX and 40.0% for MK) than polycyclic musks (29.8% HHCB and 39.3 AHTN). - Polycyclic musks seem to be readily adsorbed to biosolids: • 11-35% of the influent loadings were partitioned to the sludge after the primary treatment; • 17-58% of those were attached to the treated sludge - Nitromusks were mainly removed by biodegradation or photolysis (<10% of input amounts detected in biosolids). - Overall removal ranged from 34-75% for HHCB and AHTN. - More than 60% MK and almost all the MX entering in the WWTP were removed.	(Lv et al. 2010)
HHCB, AHTN	Germany	Urban	---	HHCB: 1374 ± 14 AHTN: 110 ± 4	---	---	(Moeder et al. 2010)
HHCB, MK, MX, ADBI, AHTN	Spain	Urban (domestic + industrial) - Primary treatment - Secondary treatment (anaerobic/anoxic/oxic biological treatment)	HHCB: <56 – 24971 (10022) AHTN: <53 - 1932 (952) ADBI: <30 MK, MX: na	HHCB: <56 – 2766 (1225) AHTN: <53 - 315 (146) MK, MX, ADBI: na	---	- Removal rates of t HHCB and AHTN ranged from 84.7 to 87.8%. - At lab scale, ozonation was tested in the effluents from the WWTP. MX was completely refractory to ozone, while MK (38%), AHTN (72%) and HHCB (83%) were partially removed with an ozone dose of 340 µM.	(Rosal et al. 2010)
ADBI, HHCB, AHTN, MK	Portugal	Urban	ADBI: <19 HHCB: 4670 AHTN: 1290 MK: <12	ADBI: <19 HHCB: 1270 AHTN: 259 MK: <12	---	---	(Silva and Nogueira 2010)
MX, MK, HHCB, AHTN, ADBI, AHMI,	UK	Urban A: Chemically-enhanced primary treatment +	---	Dissolved concentrations HHCB: 987 – 2098 AHTN: 55 – 159 ADBI: <1 – 13 AHMI: <1 – 9 MX: 4 – 7 MK: <1– 30 Pentadecanolide: nd	---	- In WWTP A, high levels of HHCB and AHTN were detected in	(Sumner et

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Pentadecanolide	Biological activated filters	ng l^{-1}	particles due to the type of treatment applied.	al. 2010)
	B: Activated sludge + UV treatment	Particulate concentrations (ng g^{-1}) HHCB: 17 – 79 AHTN: nd – 18 ADBI: nd – 6 AHMI: nd – 13 MX: nd – 5 MK: nd - <1		

Pentadecanolide: nd

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent ($ng\ L^{-1}$)	Effluent ($ng\ L^{-1}$)	Sludge ($ng\ g^{-1}$ dw)	Observations	Reference
					Dewatered sludge		
DPMI, ADBI, AHMI, ATII, HHCB, AHTN	China (Taiwan)	Urban	---	---	DPMI: 1.2 – 2.5 ADBI, AHMI, ATII: nd HHCB: 1.4 – 2.8 AHTN: 0.5 – 0.7	---	(Wu and Ding 2010)
ADBI, AHMI, ATII, HHCB, MX, AHTN, MK	Spain	Rural (agriculture) Urban (domestic, industrial) - Primary treatment - Secondary treatment (biological)	---	ADBI: 11 – 30 (23) AHMI: 13 – 16 (14) ATII: 20 – 22 (20) HHCB: 1259 – 8697 (4120) MX: 59 – 203 (104) AHTN: 56 – 981 (365) MK: 34 – 218 (107)	---	- HHCB, AHTN and MK were detected in most of the effluent wastewater. - ADBI, AHMI, ATII and MX were observed in less than 25% of the samples.	(Gómez et al. 2009)
HHCB, AHTN, MX, MK	China	Urban (domestic + industrial) - Primary treatment - Secondary treatment	HHCB: 1290.4 ± 90.4 AHTN: 378.2 ± 27.2 MX: 80.4 ± 7.1 MK: 72.1 ± 3.2	HHCB: 212.6 ± 16.5 AHTN: 38.7 ± 2.6 MX: <0.09 MK: 8.4 ± 0.5	---	- The removal efficiencies of HHCB and AHTN were 83.5 and 89.8%.	(Lv et al. 2009)
HHCB, AHTN	Germany	Urban (domestic + industrial)	HHCB: 600 – 1300 AHTN: 80 – 400	HHCB: 500 – 1000 AHTN: 70 – 95	---	- Synthetic musks followed no seasonal pattern in the effluent and were characterized by highly variable daily loads (HHCB: 10-400 g day^{-1}; AHTN: 5-45 g day^{-1}). - Significantly lower concentrations during summer months compared to winter were also reported.	(Musolff et al. 2009)
DPMI, ADBI, AHMI, ATII, HHCB, AHTN	China (Taiwan)	Urban (domestic sewage)	DPMI, ADBI, ATII: nd AHMI: nd – 19.2 HHCB: 3.2 – 37.3 AHTN: 1.2 – 22.2	---	---	---	(Wang and Ding 2009)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
HHCB, AHTN	China	Urban A: anaerobic / anoxic / oxic biological treatment B: anoxic / oxic biological treatment C: bio-selection / extended aeration oxidized ditch / anaerobic biological treatment	WWTP A: HHCB: 1649.0 AHTN: 111.9 WWTP B: HHCB: 1251.4 AHTN: 256.3 WWTP C: HHCB: 3003.8 AHTN: 286.3	WWTP A: HHCB: 492.8 AHTN: 47.3 WWTP B: HHCB: 729.9 AHTN: 190.9 WWTP C: HHCB: 1258.3 AHTN: 89.3	WWTP A: **Anaerobic:** HHCB: 3700 AHTN: 1100 **Anoxic:** HHCB: 2500 AHTN: 700 **Oxic:** HHCB: 4800 AHTN: 1000 WWTP B: **Anoxic:** HHCB: 5300 AHTN: 6100 **Oxic:** HHCB: 9000 AHTN: 13100 WWTP C: **Bio-seletion:** HHCB: 16800 AHTN: 2900 **Oxidized ditch:** HHCB: 17000 AHTN: 6100 **Anaerobic:** HHCB: 10900 AHTN: 2100	- The removal efficiencies of HHCB and AHTN were between 41.7 and 71.6% and 25.5-72.8%, respectively. - Musks concentrations in the sludge samples were several orders of magnitude higher than those in the sewage.	(Zhou et al. 2009)
DPMI, ADBI, AHMI, ATII, HHCB, AHTN, MX, MM, MK			DPMI, ADBI, ATII, MX, MM, MK: nd	DPMI, ADBI, AHMI, MX, MM: nd			

