Appendix B   Exposure considerations

B(i)   Abatement techniques

The dossier submitter has assessed potential emission abatement technologies that can be applied to industrial production, formulation, and processing of D4/D5 to limit their release to surface waters. This has considered the applicability and removal efficiency of available abatement options for industrial processes, which are generally also relevant to sewage treatment plants which treat siloxanes present in domestic and industrial waste-water.

To identify the available scientific literature, the following search string was run in both Thomson and TOXLINE on 2 August 2013:

- (cyclic volatile methylsiloxane OR cVMS OR D4 OR D5 OR D6 OR octamethylcyclotetrasiloxane OR decamethylcyclotetrasiloxane OR dodecamethylcyclohexasiloxane) AND (wastewater OR abatement OR treatment OR removal OR industrial NOT biogas)

Any papers that had already been obtained by the dossier submitter were removed, which resulted in 585 returned results, using the year limits of 2000 to July 2013. The abstracts were assessed and any relevant papers purchased and reviewed. The screened literature search results are available on request.

The project team also contacted relevant trade associations and consortia concerned with D4/D5 to discuss abatement technologies used in their industries but little information was received and this review is largely based on information from the scientific literature and reference sources such as the CEFIC risk management measures library.

B(i).1   Wastewater treatment

Previous studies (Xu *et al.* (2013), Wang *et al.* (2013a,b), Olofsson *et al.* (2013) and Bletsou *et al.* (2013)) have all demonstrated that D4 and D5 can be removed from influents to WWTPs through a variety of methods under aerobic and anaerobic conditions. From the available information, the most important removal mechanisms are likely to be volatilisation and adsorption, with volatilisation the most important for D4. Volatilisation is not usually considered to be an appropriate mechanism for the removal of potential pollutants; however, due to the low potential for these substances to redeposit to surface media, this can be considered a potential abatement option. Biodegradation is unlikely to be sufficiently rapid at WWTPs to be practical for the treatment of industrial wastewaters. Further information is provided in Section B(iii).

B(i).2 Other potential abatement techniques

To assess potential abatement techniques, the risk management measures (RMM) library version 17.2 produced by Cefic (2007) was used. Numerous techniques have also been developed for the removal of siloxanes from biogas (e.g. activated carbon, liquid or silica adsorption, refrigeration and advanced refrigeration techniques). However, the applicability of the techniques for removal from wastewater effluents is not currently known.

The Cefic RMM library is a look-up table that allows for the production of a list of potential RMM based on the exposure population and the exposure route (Cefic, 2007). The potential RMM identified from the library (Table B(i).1) have been grouped into treatments for insoluble contaminants, soluble non-biodegradable contaminants and soluble biodegradable contaminants. These three groupings were used, based on the physical-chemical properties of D4 and D5 (which have slightly differing water solubilities and potentials for biodegradation and hydrolysis (Xu *et al.* 2013)). These potential abatement techniques are applicable to industrial facilities with significant emissions of waste-water containing D4 and D5, i.e. formulation of PCPs by the cosmetics industry and use of silicone polymer anti-foaming agents (containing residual monomers) in the paper and pulp sector and in oil and gas drilling.

Table B(i).1   Potential on-site treatment options for abatement of D4 and D5 from wastewater (modified from CEFIC RMM Library, 2007).

Treatment	Treatment Description	RMM Efficiency Max (%); water
Sedimentation of solids	Mechanical separation of insoluble contaminants - used for all substances e.g. when special chemicals for coagulation or flocculation are added.	100
Air flotation	Mechanical separation of insoluble contaminants - used for dyes/pigments and heavy metal sulphides.	95
Filtration	Mechanical separation of insoluble contaminants by filtration, microfiltration and ultrafiltration	100
Chemical treatment - Oxidation	Chemical treatment for soluble non-biodegradable or inhibitory contaminants - used to treat all organic substances, oil, grease, phenols, PAHs, organic halides, dyes and pesticides oxidation by e.g. H_2O_2.	>90
Chemical treatment - Wet Air Oxidation	Chemical treatment for soluble non-biodegradable or inhibitory contaminants - used to remove organic nitro, amino-, sulphur, chlorinated compounds.	90
Chemical treatment - Supercritical Water Oxidation	Chemical treatment for soluble non-biodegradable or inhibitory contaminants - used to destroy all organics by complete conversion to CO_2.	99.9
Chemical treatment - Reduction	Chemical treatment for soluble non-biodegradable or inhibitory contaminants - used to treat H_2O_2, nitrites.	U
Chemical treatment - Hydrolysis	Chemical treatment for soluble non-biodegradable or inhibitory contaminants - used to remove organic sulphides, halides, cyanides, organophosphates, carbonates, esters and amides.	U
Chemical treatment - Precipitation	Physicochemical treatment for soluble non-biodegradable or inhibitory contaminants - used to remove heavy metals, phosphates, sulphates and fluorides.	U

Treatment	Treatment Description	RMM Efficiency Max (%); water
Crystallisation	Physicochemical treatment for soluble non-biodegradable or inhibitory contaminants - used to recover heavy metals	U
Extraction	Physicochemical treatment for soluble non-biodegradable or inhibitory contaminants - used to remove chlor aromatics, phosphoric esters	99
Nanofiltration (NR) and Reverse Osmosis (RO)	Physicochemical treatment for soluble non-biodegradable or inhibitory contaminants - used for final removal of e.g. toxic components.	>90 (NR); >99 (RO)
Adsorption	**Physicochemical treatment for soluble non-biodegradable or inhibitory contaminants - used to remove dyes, petrochemicals resins, detergents.**	**95**
Ion Exchange	Physicochemical treatment for soluble non-biodegradable or inhibitory contaminants - used to remove ionic organic / inorganic substances.	99
Thermal Treatment - Distillation / Rectification	Physicochemical treatment for soluble non-biodegradable or inhibitory contaminants - used to remove solvents, emulsions of oil and recover organics.	97
Thermal Treatment - Evaporation	**Physicochemical treatment for soluble non-biodegradable or inhibitory contaminants - used to remove volatile substances, and to concentrate mother liquors**	**99**
Waste Water treatment - Incineration	Chemical treatment (oxidation) for soluble non-biodegradable or inhibitory contaminants - used to remove all organic substances	>99
Waste Water treatment - Stripping	Physicochemical treatment for soluble non-biodegradable or inhibitory contaminants - used to remove chlorinated hydrocarbon solvents, petrol, low aromatics phenol	>99.5
Biological treatment - Anaerobic	**For soluble biodegradable contaminants.**	**90**
Biological treatment - Aerobic	**For soluble biodegradable contaminants.**	**96**
Biological treatment - Central Biological Waste Water Treatment	For soluble biodegradable contaminants.	99.8
Biological treatment - Sludge treatment e.g. thermal sludge reduction	Industrial or municipal waste water treatment plant.	98