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

	Spain	Urban		AHMI: 31 ± 2 HHCB: 718 ± 44 AHTN: 99 ± 7	ATII: < 28 HHCB: 2893 ± 269 AHTN: 334 ± 30 MK: 113 ± 6	---	---	(Reguciro et al. 2008)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
DPMI, ADBI, AHMI, ATII, AHTN, HHCB	China (Hong Kong)	Urban A. Primary treatment B. Secondary treatment (biological) C. Chemically-enhanced primary treatment	---	---	Dewatered sludge WWTP A DPMI, ATII: nd ADBI: <0.021 AHMI: <0.02 AHTN: 932 – 3220 (2120±1150) HHCB: 4140 – 7240 (6110±1710) ∑Musks: 5180 – 10600 (8340 ±2810) WWTP B DPMI, ATII: nd ADBI: <0.021 - 186 AHMI: <0.02 - 670 AHTN: 475 – 12500 HHCB: 3580 - 58100 ∑Musks: 4190 – 71000 WWTP C DPMI, ATII: nd ADBI: 83 - 351 AHMI: 71 - 209 AHTN: 5830 - 13900 HHCB: 22400 – 78600 ∑Musks: 28400 - 93000	- Total musks levels in sludge from plants with chemically enhanced primary treatment were significantly higher than those using secondary or simple primary treatment. - Musks were mainly removed through sorption to sewage sludge.	(Shek et al. 2008)
HHCB, AHTN, MX, MK, DPMI, ATII, AHMI, ADBI	China	Urban - Primary treatment - Secondary treatment (activated sludge)	HHCB: 1467 – 3430 (2300) AHTN: 435 – 1043 (717) MX: <4 MK: 418 – 1010 (743) DPMI, ATII, AHMI, ADBI: nd	HHCB: 233 – 336 (297) AHTN: 74 – 94 (86) MX: <4 MK: 43 – 101 (80) DPMI, ATII, AHMI, ADBI: nd	---	---	(Zhang et al. 2008)
DPMI, ADBI, AHMI, ATII, AHTN, HHCB	China	Urban (industrial - cosmetic plant)	DPMI: 20340 – 29540 (24940) ADBI: 5350 – 7730 (6540) AHMI: 3730 – 5660 (4700) HHCB: 503880 – 595480 (549680) AHTN: 61090 – 68120 (64600) ATII: nd ∑ Musks: 590650 – 700870	Primary sludge DPMI: 40750 – 50430 (45590) ADBI: 1460 – 2590 (2030) (645760)	DPMI: 1730 – 2220 (1970) ADBI: 500 – 730 (620) HHCB: 30570 – 33540 (32060) AHTN: 4840 – 5970 (5410) AHMI, ATII: nd ∑ Musks: 37640 – 42460 (40050)	AHMI: 1380 – 2120 (1780) HHCB: 479730 – 545170 (512450) AHTN: 49690 – 68130 (58910) ATII: nd

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Secondary sludge DPMI: 42640 – 52380 (47510) ADBI: 2120 – 4010 (3070) AHMI: 2130 – 3650 (2890) HHCB: 530080 – 601270 (565670) AHTN: 82870 – 107610 (95240) ATII: nd	- Average removal efficiencies of 92.1, 90.6, 94.2, 91.6 and 93.8 for DPMI, ADBI, HHCB, AHTN and total polycyclic musks, respectively. - Polycyclic musk concentrations increased quickly from the primary to the secondary sludge - adsorption to sludge.	(Chen et al. 2007)	

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
HHCB, AHTN, HHCB-lactone	USA	A: Rural (domestic + commercial) B: Urban (domestic + commercial) - Primary treatment - Secondary treatment - Tertiary treatment	WWTP A: HHCB: 43 – 7032 (2499) AHTN: 112 – 5396 (1914) HHCB-lactone: 140 – 300 (232) WWTP B: HHCB: 284 – 522 (420) AHTN: 257 – 572 (388) HHCB-lactone: 107 – 766 (371)	WWTP A: HHCB: 10 – 67 (44) AHTN: 13 – 225 (130) HHCB-lactone: 73 – 467 (229) WWTP B: HHCB: 28 – 98 (55) AHTN: 38 – 192 (139) HHCB-lactone: 267 – 545 (378)	WWTP A: HHCB: 2000 - 21000 (9500) AHTN: 1200 - 6700 (3100) HHCB-lactone: 5600 - 10000 (7200) WWTP B: HHCB:<20 AHTN: <20 - 21 (21) HHCB-lactone: <50	- The highest concentrations of HHCB and AHTN were detected in the influent of WWTP A. - Estimated mass of total musks in the sewage entering each WWTP was between 74 and 81 g day^{-1}. - Estimated discharge was between 21 and 31 g day^{-1}. - Removal efficiencies of HHCB and AHTN ranged from 72 to 98%. - Mass of HHCB-lactone increased, suggesting oxidation of HHCB.	(Horii et al. 2007)
HHCB	Germany	Urban	---	HHCB: 1810	---	---	(Osenbruck et al. 2007)
MX, MM, MT, MK	Spain	Urban	Raw water: MX: 6.2 – 15 MM, MT: nd MK: <3.5 – 6.3 Influent MX: 7.1 ± 0.8 MM, MT: nd MK: 3.8 ± 0.4	MX: 2.4 MM, MT: nd MK: <3.5	---	---	(Polo et al. 2007)
HHCB, AHTN, HHCB-lactone	USA	Urban A: Domestic, commercial and industrial sewage B: Domestic and commercial sewage - Primary treatment - Secondary treatment	WWTP A HHCB: 4760 –12700 (9030±3010) AHTN: 1030 – 2590 (1900±629) HHCB-lactone: 741 – 1150 (897±153)	WWTP A Primary effluent HHCB: 4120 – 8150 (6730±1650) AHTN: 877 – 1660 (1400±331) HHCB-lactone: 620 – 854 (763±116) Final effluent HHCB: 2810 – 3730 (3350±455) AHTN: 585 – 807 (713±106) HHCB-lactone: 823 – 4000 (1740±1290)	Mixture of primary and secondary sludge WWTP A HHCB: 63400 – 117000 (88600±22400) AHTN: 10400 – 16800 (12600±2650) HHCB-lactone: 12900 – 22000 (17900±3960)	- The highest concentrations were measured in plant A. - HHCB and AHTN levels decreased from influent to effluent in both WWTPs (A: 63% for HHCB and AHTN, B: 46% for HHCB, 56% for AHTN). - The average concentrations of HHCB-lactone increased from influent to effluent (A: increase of 48%, B: 69%)	(Reiner et al. 2007)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

	WWTP B HHCB: 1780 – 11500 (5940±3770) AHTN: 304 – 1870 (994±613) HHCB-lactone: 146 – 942 (505±300)	WWTP B Primary effluent HHCB: 2950 – 6820 (5310±1740) AHTN: 571 – 1300 (1010±326) HHCB-lactone: 445 – 1030 (683±234) Final effluent HHCB: 2360 – 3310 (2700±358) AHTN: 495 – 673 (555±69) HHCB-lactone: 820 – 3080 (1620±882)	WWTP B HHCB: 7230 – 46100 (26600±14000) AHTN: 809 – 3250 (2730±1090) HHCB-lactone: 3160 – 19400 (12600±6210)	- HHCB, AHTN and HHCB-lactone were detected in all sludge samples. - WWTP A showed a mass load loss of 457 g day^{-1} of HHCB and 101 g day^{-1} of AHTN, whereas WWTP B a mass load loss of 286 g day^{-1} of HHCB and 39.6 g day^{-1} of AHTN.

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
					Air-dried sludge Primary sludge DPMI: nd ADBI: 173 - 278 ATII: 416 - 495 HHCB: 17500 - 25600 AHTN: 4240 - 7040 MX: nd MK: 170 – 196 Activated sludge DPMI: nd ADBI: 195 - 219 ATII: 472 - 586 HHCB: 20500 - 23800 AHTN: 4910 - 5870		
DPMI, ADBI, AHMI, ATII, HHCB, AHTN, MA, MX, MM, MT, MK	41 42	Canada	Urban - Primary treatment - Secondary treatment (activated sludge)		--- ---	MX: nd-138 MK: 306 – 445 Centrifuged sludge Primary sludge DPMI: nd ADBI: 199 - 361 ATII: 435 - 1220 HHCB: 20100 - 36500 AHTN: 6130 - 9300 MX: 50 - 392 MK: 150 – 619 Activated sludge DPMI: nd ADBI: 470 - 729 ATII: 1980 - 3210 HHCB: 45300 - 73700 AHTN: 10900 - 17000 MX: 284 - 1230 MK: 619 – 1630	- Proportions of synthetic musks present in the liquid phase of sludge samples were less than 5% compared to concentrations in the sludge solids.