Key;	Potential treatment option based on low water solubility of D4 and D5	Potential treatment option based on low biodegradability of D4 and D5, although low water solubility may reduce efficiency	Potential treatment option based on potential for biodegradation of D4 and D5, although low water solubility and high half lives may reduce efficiency	**Bold = potential RMMs**

From Table B(i).1, it can be seen that there are various RMM that could be applied for the abatement of siloxanes, with maximum treatment efficiencies of up to 100%

achieved depending on the RMM selected. However, some of the techniques detailed in the table may also require the integration of other measures, although these may not be directly applicable to siloxane abatement. For example, the additional RMM for gas treatment from various biological treatments will not be applicable as the substances are not expected to be readily biodegradable. Removal by volatilisation is not a RMM considered by Cefic (2007).

Due to the high volatility of D4 and D5 and their expected release to air during WWTP processes, some further RMMs may be applied to reduce and clean air emissions (Table B(i).2).

Table B(i).2   Potential RMMs for reduction and cleaning of air emissions for abatement of D4 and D5 (modified from CEFIC RMM Library, 2007)

Treatment	Treatment Description	RMM Efficiency Max (%)
Air filtration - Mist filter	Recovery and abatement technique for aerosols	99
Waste gas membrane separation	Recovery technique for alkanes, olefin aromatics, alcohols, ethers, esters, ketones.	99.9
Waste gas treatment - thermal oxidation	Abatement technique for VOCs.	>99.9
Waste gas treatment - catalytic oxidation	Abatement technique for VOCs and solvents.	99.9
Waste gas treatment - adsorption	Recovery technique for VOCs e.g. emissions from point spraying, degreasing etc.	95
Waste gas treatment - condensation	Recovery technique for all VOCs and volatile inorganics	90

The RMMs identified in Table B(i).2 for the reduction of air emissions are generally in good agreement with the siloxane abatement techniques applied to landfill and biogases (typically adsorption to activated carbon, liquids or silica gels or through the use of refrigeration and advanced refrigeration techniques).

From the information presented in Tables B(i).3 and B(i).4, it is suggested that the most suitable RMMs for potential siloxane abatement are;

- Adsorption; Maximum treatment efficiency = 95 %
- Thermal Treatment – Evaporation; Maximum treatment efficiency = 99 %
- Biological treatment – Aerobic; Maximum treatment efficiency = 96 %
- Biological treatment – Anaerobic; Maximum treatment efficiency = 90 %

B(i).3   Currently applied abatement techniques

From the reviewed literature, the most commonly used abatement technique for the reduction in D4 and D5 emissions from industrial formulation sites is the use of biological WWTP, which are considered to be comparable to a municipal WWTP in terms of their potential for removal. On the face of it, it would seem that the type of WWTP treatment applied (i.e. primary, secondary or tertiary treatment) has minimal influence on the removal efficiency of D4 and D5, with the study authors stating that there is little apparent difference in WWTPs with different treatment types (e.g. Sanchís *et al.*, 2013; Wang *et al.*, 2013a). A closer look at the results suggests that there is a consistently better removal of D4 and D5 at the lagoon sites than at the secondary activated sites or the primary sites. This potential for better removal may arise from the fact that activated sludge mixing aerates the sludge and therefore there is greater potential for volatilisation, especially if it is then allowed to sit in a lagoon rather than discharged immediately. Differences in removal efficiencies can be observed at different sites employing the same treatment types. The aerobic/anaerobic conditions during treatment and dissolved organic matter (DOM) content of the waste can have an effect on the removal efficiencies and degradation pathways (Xu *et al.* 2013). The use of biological wastewater treatment is similar to the use of activated sludge treatment at municipal WWTPs, which is commonly used on industrial sites to treat a wide variety of organic substances.

B(i).4   Recommendations

From the information in Cefic (2007) and published literature, it is acknowledged that the major abatement technique for waste waters is aerobic and anaerobic biological treatment (i.e. secondary sludge treatment). Reported removal efficiencies are high (up to 99%), especially if there is an aeration step.

If removal efficiency needed to be increased, adsorption to a suitable adsorbent (i.e. activated carbon) or thermal treatment of the sludge could also be applied. Another alternative technique would be to remove DOM where possible from the influent, which would have the effect of increasing dissolved D4/D5 concentrations (Xu *et al.*, 2013). However, the effectiveness of performing these additional potential RMMs is unknown.

B(ii)   Studies of D4/D5 emissions to water during use of Personal Care Products (PCPs)

This section summarises studies that have assessed the quantities of D4 and D5 released to domestic wastewater during the use of PCPs. The focus of the studies has been mainly on leave-on PCPs.

1. Jovanovic *et al.* (2008) studied the *in vitro* percutaneous absorption of ^{14}C-D4 and ^{14}C-D5 in flow-through diffusion cells. Single doses were applied neat and in antiperspirant formulations to dermatomed human skin, which were then left for 24 hours (h). The majority of applied D4 and D5 (approximately 90%) volatilized before being absorbed. Only 0.5% of applied D4 was absorbed while the absorption of D5 was one order of magnitude lower (0.04%). A further *in vivo* study involved the topical application of a single dose of ^{14}C-D4 (10, 4.8 and 2 mg/cm^2) and ^{14}C-D5 (10 mg/cm^2) to the skin of rats inside a dosing chamber attached to their dorsal area. Rats were housed in metabolism cages up to 24 h to enable collection of urine, faeces, expired/escaped volatiles. The majority of applied D4 or D5 had volatilized from the skin surface. Less than 1% of the applied D4 and only 0.2% of applied D5 was absorbed. The amount absorbed into the skin decreased with time showing that residual D4 and D5 diffused back to the skin surface and continued to evaporate.

2. Gouin *et al.* (2013) performed application and wash off studies using five different leave-on deodorant/antiperspirant products (a soft solid, an aerosol and three types of stick) on six male participants during summer time. The soft solid product had the highest D5 content (43.3 ± 3.8 µg/g, or 51%), the aerosol had the lowest D5 content (5.7 ± 0.75 µg/g, or 7%), and the sticks had similar intermediate contents (between 20 and 25 µg/g, or 23 – 32%).