(Smyth et al. 2007)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent ($ng\ L^{-1}$)	Effluent ($ng\ L^{-1}$)	Sludge ($ng\ g^{-1}$ dw)	Observations	Reference
DPMI, ADBI, AHMI, ATII, HHCB, AHTN	China	Urban (domestic + industrial) - Primary treatment - Secondary treatment (activated sludge)	DPMI: 0.19 – 0.34 ADBI: nd – <10 AHMI, ATII: nd HHCB: 1.01 – 3.08 AHTN: 0.12 – 0.16	Primary effluent DPMI: 0.21 – 0.32 ADBI: nd – <10 AHMI, ATII: nd HHCB: 1.15 – 3.19 AHTN: 0.12 – 0.16 Final effluent DPMI: 0.06 – 0.10 ADBI, AHMI: <10 ATII: nd HHCB: 0.95 – 2.05 AHTN: 0.10 – 0.14	---	- After gravitational settling in the primary settler, about 50% DPMI, < 57% AHTN and 20.7-74.5% HHCB were removed with particles sedimentation. - After primary and secondary treatment 61.3-74.5% DPMI, 85.6-96.9% HHCB and 87.7-95.9% AHTN were removed.	(Zeng et al. 2007)
HHCB, AHTN, ADBI, AHDI, DPMI, ATII	Switzerland	Rural (domestic + industrial) - Primary treatment - Secondary treatment (activated sludge)	HHCB: 2290 - 6810 AHTN: 1130 - 2000 ADBI: 90 - 330 AHDI: 30 - 110 DPMI: 60 - 100 ATII: nd	HHCB: 570 - 1030 AHTN: 190 - 500 ADBI: nd - 40 AHDI: 30 - 110 ATII, DPMI: nd	Raw sludge HHCB: 9420 - 11670 AHTN: 2950 - 3870 ADBI: 180 - 440 AHDI: 90 - 260 ATII: 150 - 210 DPMI: 10 - 20 Digested sludge HHCB: 9390 AHTN: 3220 ADBI: 250 AHDI: 110 ATII: 180 DPMI: 30	---	(Kupper et al. 2006)
ADBI, AHMI, ATII, HHCB, AHTN	Canada	Urban (domestic + industrial) - Primary treatment - Secondary treatment (activated sludge, lagoons or activated sludge followed by media filtration)	ADBI: 37.2 AHMI: 42.0 ATII: 168 HHCB: 2031 AHTN: 804	ADBI: 25 AHMI: nd ATII: 45 HHCB: 751 AHTN: 274	---	- Lagoon systems were the most effective type of treatment for musks reduction (98-99% for HHCB and AHTN). - Activated sludge systems reduce the musks concentrations between 37 and 65%.	(Lishman et al. 2006)
HHCB, AHTN, ADBI, AHDI, ATII, AETT	42 43 44	_____	*Concentration in ng g^{-1}* HHCB: 1.44 – 1.79 Germany an (domestic +	*Concentration in ng g^{-1}* HHCB: 0.14 – 0.36 industrial) Urb R u r a	Activated sludge HHCB: 2700 – 14400 AHTN: 800 - 4700 ADBI: 30 - 180 AHDI: 80 - 310 ATII: 110 - 360 l	- In the water line, higher removal rates were found during summer (66.5-85.9%). - In winter, synthetic musks concentrations in activated sludge samples were generally higher compared to summer AHTN: 0.41 – 0.57 ADBI: 0.017 – 0.018 AHDI: 0.025 – 0.059	ATII: 0.021 – 0.032

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

AHTN: 0.05 – 0.08 ADBI: 0.005 – 0.007 AHDI: 0.009 – 0.010 ATII: 0.004 – 0.005	AETT: 30 – 460 Dried sludge HHCB: 6020 – 23000 AHTN: 1970 - 6940 ADBI: 80 - 340 AHDI: 150 - 320 ATII: 150 - 590	measurements. - Dried sludge present higher contamination levels that may be caused by degradation of organic matter (24-57% of increase over values determined for liquid sludge). - Treatment process led to a dramatic reduction of the compounds in effluent, and accumulation in the solid phase.	(Müller et al. 2008)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent ($ng\ L^{-1}$)	Effluent ($ng\ L^{-1}$)	Sludge ($ng\ g^{-1}$ dw)	Observations	Reference
DPMI, ADBI, AHMI, ATII, HHCB, AHTN, MA, MX, MM, MT, MK	Canada	Urban (domestic + industrial) - Primary treatment - Secondary treatment (activated sludge) - Tertiary treatment (UV disinfection)	DPMI: 6.3 – 13.5 (8.5) ADBI: 4.8 – 8.2 (5.8) AHMI: 4.3 – 5.5 (4.8) ATII: 13.2 – 31.2 (18.9) HHCB: 246.7 – 567.5 (390.2) AHTN: 47.2 – 136.7 (85.9) MX: 10.8 – 16.0 (13.6) MK: 12.5 – 15.5 (14.5) MA, MM, MT: nd	Primary effluent DPMI: 5.1 – 9.4 (7.0) ADBI: 3.5 – 5.8 (4.4) AHMI: 2.8 – 3.5 (3.2) ATII: 9.2 – 24.1 (14.8) HHCB: 214.3 – 472.1 (324.8) AHTN: 41.0– 100.7 (66.3) MX: 8.8 – 11.4 (9.7) MK: 9.8 – 10.9 (10.5) MA, MM, MT: nd Final effluent DPMI: 2.5 – 4.7 (3.9) ADBI: 2.3 – 4.0 (2.9) AHMI: 2.3 – 3.3 (2.7) ATII: 5.9 – 10.0 (7.3) HHCB: 138.8 – 234.0 (173.1) AHTN: 24.7 – 62.8 (41.5) MX: 4.3 – 7.6 (6.4) MK: 8.3 – 8.5 (8.4) MA, MM, MT: nd	Raw sludge DPMI: 12.8 – 48.4 (31.4) ADBI: 16.1 – 29.3 (23.6) AHMI: 11.3 – 30.0 (20.1) ATII: 92.8 – 244.3 (198.5) HHCB: 2482.4 – 4514.1 (3302.5) AHTN: 408.6– 929.4 (720.1) MX: nd – 83.7 (76.6) MK: nd – 48.1 (39.8) MA, MM, MT: nd Digested sludge DPMI: 38.8 – 68.4 (57.3) ADBI: 44.5 – 61.4 (51.2) AHMI: 21.2 – 43.0 (33.8) ATII: 501.9 – 259.4 (413.2) HHCB: 5772.7 – 7896.7 (6788.4) AHTN: 1040.2– 1569.0 (1349.4) MX: 62.0 – 133.5 (95.1) MK: nd – 71.6 (53.0) MA, MM, MT: nd	- ADBI, AHMI, ATII, HHCB and AHTN were detected in all samples of sludge/biosolids. - In the solid phase, there was a clear trend for musks to accumulate in return activated sludge. - Most musks exhibited decreasing concentration during the colder months. - The removal efficiencies in the primary treatment ranged from 17.9 to 26.3%. - The average overall removal (primary + secondary treatment) ranged from 51.6 to 68.1%. - UV disinfection failed to remove musks. - The removal of synthetic musks is associated with the removal of total suspended solids. - The mass balance to HHCB and AHTN showed that 3% of these musks were discharged via suspended solids in final effluent, 73% in the form of biosolids and only 24% remained in the final aqueous effluent.	(Yang and Metcalfe 2006)
AHTN, HHCB, HHCB-lactone	Germany	? - Primary treatment - Secondary treatment (activated sludge)	---	AHTN: 20 – 300 HHCB: 100 – 600 HHCB-lactone: 20 – 300	---	- HHCB may be transformed to some extent to HHCB-lactone by biological processes. - Removals between 76 and 87% were reached for HHCB and AHTN.	(Bester 2005)
AHTN, HHCB	Austria	Rural (domestic) - Primary treatment - Secondary treatment A: activated sludge + membrane bioreactor at pilot scale B: Activated sludge	WWTP A AHTN: 989 – 1106 HHCB: 3060 – 4443 WWTP B AHTN: 210 - 450 HHCB: 830 - 1400	WWTP A Activated sludge AHTN: 144 – 170 HHCB: 451 – 652 Activated sludge + Membrane bioreactor AHTN: 92 - 163 HHCB: 373 - 536 WWTP B AHTN: 160 - 170 HHCB: 535 - 870	---	- 80-95% removals were achieved for AHTN and HHCB in WWTP A. - In WWTP B, none or only slight removal rates were observed (about 60%).	(Clara et al. 2005)
		Urban			Activated sludge AHTN: 2300 - 4300 HHCB: 4500 - 8500	- During digestion the solid mass is reduced up to	

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

AHTN, HHCB	Switzerland	- Primary treatment - Secondary treatment (activated sludge)	---	----	Digested sludge AHTN: 6600 HHCB:15000	50-70%, leading to an increase in synthetic musks levels.	(Ternes et al. 2005)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent ($ng\ L^{-1}$)	Effluent ($ng\ L^{-1}$)	Sludge ($ng\ g^{-1}$ dw)	Observations	Reference
AHTN, HHCB	Germany	Urban - Primary treatment - Secondary treatment (activated sludge) - Tertiary treatment	---	----	Activated sludge AHTN: 1400 - 2600 HHCB: 5200 - 6500	- Same as previous row.	(Ternes et al. 2005)
DPMI, ADBI, AHMI, ATII, HHCB, AHTN	China	Urban A: Domestic + industrial B: Domestic C: Industrial - cosmetic plants D: Industrial - food plant	---	---	WWTP A DPMI: 599 – 1004 ADBI: 192 - 210 AHMI: <LOD – 227 ATII: nd HHCB: 5656 - 21214 AHTN: 768 - 6195 WWTP B DPMI: 1004 ADBI: 207 AHMI: 112 ATII: nd HHCB: 5416 AHTN: 715 WWTP C DPMI: 2705 - 51604 ADBI: 302 - 4275 AHMI: <LOD - 4888 ATII: nd HHCB: 32061 - 703681 AHTN: 8557 - 169284 WWTP D DPMI: 972 ADBI: <LOD AHMI, ATII: nd HHCB: 82 AHTN: 54	- Concentrations were high in samples from WWTP C - plant producing household and personal care products.	(Zeng et al. 2005)
DPMI, AHDI, ATII, AHTN, HHCB, HHCB-lactone	42 43 44	Switzerland	Urban (domestic + industrial)	HHCB: 5390 – 9020 (6900±1500) AHTN: 1240 – 2280 (1520±380) ADBI: 50 – 110 (80±20) AHDI: 100 – 340 (200±80) ATII: 90 – 320 (170±80) DPMI: 20 – 50 (30±10)	Activated sludge HHCB-lactone: 390 – 500 (430±40)	HHCB: 730 – 1080 (860±130) AHTN: 180 – 370 (250±70) ADBI: <20 (20) AHDI: 50 – 90 (70±10) ATII: 15 – 30 (20) DPMI: <10	HHCB-lactone: 680 – 1190 (900±220)