    Test items were applied to the axilla in accordance with the recommended dosage on the product packaging. This involved two clicks for a soft solid product (equivalent to 0.4 g per axilla, or approximately 0.2 g of D5), a 2-second spray of an aerosol product (approximately 1.7 g of product or 0.12 g D5) and 0.7 g per axilla for each of three stick products applied to the axilla in a wiping up and down motion (6 wipes total) (equivalent to approximately 0.2 g D5). Accurate weights of each product before and after application were recorded to calculate the weight of material applied. The product was worn for a period of 24 h without washing. Each participant then washed each axilla separately using 1 mL of shower gel that did not contain D5, allowing thorough contact. The wash water (1 L, 35 ± 10 °C) used to thoroughly rinse off the applied shower gel was collected via a stainless steel funnel in a 1 L Duran placed under the sink (waste pipe disconnected). The volume of water collected was 1000 ± 50 mL. A second wash was carried out in a repeat procedure. The participant was then able to re-apply another product to commence another 24 h testing cycle. To avoid cross-contamination between samples, the sink was flushed with copious amounts of water. Separate sinks were used for the first and second wash samples. To monitor for background levels of D5 in experiments, sink blank samples were taken by washing 1 mL of shower gel into a 1 L Duran as described above.

All wash water samples and blanks were sealed immediately following collection. Samples were homogenised by gentle shaking to minimise foaming of the surfactant from the shower gel. Analysis was by headspace gas chromatography/mass spectrometry. The method performed well for samples in the low µg/L range, with mean spike recovery for samples containing 0.1% v/v shower gel and other wash off products of 81.0 ± 8.2% (n = 12).

Sink blanks were typically found to contain <0.1 µg/L of D5. Concentrations measured on participants prior to commencing application of products were in the range <0.1 – 1.021 µg/L, depending when a D5-containing product was last used. In one case, 5 days had passed between product use and testing, and the concentration was still 0.13 – 0.26 µg/L. This suggests that D5 may remain on the skin for a substantial period following product use (although the amounts are relatively small).

The results for the product trials are summarised below.

Product	Measured D5 (%) [no. of replicates]	Spike recovery (%) [no. of replicates]	Recovery corrected D5 (% mean)	Product specification (% w/w D5)
Soft solid	43.3±3.8 [n=18][c]	84.1±12 [n=3][f]	51.5	51.26
Aerosol	5.7±0.75 [n=14][d]	94.0±0.65 [n=3][g]	6.06	7.13
Stick (1)	21.9±2.5 [n=15][a]	75.3±6.6 [n=3][e]	29.1	29.95
Stick (2)	20.0±1.6 [n=12][b]	82.0±18 [n=3][e]	24.4	23.45
Stick (3)	24.5±2.5 [n=15][a]	88.4±7.8 [n=3][e]	27.7	31.78

Note: a – Five sub-samples analysed in triplicate.
       b – Four sub-samples analysed in triplicate.
       c – Six sub-samples analysed in triplicate.
       d – Five sub-samples analysed in triplicate with one excluded result.
       e – Triplicate 1 mL aliquot of a 40 mL hexane extract of these samples was spiked with 10 µL into 20 mL and compared to the unspiked sample.
       f – Three additional weighings of 0.3 g of this product were extracted in 40 mL of hexane and spiked with 400 µL (0.383 g) of D5 before being diluted 10 µL into 20 mL and compared to the unspiked sample.
       g – Triplicate 1 mL aliquot of the 100 mL hexane extract of this product sample was spiked with 3 µL (0.002874 g) of D5 diluted 10 µL into 10 mL and compared to the unspiked sample.

After use of the soft solid product for 24 h, measured D5 concentrations were in the range 0.506–12.0 µg/L in the first wash and 0.208–1.94 µg/L in the second wash. The mass of D5 going down the drain was calculated to be in the range of 0.766–13.5 µg, which was 0.0003–0.006% w/w of the amount of D5 initially applied.

The mass of D5 going down the drain following use of the aerosol product was in the range of 0.194–8.47 µg, which was 0.0002–0.009% w/w of the amount of D5 initially applied.

The mass of D5 going down the drain for the three stick products was in the range of 1.84–9.24, 0.858–4.43 and 0.364–9.86 µg, respectively, which was 0.0008–0.004, 0.0005–0.003 and 0.0002–0.005% w/w of the amount of D5 initially applied.

The relationship between the losses and recorded levels of exercise is unclear.

The soft solid test item was also used to assess the temporal loss of D5, as it contained the highest amount of D5 on a per weight basis, enabling better

quantification compared to the lower concentrations in the other products. The experiment was carried out as described above with the exception that the following periods between application and wash-off times were added to the testing procedure: 0, 1, 2, 4 and 7 h. At the 0 h time point the product was applied to the left axilla then washed with two consecutive washes, before repeating procedures with the right axilla. This ensured minimal contact time at T = 0.

At 0 h, recovery of D5 was only 5.5–17.7% w/w, which was thought to be due to a matrix effect associated with the freshly applied product (relating to attempting to dissolve the freshly applied product in an aqueous solution). Unlike the washes at other time intervals, at 0 h the amount removed in the first wash was lower than that in the second wash, implying that the capacity of the soap and water to effectively remove the freshly applied product was initially hindered, with the second wash being significantly more efficient. This part of the experiment therefore cannot be used to estimate the typical wash-off rates for PCPs that are intended to be washed off immediately.

The time course experiment was further complicated by the relatively large variability in D5 levels measured at 7 h between individual subjects, in the range 7.96–16,700 µg/L for wash 1. The calculated D5 wash-off figures expressed as a percentage of the amount of D5 initially applied were in the range 0.004–5.8% w/w. Despite this lack of consistency, the study suggests that >94% of D5 was lost during the first 8 h following application.

To assess the potential for D5 residues on clothing worn by participants, the axilla area of selected shirts worn by two of the participants during the 24 h period following the aerosol treatment were washed with shower gel. The collection of water was as described above. It is not stated whether the shirts were worn for the whole period (i.e. during sleeping), although it is stated that they were worn "throughout most of the 24 h period". The results show that the traces of D5 present were of a similar order of magnitude compared to the residual amount left on the axilla (i.e. around. The authors recommended a more comprehensive mass-balance study to establish the actual losses given the low sample numbers and limited extraction technique.

Despite the small sample numbers, the study suggests that much less than 0.1% w/w of the D5 applied in leave-on PCPs is available for wash off after 24 h. A similar amount may also be present on clothing that could then be laundered.

3. Montemayor *et al.* (2013)[1] investigated releases of D5 from three PCP groups: I) antiperspirants, II) skin care products, and III) hair care products (including one wash-off conditioner), using realistic application and wash-off times designed to replicate standard use patterns. Testing took place in the early autumn. Chemical analysis followed the method developed by Sparham *et al.* (2008) with a limit of detection and quantification of 0.07 and 0.023 µg/L, respectively.