Table 1 Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

HHCB: 3170 – 5270 (4300±640) AHTN: 1250 – 2060 (1720±260) ADBI: 50 – 70 (60±10) AHDI: 170 – 240 (210±30) ATII: 120 – 210 (170±30) DPMI: nd HHCB-lactone: 1280 – 1570 (1410±90)	- The highest daily loads in influents were observed for HHCB, AHTN and HHCB-lactone. The loads were highest during the weekend and on Monday. - Mean removal rates ranged from 61% (AHDI) to 87% (HHCB and ATII).	(Berset et al. 2004)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
AHTN, HHCB, HHCB-lactone	Germany	Urban (domestic + industrial – brewing) - Primary treatment - Secondary treatment (activated sludge)	AHTN: 427 – 713 (583±103) HHCB: 1409 – 2325 (1941±352) HHCB-lactone: 170 – 270 (231±42)	AHTN: 197 – 240 (212±17) HHCB: 652 – 795 (695±58) HHCB-lactone: 335 – 420 (367±34)	Digested sludge AHTN: 1343 – 1746 (1525±145) HHCB: 2709 – 3342 (3068 ±244) HHCB-lactone: ---	- Removals of 64% for AHTN and HHCB were reached. - HHCB-lactone concentration increased within the plant - HHCB is transformed to HHCB-lactone during the sewage treatment process. - Most of the AHTN (80%) and HHCB (50%) were transferred to the sludge.	(Bester 2004)
HHCB, AHTN	Spain	Urban - Primary treatment - Secondary treatment (activated sludge)	HHCB: 2100 - 3400 AHTN: 900 - 1690	Primary effluent HHCB: 1400 - 1820 AHTN: 600 - 970 Biological effluent HHCB: 17720 - 45400 AHTN: 3250 – 14780 Final effluent HHCB: 490 - 600 AHTN: 150 – 200	---	- HHCB and AHTN are well removed during the primary treatment (about 40%) - adsorption onto solid particles is the key mechanism involved. - Musks were also removed during biological treatment (30-40% for HHCB and 45-50% for AHTN) mainly by sorption on activated sludge. - The overall removal efficiencies from the water phase were 70-85% for HHCB and 75-90% for AHTN.	(Carballa et al. 2004)
MK, MM, MA, MX, MT, 2-AMK, 4-AMX, 2-AMX, HHCB, AHTN, ATII, ADBI, DPMI, AHMI, AETT	USA	Urban	---	HHCB: 32.6 – 97.9 (56.9) AHTN: 21.7 – 49.7 (34.0) AHMI: 1.0 – 3.8 (2.8) ATII: nd – 51.0 (26.6) ADBI: 0.4 – 6.0 (2.7) MX: nd – 1.6 (1.1) MK: 18.0 – 45.7 (27.4) 4-AMX: nd – 33.0 (13.5) 2-AMX: nd – 1.7 (1.6) 2-AMK: nd – 4.7 (3.2)	---	---	(Osemwengie and Gerstenberger 2004)
AHTN, HHCB	Netherlands	Urban - Primary treatment - Secondary treatment (activated sludge)	Free amount AHTN: 210±3 – 480±10 HHCB: 790±10 – 1630±60	Primary effluent (soluble content) AHTN: 300±10 – 480±20 HHCB: 1050±40 – 1750±60 Primary effluent (overall amount) AHTN: 810±10 – 1640±230 HHCB: 2060±130 – 3980±460	Primary sludge (soluble content) AHTN: 310±40 – 470±60 HHCB: 1080±120 – 1590±170 Primary sludge (overall amount) AHTN: 15260±2180 – 92250±36530 HHCB: 39300±8120 – 257730±107880 Overall amount AHTN: 540±50 – 1760±90 HHCB: 1420±120 – 4300±230	- Neither biodegradation nor volatilisation contribute significantly to the removal of these synthetic musks. Removal occurs mainly via AHTN: 1240 – 1760	(Artola-Garicano et al.