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[1] The dossier submitter has also seen a draft version of the underlying study report (HTR, 2011), which contains additional details.

A series of quality control procedures were used across all studies to minimize laboratory background levels of D5. All subjects, clinical and analytical staff were prohibited from using products containing D5 for at least 24 h before the studies and throughout the study. Additional controls included the physical separation of product application and washing rooms with separate, dedicated staffing to minimize any cross-contamination. At each time point, study design included random panelists with no product application (placebo control) and laboratory basin/bottle blank controls to assess laboratory background levels. Sample collection bottles were pre-cleaned with detergent and equipped with foil-lined closures to minimize potential contamination or loss of D5 during sampling, transport and analysis.

- *Group I (antiperspirants)*: Two types of product were investigated (an invisible solid and a soft solid antiperspirant). They were chosen to cover the typical distribution of available products on the North American market and allowed for the assessment of the impact of non-polar emollients on the volatilisation of D5 (solid forms typically contain the highest levels of both emollients and D5 across this market category). The product (0.4 g) was applied to each axilla of five test subjects consistent with standard clinical application techniques. The subjects were provided with a long-sleeved cotton t-shirt to wear until the specified wash-off time (8 ± 0.5 and 24 ± 1 hours after application). Between application and sampling, subjects were permitted to leave the facility and perform typical daily tasks with the exception of washing the product application area or removing provided clothing (t-shirt) that might come into direct contact with the application area.

  At the designated wash-off time the t-shirt was removed and the treated skin area was washed manually using 1 g of a silicone-free liquid soap and 900 mL water; this step was performed twice by clinical staff wearing nitrile gloves, and the rinsate included any residual lather on the gloves. (The temperature of the water was not stated, but appears to have been at room temperature). The combined wash and rinse water (1800 mL) was collected in a two-litre glass bottle, leaving a small head-space (to accommodate the foam) and then capped. Each product and sampling time was initially designed to include 20 subjects and three blank controls. Subjects who did not arrive within the scheduled sampling time window were removed from the study.

  Additionally, physical transfer of D5 to clothing of five subjects was also assessed by removing a 400 cm^2 sample from the t-shirt in contact with the axilla area. This was placed in a 150 mL glass jar which was filled with water and 1 g of liquid hand soap and agitated for 5 minutes before being allowed to sit for 4 hours at room temperature to extract the D5. The liquid hand soap solution was preferred over commercial laundry detergent since prior analytical assessments confirmed the solubility and stability of D5 in the system and found the matrix free of background interference. Subsequently, a sub-sample of the t-shirt wash water was collected for analysis. There is no information to indicate whether this method would have effectively removed all of the D5 present.

To assess initial D5 application levels, 0.4 g of product was applied to a forearm area and washed off within 10 minutes of application.

Releases to wastewater were estimated by comparing the mean concentrations in the treatment rinsates with the mean concentrations in the control rinsates 10 minutes after application. Given that significant evaporation appears to have occurred after 3 minutes for a wash-off hair conditioner (see below), this method potentially underestimates the initial dose (i.e. the relative amounts left on the skin after longer periods will be over-estimated).

Residual mean D5 concentrations from untreated control subjects ranged from 22 µg/L at initial sampling to 0.7 µg/L at the 24 h sampling time, corresponding to an overall study background concentration. Higher levels during initial sampling were considered to be consistent with cross-contamination from treated subjects being washed concurrently in the facility.

Mean D5 concentrations (±95th percent confidence intervals) for the invisible solid antiperspirant from treated subjects were 38,020 (±11,750) µg/L (n=22) at initial sampling, 153 (±167) µg/L at the 8 h sampling time (n=21) and 12 (±15) µg/L at the 24-h sampling time (n=21). The residual amount of D5 relative to the initial sampling was in 0.8% after 8 hours and 0.07% after 24 hours (based on the initial mean and the upper 95th confidence interval of the mean at the specified time point).

For the soft solid antiperspirant, the D5 concentrations from treated subjects (±95th percent confidence intervals) were 468,500 (±261,750) µg/L (n=22) at initial sampling, 137 (±110) µg/L at the 8 h sampling time (n=22) and 26 (±1) µg/L at the 24 h sampling time (n=19). The residual amount of D5 relative to the initial sampling was in the range of 0.05% after 8 hours and 0.01% after 24 hours (based on the initial mean and the upper 95th confidence interval of the mean at the specified time point).

These results suggest that the residual mass of D5 available to wash-down the drain at both 8- and 24-hours is fairly independent of the form in which it is applied. Additionally, the results suggest a retention rate that is an order of magnitude lower than previously reported in an *in-vitro* evaluation of antiperspirant products (Jovanovic *et al.*, 2008).

T-shirt wash concentrations ranged from 2 to 36 µg/L, but the t-shirt water volume was only approximately 10% of the subject wash water volume, so transfer to fabric was determined to be negligible by the study authors.

- *Group II (skin care products)*: Three skin care products were investigated: oil dominated lotion, water dominated lotion and anhydrous serum. The serum solution was selected due to the high concentrations of D5 present. The two types of lotion were chosen to assess whether emulsion type or the magnitude of D5 content has an effect on its evaporative fate. The investigation was performed following US FDA clinical application techniques for sunscreens. A 50 cm^2 area was marked on the subject's

forearm and 100 mg of the test product was uniformly applied over the area by trained clinical staff. Each subject was provided with a long-sleeved cotton t-shirt to wear until the specified wash off time. Due to the increased frequency of hand and face washing in comparison to bathing/showering, an additional wash-off time of 4 hours (±0.5 hrs) was included, as well as the time intervals of 8- and 24-hours performed previously.

At the designated wash time, subjects returned, the t-shirt was removed and the application area was washed with two sequential wash–rinse steps each using 1 g of liquid handsoap with a total of 900 mL of water. The combined wash and rinse water solution (1800 mL total) was collected in a dedicated 2 L collection bottle that was immediately capped. For each product and sampling time, a total of at least 20 subjects and three blank controls were collected.

The t-shirt (500 cm^2 samples from the region in contact with the forearm) was also subjected to the same extraction procedure as the t-shirts used in the antiperspirant testing.

To assess initial D5 application levels, four panelists per product were randomly selected to have the application area washed off within 10 minutes of application.

Releases to wastewater were estimated by comparing the mean concentrations in the treatment rinsates with the mean concentrations in the control rinsates 10 minutes after application. Given that significant evaporation appears to have occurred after 3 minutes for a wash-off hair conditioner (see below), this method potentially underestimates the initial dose (i.e. the relative amounts left on the skin after longer periods will be over-estimated).

The residual D5 concentrations from untreated control subjects across the whole study ranged from a maximum of 6.2 μg/L (initial) to 0.30 μg/L by the end. Similar to the antiperspirant study, t-shirt samples contained low residual levels of D5, with wash water concentrations ranging from a maximum of 37.3 μg/L for a single subject at the 4 h sampling to a typical value of 0.75 μg/L at 24 h.

Residual D5 concentrations measured in wash water associated with the skin product testing were as follows:

Product	Time	Treated subject mean (±95th % confidence intervals), μg/L	N
Oil dominant lotion	Initial	6,650 (±2,860)	3
	4 h	1.7 (±0.2)	24
	8 h	0.84 (±0.1)	22
	24 h	1.1 (±1.7)	21
Water dominant lotion	Initial	2,480 (±2,960)	4
	4 h	4.2 (±0.9)	23
	8 h	2.4 (±0.45)	24
	24 h	2.3 (±0.39)	23
Anhydrous serum	Initial	24,800 (±19,500)	4
	4 h	1.65 (±0.2)	24
	8 h	0.92 (±0.38)	24
	24 h	1.49 (±0.77)	24

The results show that after four hours, a maximum of 0.21% w/w of the initially applied D5 is available for washing-off (based on the initial mean and the upper 95th confidence interval of the mean at the specified time point). At the 8- and 24-hour sampling times, D5 concentrations were comparable to the background levels, representing around 0.1% w/w of the initially applied dose for the water dominant lotion, and 0.01-0.02% w/w for the other two product types.

- *Group IIIa (leave-on hair care products)*: This product category is extremely diverse in D5 levels, as well as additional additives that could affect the volatilisation of D5. Three leave-on products were investigated (a leave-on spray serum, a styling spray and a leave-on styling gel).

Due to the many variables associated with hair and the testing of hair products on human subjects, human hair tress testing methods were used. Flat virgin brown European human hair tresses were pre-wetted under running water at 40 °C for 30 seconds, followed by application of 0.5 mL of sodium lauryl sulphate pre-conditioning solution per gram of hair for 30 seconds, which was then rinsed out under running water for 60 seconds. The squeezed and combed tresses were then clipped onto racks, and allowed to dry prior to use.

The treatments involved two techniques, depending on the application method. For pump spray products, two pumps were applied to the centre of 4 g hair tresses. Gel styling products (0.4 g) were applied by hand to 2 g tresses. For each product tested 15 separate tresses were prepared, and the wash-off times used were 8- and 24-hours.

Washing was performed manually as before, using 1 g of a silicone-free liquid soap and a total of 900 mL of water, with two sequential wash–rinse steps (i.e. 1800 mL of combined wash and rinse water). All washings were collected in a pre-rinsed stainless steel basin, and sampled for analysis.

Initial dosing levels were established by washing treated tresses within 10 minutes of product application (n=4 per product).

The concentrations of D5 in rinsate from blank tress controls ranged from 0.38 to 3.3 µg/L across the entire study. Residual D5 concentrations measured in wash water from the hair tress testing are summarized below.

Product	Time	Treated tress mean (±95th % confidence intervals), µg/L	n
Spray serum	Initial	22,600 (±16,200)	4
	8 h	2.7 (±0.41)	14
	24 h	0.79 (±0.13)	15
Spray styling	Initial	90,200 (±55,000)	4
	8 h	2.0 (±0.68)	15
	24 h	0.68 (±0.08)	15
Gel styling	Initial	135,000 (±57,300)	4
	8 h	1.6 (±0.37)	15
	24 h	0.60 (±0.08)	15

Releases to wastewater were estimated by comparing the mean concentrations in the treatment rinsates with the mean concentrations from the initial dosing rinsates that were collected 10 minutes after application. Given that significant evaporation appears to have occurred after 3 minutes for a wash-off hair conditioner (see below), this method potentially underestimates the initial dose (i.e. the relative amounts left on the hair after longer periods will be over-estimated).

The results show that after eight hours, a maximum of 0.01% w/w of the initially applied D5 is available for washing-off (based on the initial mean and the upper 95th confidence interval of the mean at the specified time point). At the 24-hour sampling time, D5 concentrations were comparable to the background levels, representing around 0.004% w/w or less of the initially applied dose.

- *Group IIIb (wash-off hair conditioner)*: Human hair tresses (2 g) (n=15) (pre-wetted as before) were treated with 1 g of a non-spray rinse-off conditioner for 30 seconds using gentle vertical strokes. The tresses were allowed to stand for one to three minutes (one tress was left for 6 minutes) and then washed following the same method as described for the other hair care products (1,800 mL of rinsate in total).

Sample loading controls were prepared by dispensing 1.0 g of product directly to a collection bottle, and adding 1 mL of silicone-free liquid soap plus 900 mL of water, twice (so 1,800 mL of water in total) (n=4). Blank controls were prepared following the rinse procedure with tresses that were not loaded with product (n=4). Pre-rinse basin controls were also performed (n=3).

The mean D5 concentration detected in the rinsate was 5,725 µg/L (95% confidence interval: 4,199 –7,252 µg/L, median: 4,522 µg/L, range: 3,590 – 12,330 µg/L). The mean D5 concentration in the loading controls was 18,370 µg/L (range: 6,394 – 50,061 µg/L); the highest concentration was six times greater than the next highest one (8,681 µg/L), implying a dosiing error (neither the paper nor the report discuss this). Excluding the highest loading control concentration gives a mean of 7,807 µg/L. Blank control

concentrations were below 3 µg/L and basin controls were below 1 µg/L; the results do not appear to have been corrected, but this would make no difference.

Releases to wastewater were estimated by comparing the concentrations in the rinsate with the concentrations in the loading controls. The average release appears to have been around 73% based on the average loading concentration excluding the highest value (using the 95% confidence intervals, the range is 54 – 93%)[2].

It is unclear whether the method accurately mimics the use of the product by the majority of people (e.g. in terms of the amount of product applied or the time the product is left on the hair), or the volume/temperature of water normally used to wash hair, although the paper points out that the normal use instructions do not require washing with surfactant after application so the results may be a worst case.

It is not known how representative this study is for these particular product types given the relatively small sample numbers involved (which is also reflected in the wide confidence intervals for some time points). However, it appears to be the best study currently available for wash-off PCPs.