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Biological effluent (soluble content) AHTN: 310±10 – 550±70 HHCB: 1210±40 – 1970±120 Biological effluent (overall amount) AHTN: 420±60 – 1200±180 HHCB: 1250±20 – 2220±90 AHTN: 570 – 1200			Waste sludge (soluble content) AHTN: 380±70 – 460±10 HHCB: nd – 1800±480 Waste sludge (overall amount) AHTN: 12380±190 – 82670±43090 HHCB: 29470±10840 – 234600±111860	sludge adsorption.	2003a) (Artola-		
AHTN, HHCB	Netherlands	Urban	HHCB: 3260 – 4300	HHCB: 1430 – 2220	---	---	Garicano et al. 2003b)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
AHTN, HHCB	Switzerland	Urban - Primary treatment - Secondary treatment (activated sludge) - Tertiary treatment	---	AHTN: 0.31 - 0.76 HHCB: 0.72 -1.95	---	---	(Buerge et al. 2003)
HHCB, AHTN, ATII, ADBI, AHMI, DPMI, MK, MX	Canada	Urban (domestic + industrial) - Primary treatment - Secondary treatment	---	DPMI, ATII, MX, MK: <1 ADBI: 4 – 19 AHMI: 2 – 6 HHCB: 205 – 1300 AHTN: 110 – 520	---	- The highest concentrations for all compounds were measured in the effluents from the WWTP that serves the most populated area (350 000 inhabitants).	(Ricking et al. 2003)
HHCB, AHTN, ATII, ADBI, AHMI, DPMI, MK, MX	Sweden	Urban (domestic + industrial) - Primary treatment - Secondary treatment -Tertiary treatment	---	DPMI, ATII, MX, MK : <1 ADBI: 2 – 8 AHMI: 2 – 5 HHCB: 157 – 423 AHTN: 42 – 104	---	- The highest concentrations for all compounds were measured in the effluents from the WWTP that serves the most populated area (79 000 inhabitants).	(Ricking et al. 2003)
MA, MX, MM, MT, MK, DPMI, ADBI, AHMI, ATII, HHCB, AHTN	UK	Urban and Rural (domestic + industrial) - Primary treatment - Secondary treatment (activated sludge or percolating filter treatments)	---	---	Digested sludge ADBI: 0.010 – 0.260 (0.071) AHMI: 0.032 – 1.100 (0.410) ATII: 0.044 – 1.100 (0.450) HHCB: 1.9 – 81 (27) AHTN: 0.120 – 16 (4.700) MA, MX, MM, MT, MK, DPMI: nd Σ Musks: 2.1 – 99 (32)	---	(Stevens et al. 2003)
HHCB, AHTN, ADBI, AHMI	Germany	Urban	HHCB: 970 AHTN: 320 ADBI: 20 AHMI: 20	HHCB: 1400 AHTN: 360 ADBI: <10 AHMI: 60	---	---	(Dsikowitzky et al. 2002)
DPMI, ADBI, AHMI, ATII, HHCB, AHTN, Ambrettolide	Spain	Urban	---	ADBI: 9.1±0.6 AHMI: 5.3±0.6 ATII: 12.9±0.3 HHCB: 372±26 AHTN: 102±1 DPMI, Ambrettolide: nd	---	---	(García-Jares et al. 2002)
HHCN, AHTN, MX, MK, 4-AMX, 2-AMK	Germany	Urban	---	HHCN: 210 – 4200 AHTN: 140 – 1900	HHCB: 4800 AHTN: 2000		

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

	MX: nd – 3 MK: 15 – 94 4-AMX: 7 – 15 2-AMK: 15 – 20	MX: <10 MK: <10 4-AMX: <10 2-AMK: nd	---	(Gatermann et al. 2002)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent ($ng\ L^{-1}$)	Effluent ($ng\ L^{-1}$)	Sludge ($ng\ g^{-1}$ dw)	Observations	Reference
AHTN, HHCB, MX, MK	USA	Urban (different type of WWTPs) - Primary treatment - Secondary treatment	AHTN: 12500±7350 HHCB: 16600±10400 MX: 386±299 MK: 640±395	Primary + Activated sludge effluent AHTN: 1326±270 HHCB: 2053±1314 MX: 10±4 MK: 58±28 Oxidation ditch effluent AHTN: 890 - 1130 HHCB: 1490 - 1500 MX: 6 - 14 MK: nd Primary + Trickling filter effluent AHTN: 1555±522 HHCB: 2056±655 MX: 112±172 MK: 67±27 Primary + Rotating biological contactor effluent AHTN: 1710 HHCB: 2210 MX: 32 MK: 55 Lagoon treatment AHTN: 24 - 130 HHCB: 32 - 73 MX: nd - 1 MK: 10 - 27	---	- See following row	(Simonich et al. 2002)
AHTN, HHCB, MX, MK	Europe (UK + Netherlands)	Urban (different type of WWTPs) - Primary treatment - Secondary treatment	AHTN: 5970±3880 HHCB: 9710±5090 MX: 248±136 MK: 996±741	Primary + Activated sludge effluent AHTN: 1440 HHCB: 4620 MX: 10 MK: 60 Primary + Carousel effluent AHTN: 1170 - 1300 - 1150 MX: 10 MK: 640 – 770 Primary + Trickling filter effluent AHTN: 620 – 2670 HHCB: 1050 - 3750	HHCB: 980	- USA and European influent concentrations are similar. - Primary treatment leads to lower removal rates (27% MK, 41% MX, 29% AHTN and 30% HHCB). - The overall removal (primary + secondary treatment) ranged from 88-98% for activated sludge plants, 59-	MX: 20 - 170 MK: 40 - 200