For all leave-on products tested, residual D5 concentrations decreased to levels of 0.8% w/w at most (generally below 0.1% w/w, depending on the number of hours before washing occurs) of the initial applied amount eight hours after application. This could be an under-estimate due to the way that the applied dose was estimated in this study. This suggests that evaporation of D5 from hair and skin is relatively rapid compared to typical washing frequencies (the paper cites other studies that indicate that dermal absorption accounts for less than 0.2% of the total applied D5). D4 is more volatile so would be expected to be lost even quicker. This study therefore suggests that less than 1% w/w of the applied amount of D5- (and D4-)containing leave-on PCPs will be available for wash-off during typical consumer use scenarios. The study also shows that use of leave-on PCPs can lead to some contamination of clothing, which could theoretically lead to additional wastewater emissions during laundering, although the amounts are relatively small. It is not known whether additional clothing layers would increase the amount of D5 retained (e.g. due to reduced air movement).

For PCPs that are intended to be left on the body for a few minutes prior to washing off, this study suggests that around 75% of the applied dose would be released via the drain, although the confidence intervals are wide. The implication is that the release rate would be higher if the product is washed off almost immediately.

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[2] The paper assumes that the concentrations are comparable, and cites a release of around 40% based on the non-corrected average loading control concentration.

B(iii)   Measured Concentrations of Siloxanes in the Aquatic Environment and WWTPs

B(iii).1   Literature review

The available scientific literature has been evaluated for measured concentrations of D4 and D5[3] in wastewater treatment plant (WWTP) influent, effluent, sludge, receiving waters and receiving water sediments. Summary tables of measured concentrations, as well as treatment type performed at each WWTP (where relevant), are presented in Annex 1 and 2, and the key findings of the individual studies are detailed in the text. The focus has been on European data collected within the last ten years, to minimise the influence of any changes in use pattern[4], with North American data cited where relevant (Asian data have not been summarised as the conditions of use and wastewater treatment approaches may be significantly different to the EU).

The following search strings were run in both Thomson and TOXLINE on 18 February 2013:

- (556-67-2 OR octamethylcycloterasiloxane OR D4) AND (Receiving Water OR Concentration OR Sediment)

- (541-02-6 OR decamethylcyclopentasiloxane OR D5) AND (Receiving Water OR Concentration OR Sediment)

- (540-97-6 OR dodecamethylcyclohexasiloxane OR D6) AND (Receiving Water OR Concentration OR Sediment)

The returned results for the above search strings were then combined, any duplicate results removed, which resulted in 315 returned results. The returned results were then assessed for their relevance based on the reporting of measured concentrations of D4 or D5 in the receiving environment, with any relevant papers being purchased and reviewed.

Precautions need to be taken during sample collection (e.g. avoiding aeration and/or bubbling of the sample and through the use of sealed containers with no headspace for storage) and analysis to avoid losses through volatilisation.

B(iii)1.1   Measured concentrations

B(III).1.1.1 Sparham *et al*. (2008), Determination of D5 in river water and final effluent.

The objective of this study was the validation of a new analytical technique for measuring D5 in aqueous environmental samples at concentrations below 100 ng/L. Sampling was conducted on the River Nene in the vicinity of the Great Billing sewage treatment works (STP) near Northampton, UK in June 2006. Samples were collected at one station upstream of the effluent outfall, from the final effluent stream and at three stations downstream. Additional sampling on the River Nene was

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[3] D6 concentrations have been reported for completeness, where studies have reported these results alongside D4 and D5 concentrations.
[4] Monitoring data from prior to 2005 are summarised in Environment Agency (2009a&b).

conducted in December 2006. A number of STPs discharge into the river over the sampling reach. Samples were also taken from the River Great Ouse (Buckinghamshire and Bedfordshire, UK) in October 2006. Samples were collected upstream and downstream of STPs. River water samples were taken at a depth of 10-50 cm and immediately prepared, without preservatives for analysis in headspace vials in the field. From the validation and field work performed on the HS-GC/MS method, a limit of detection for D5 in water samples of 6.2 – 10 ng/L was determined, and recoveries of 88.4 – 94.7%, 89.3 – 98.7% and 80.5 – 85.9% were observed for spiked blank water, spiked effluent and spiked river water, respectively. The internal standard recovery in the samples ranged from 71 – 125% for all the various sample types analysed. The stability of the samples was assessed via analysis of samples on the day of sampling and seven days after sampling after storage in refrigerator, and excellent stability was observed, with the Ouse Farm river level sample being analysed as 59.2 ± 6.9 ng/L on Day 0 and 60.2 ± 2.0 ng/L on Day 7, and the River Great Ouse at Roxton Lock (replicate 2) sample being 22.6 ± 0.3 ng/L and 25.5 ± 2.3 ng/L on Day 0 and 7, respectively. Overall, measured levels of D5 were typically in the range <10 (the limit of quantification, LoQ) to 29 ng/L in the River Great Ouse and < 10 to 151 ng/L (June 2006) and 12.9 to 26.8 ng/L (December 2006) in the River Nene. The levels below LoQ were found in samples upstream of the STPs. The measured concentration of D5 in treated effluent was 400 ng/L (Sparham *et al*. 2008). Forty samples out of 129 (31%) had concentrations below the LoQ of 10 ng/L.

The paper is published in a peer-reviewed journal using a validated method for the analysis of D5. The GLP status of the work is unknown but the results are considered acceptable.

B(iii).1.1.2 Sparham *et al*. (2011), Determination of D5 in river and estuarine sediments in the UK

The objective of this study was to develop suitable methods to measure levels of D5 in river and estuarine sediments and the application of novel approaches to minimise commonly reported artefacts in previous analytical methods. Samples were collected from two locations on the River Great Ouse (Felmersham and Tyringham Bridge), UK on 27/08/2008 and 23/09/2008, respectively, and from six locations on the Humber estuary (Chowder Ness, Paul Holme, Stone Creek, Welwick, Cleethorpes and Skeffling) between 24/09/2009 and 15/10/2009 (all UK) alongside a blank sediment from Sanford Lake, MI, USA (this lake is not subject to an effluent discharge). River sediment samples were taken with a small grab sampler and sieved (2 mm) using an acetone-cleaned stainless sieve and collection tray. Sediments were stored in 1 L solvent-cleaned glass straight sided jars and sub-sampled by transferring into centrifuge tubes as required, in the field. Intertidal sediment samples (surface, 1–2 cm) were obtained using a solvent-cleaned stainless steel scoop and stored as for the river samples. Method validation samples (n=3) were also prepared, by spiking a lake and estuarine sediment with D5, mean percentage recoveries reported as 85 ± 18% and 113 ± 12%, for lake and estuarine sediments respectively.

For river samples taken from Felmersham, concentrations were in the range 820 – 14,500 ng/g dry weight (dw) for D5 and 12 – 24 ng/g dw for D4. The results for D4 lie between the limit of detection (LoD) and LoQ but are at a lower risk of ambient contamination compared to D5. The LoQ for D5 was 110 ng/g dw. When expressing

the Felmersham concentrations of D5 normalised to the organic carbon (OC) content, a much narrower range of 18 – 26 µg/g OC dw was determined, demonstrating the affinity of D5 with organic material in sediment. For Tyringham bridge, concentrations were in the range 186 – 695 ng/g dw for D5 (LoQ 57 ng/g dw), which corresponds to 11 – 22 µg/g OC dw, and less than the LoD of 19 ng/g dw for D4.

Concentrations measured in the estuarine sediment samples taken from the Humber estuary were in the range 49 – 256 ng/g dw (LoQ 4 ng/g dw), equivalent to 4 – 15 µg/g OC dw. No values were reported for D4.

From all the sediment results reported from Tyringham Bridge, Felmersham and the Humber Estuary, it can be calculated that 10% of samples had concentrations below the LoQ for D4 (9 of 90), and no samples were <LoQ for D5.

The paper is published in a peer-reviewed journal using a validated method for the analysis of D4 and D5 in river and estuarine sediment. The GLP status of the work is unknown but the results are considered acceptable.

B(iii).1.1.3 Wang *et al.* (2013a), Concentrations of cVMS in biosolid amended soil, influent, effluent, receiving water, and sediment of wastewater treatment plants in Canada

A monitoring programme was conducted to determine the occurrence of D4, D5 and D6 in environmental compartments impacted by wastewater effluent discharges. Eleven WWTPs representative of those found in southern Ontario and southern Quebec, Canada were sampled. In addition, receiving water and sediment impacted by WWTP effluents, and biosolid-amended soil from agricultural fields were also analysed. The quality control samples run with this analysis returned recoveries in water of 100 ± 21%, 103 ± 21% and 107 ± 29% for D4, D5 and D6, respectively. For sediment recoveries were 69 ± 10%, 71 ± 9% and 74 ± 8% for D4, D5 and D6 respectively and for sludges recoveries were 70 ± 12%, 78 ± 11% and 76 ± 29% for D4, D5 and D6 respectively.

Concentrations in influents to the 11 WWTPs were in the range 0.282 – 6.69 µg/L, 7.75 – 135 µg/L and 1.53 – 26.9 µg/L, for D4, D5 and D6 respectively. The D4, D5 and D6 concentration ranges in effluent were <0.009 – 0.045 µg/L, <0.027 – 1.56 µg/L and <0.022 – 0.093 µg/L, respectively. The concentrations in receiving waters, taken from 0.005 to 3.1 km downstream of WWTP outfalls were lower compared to effluent in most cases, with ranges <0.009 – 0.023 µg/L, <0.027 – 1.48 µg/L and <0.022 – 0.151 µg/L for D4, D5 and D6, respectively. Sediment concentrations ranged from < 0.003 – 0.049 µg/g dw, 0.011 – 5.84 µg/g, and 0.004 – 0.371 µg/g for D4, D5 and D6, respectively. The concentrations in sewage sludge amended soils ranged from <0.008 – 0.017 µg/g dw, <0.007 – 0.221 µg/g dw and <0.009 – 0.711 µg/g dw for D4, D5 and D6, respectively, which are lower than the concentrations observed in the sediment, though approximately ten fold of the control soil concentrations.

D5 was the dominant cVMS found in the analysed samples, followed by D6 then D4, and there was good agreement between the predicted concentrations from the empirical model of the fate of siloxanes during sewage treatment of Fendinger *et al.*

(1997) and measured influent concentrations for D5 and D6. However, predicted concentrations for D4 were ten-fold higher than the measured D4 concentrations. The authors considered that the observed difference may have been due to higher hydrolysis and volatilisation rates for D4 in comparison to D5 and D6. However, the amount of cVMS lost via volatilisation was not been or estimated, so it is not possible to quantify the amount of substance lost via volatilisation.

Approximate removal efficiencies were reported as follows:

Site No.	Treatment type	Removal efficiency	
		D4	D5
9	Chemically-assisted primary treatment	97	92
1	Secondary Activated sludge	97	99
6	Secondary Activated sludge	98	98
7	Secondary Activated sludge	96	98
2	Lagoon	97	99
3	Lagoon	99	100
4	Lagoon	97	99
5	Lagoon	99	100
8	Lagoon	99	99
10	Lagoon	99	99
11	Lagoon	99	98

The mean removal efficiency at all sites was 98 and 99% for D4 and D5, respectively. Removal efficiencies at the site performing only primary treatment (Site 9) were ~92% for D4 and D5, while at sites with secondary activated sludge plants removal efficiencies for D5 were ≥ 95.8 % for D5.

From the results of the study both the influent concentration and the treatment type influenced the concentrations of D4 and D5 in effluent. The authors conclude that the higher concentrations in the effluent observed at site 9 were due to the chemically-assisted primary treatment performed providing a lesser degree of treatment than the other WWTPs investigated. Site 9 utilised a lower retention time and no aeration of the wastewater, giving fewer opportunities for adsorption or volatilisation removal mechanisms. The other mechanical treatment plants investigated in this study (n = 3) also perform secondary activated sludge treatment with aeration and longer hydraulic retention after primary treatment, and exhibit removal efficiencies of >96% for both D4 and D5. The increased efficiencies observed at sites undergoing lagoon treatment compared to sites not performing this treatment, is believed to be due to the increased potential for volatilisation after primary and secondary treatment.

However, the authors state that there is little influence on the removal efficiency of D4 and D5 by different techniques, with the removal mechanisms of volatilisation to air and adsorption to sewage sludge providing approximately equal contributions to removal. The authors also conclude that biodegradation plays a small role in the

removal due to the very low water solubilities of these substances, which limits their biological availability.

From the available information, effluent and receiving water concentrations are typically within a factor of 3 or 4 of each other, although this does not hold for sites 8 and 9. The WWTP at site 8 received about 80% municipal wastewater coming from >10,000 residences and 20% industrial wastewater including a facility manufacturing cosmetic and PCPs incorporating cVMS. In general, higher levels of cVMS are found in the sediments than the waters.

Due to the high log K_{OW} of cVMS, they have been shown to have a strong affinity for dissolved organic carbon (DOC) in water, with increasing DOC concentrations resulting in a decrease in the volatilisation of D5, because interactions with the colloidal DOC maintain a higher concentration in solution. A strong positive correlation (using Pearson's correlation analysis) was observed between the log D4, D5 and D6 concentrations and total organic carbon (TOC) in water, which suggests that high levels of TOC in water results in high concentrations of cVMS in the water column.