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

	89% for carousel plants, 89-97% for oxidation ditch plants, 78-88% for trickling filter plants, 81-89% for a rotating biological contactor plant, and 97-100% for lagoons. - Lagoons yielded the most effective removal due to the long retention times (90-120 days) that enable biodegradation, photodegradation, sorption and settling and/or volatilisation.	(Simonich et al. 2002)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent (ng L^{-1})	Effluent (ng L^{-1})	Sludge (ng g^{-1} dw)	Observations	Reference
HHCB, AHTN, ADBI, ATII, AHMI	Germany	Urban	---	HHCB: 6850 AHTN: 2240 ADBI: 110 ATII: 310 AHMI: 270	---	---	(Fromme et al. 2001)
HHCB, AHTN, ATII, ADBI, DPMI, AHMI, AETT, MK, MM, MA, MX, MT, 2-AMK, 4-AMX, 2-AMX	USA	Urban - Primary treatment - Secondary treatment - Tertiary treatment	---	MX: <0.02 – 1.3 MK:<0.20 - 27.5 MA: <0.30 MM: <0.03 MT: <0.02 AETT: <0.02 HHCB: 35.0 – 152 AHMI: 2.4 – 5.0 DPMI: <0.02 ADBI: 0.3 – 2.1 ATII: < 0.02 - 126 AHTN: 26.6 – 92.2 4-AMX: < 0.30 - 31.5 2-AMX: <0.25 - 0.9 2-AMK:<0.25	---	---	(Osemwengie and Steinberg 2001)
DPMI, ADBI, AHMI, MA, MX, HHCB, AHTN, MM, AMA, MT, AMM, MK, AMT, AMK, AMX	Switzerland	Urban A. Domestic B. Domestic + Industrial			Wet sludge WWTP A MA, MX, MM, MT, AMA, AMT, AMK : nd MK: nd – 6.9 AMX: nd – 49.1 AMM: nd – 7.9 DPMI: 47.2 – 332 ADBI: 61.6 – 245 ---- ---	AHMI: 103 – 843 HHCB: 2347 – 12157 AHTN: 973 - 4161 WWTP B MA, MM, MT, AMA, AMT: nd MX: nd – 32.5 MK: nd – 7.0 AMX: nd – 31.5 AMM: nd – 36.2 DPMI: 38.4 – 147 ADBI: 41 – 330 AHMI: 64.9 – 266 HHCB: 2293 – 4074	AHTN: 741 - 1418

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

						- Among nitromusks MK was predominantly detected whereas MX was found only in one sample.	
						- Besides adsorption to sewage particles, transformation processes seem to play an important role with respect to nitromusks removal	
						- The two most frequently detected compounds were HHCB and AHTN.	(Herren and Berset 2000)

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

Compounds	Country	Type WWTP	Influent ($ng\ L^{-1}$)	Effluent ($ng\ L^{-1}$)	Sludge ($ng\ g^{-1}$ dw)	Observations	Reference
AHTN, HHCB, MK, MX	USA	Urban A: Activated sludge wastewater treatment B: Trickling filter wastewater treatment	WWTP A AHTN: 10700±619 HHCB: 13700±1500 MK: 569±114 MX: 376±96 WWTP B AHTN: 10000 HHCB: 9810 MK: 488 MX: 339	A: Primary effluent AHTN: 6990±1340 HHCB: 7760±1600 MK: 332±174 MX: 230±136 A: Final effluent AHTN: 1180±74 HHCB: 1170±100 MK: 99±15 MX: 5±1 B: Primary effluent AHTN: 7030 HHCB: 6660 MK: 419 MX: 165 B: Final effluent AHTN: 1660 HHCB: 1630 MK: 96 MX: 31	---	- The removal following the primary treatment was slightly lower at WWTP B (14% MK, 51% MX, 30% AHTN, 32% HHCB) than WWTP A (42% MK, 39% MX, 35% AHTN, 43% HHCB). - This reduction is likely due to a shorter hydraulic residence time in the primary clarifiers. - After secondary treatment the removal was also lower in WWTP B (80% MK, 90% MX, 84% AHTN, 84% HHCB)	(Simonich et al. 2000)
MX, 2-AMX, 4-AMX, MK, 2-AMK	Germany	?	4-AMX, 2-AMX, 2-AMK: nd MX:150 MK: 550	4-AMX: 34 2-AMX: 10 MX: 10 MK: 6 2-AMK: 250	---	---	(Gatermann et al. 1998)
HHCB, MK	Sweden	Urban (domestic + industrial) - Primary treatment - Secondary treatment (activated sludge)	---	HHCB: 1000 – 6000 MK: 1000 – 5000	----	---	(Paxéus 1996)

nd - not detected, na - not available, concentration in brackets - mean values

Table 1. Occurrence of synthetic musk fragrances in wastewater treatment plants (*cont.*)

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