From the reported analytical results from the 11 WWTPs in Canada, based on triplicate analysis of single samples, 36.4% of receiving water samples (4 of 11), 50% of receiving water sediment samples (5 of 10) and 27.3% of effluent samples (3 of 11) had concentrations below LoQ for D4. For D5, 54.5% of receiving water samples (6 of 11) and 18.2% of receiving water sediment samples (2 of 11) had concentrations below LoQ. For the soil samples of the 13 samples, 69.2 % (9 of 13) and 7.7% (1 of 13) had concentrations below LoQ for D4 and D5, respectively.

The paper is published in a peer-reviewed journal using a validated method for the analysis of D4 and D5 in river and estuarine sediment and the results are considered to be reliable, although the GLP status is unknown.

[A further paper by Wang *et al*. (2013b) contains a few additional data but these are less relevant so only recorded in the Annexes.]

B(iii).1.1.4 Bletsou *et al*. (2013), Mass Loading and Fate of Linear and Cyclic Siloxanes in a WWTP.

Bletsou *et al*. (2013) investigated the occurrence and fate of five cVMS including D4, D5 and D6 in raw and treated wastewater and sludge from a WWTP in Athens, Greece. Additionally, the overall removal efficiencies were calculated and the solid-liquid distribution co-efficients for each cVMS were estimated at each sampling point. cVMS were detected in all WWTP influent and sludge samples. D5 and D6 were major components of the total siloxane load in the WWTP with concentrations of 2.60 and 1.83 µg/L, respectively, determined in the influent. However, the D3-D7 siloxanes contributed 59% to the total concentration determined in the effluent, with D5 being the major cyclic siloxane present at a mean concentration of 1.79 µg/L (range: 0.125 – 6.02 µg/L). The cyclic siloxanes were mainly detected in the dissolved phase of the influent samples, suggesting adsorption to particulate matter was not particularly significant. It was also noted that although there is no discernible pattern regarding daily variation, two-fold higher concentrations were observed for D5 and D6 at weekends. In sludge samples, D5 was the major compound detected

with mean concentrations of 15.1 mg/kg. However, in sludge samples 72% of the total siloxane concentrations related to the linear compounds. cVMS log K_d values are lower than linear siloxane values, with cyclic siloxane log K_d's not exceeding 3.8 L/kg, with results staying relatively consistent for all sample points, though siloxanes D5 –D7 do exhibit a greater affinity for secondary sludge than some other non-siloxane contaminants; it was suggested that this is due to the secondary sludge characteristics.

From the reported influent and effluent results from samples taken from the WWTP in Athens 0% of samples (0 of 7) had concentrations below LoD for both D4 and D5 in both influent and effluent. All dewatered sewage sludge samples had concentrations above the LoD for both D4 and D5.

The fate of cVMS substances in WWTPs are variable depending on the cyclic siloxane investigated. D3 and D4 were not removed during the treatment process while D5 and D6 showed removal efficiencies of 34.2 and >97 %, respectively. The authors suggest that the low removal efficiency of D5 is possibly due to the increased sorption potential of D5 compared to other cVMS. The results from the analysed samples showed that 68% of the total siloxanes present in the influent were sorbed to sludge, and 29% discharged in the effluent, with only a small proportion lost via volatilisation, degradation and transformation. Cyclic siloxane sorption was not significant, except for D5 where the mass balance shows that 66% of the influent concentration of D5 is present in the effluent. The authors concluded that D5 appears stable in the wastewater treatment process, and that the fraction that sorbs to the sludge hampers volatilisation. It is concluded that D4 does not undergo any apparent loss. However, the increased concentration of D3 in the effluent compared to the influent indicates an increase in loading and suggests that possible sources of additional D3 could be the breakdown of larger siloxane molecules or precursor compounds.

The paper is published in a peer-reviewed journal using an optimised and validated method for the analysis of D4, D5 and D6 in raw and treated wastewater and WWTP sludge and the results are therefore considered to be reliable although the GLP status is unknown.

B(iii).1.1.5 Sanchís *et al*. (2013), Occurrence of IVMS and cVMS in wastewater, surface water and sediments

Sanchís *et al*. (2013) proposed a new method for the analysis of cVMS by GC-MS/MS using a triple quadrupole analyser, and the method was then used to analyse surface waters and sediments from the Llobregat River and Riera de Rubí, Catalonia, Spain and the influents and effluents of 17 WWTPs. All the sites were equipped with secondary treatment with additional tertiary treatment for nitrogen and phosphorous removal, and some sites had tertiary treatment.

D4 and D5 were present in all the wastewater samples taken from the WWTPs, with D5 found at the highest concentration in 16 out of the 17 influents, with a median concentration of 8,915 ng/L. A significant reduction was observed during wastewater treatment. The highest D5 concentration in surface waters was 468 ng/L for the Rubi Brook at site E, while the highest D5 sediment concentration was 1,270 ng/g dry weight at site F (see Annex 2). The authors explained the high D5 concentration at

site F as being due to sediment sampled from a stagnant section of the river where accumulation is expected. In general, the sediment D4 and D5 concentrations were in agreement with the results of the previous studies of Zhang *et al.* (2011)[5], Sparham *et al.* (2011) and Kaj *et al.* (2005b).

From the reported wastewater influent samples results, 13.3% (6 of 45) and 6.7% (3 of 45) had concentrations below the LoQ for D4 and D5, respectively. For the effluent samples, 25% (12 of 48) and 0% (0 of 48) had concentrations below the LoQ for D4 and D5, respectively. The surface water results show that 0% (0 of 6) of samples were <LoQ for both D4 and D5 while for sediment 16.7% (1 of 6) and 0% of samples were <LoQ for D4 and D5, respectively.

The authors observed a 77 and 94% reduction in the effluent samples in comparison to the influent for D4 and D5, respectively. No significant differences were observed between the sites performing only secondary treatment and the sites performing secondary and tertiary treatment. A municipal WWTP near to Barcelona (sampled daily for a week) exhibited concentrations in the secondary effluent around 10 and 30 times lower than in the influent samples for D4 and D5, respectively. Complete elimination was not achieved at this site. Furthermore, concentrations in the tertiary effluents were around 1.1 and 3.1 times lower than in the secondary effluent for D4 and D5, respectively, which would seem to indicate that there is a difference in the treatment efficiencies of secondary and tertiary effluents. However, the authors do not provide any further information regarding the retention time, degree of aeration, or the quantity of sludge provided at each site, so, the impact of changes to these parameters for the sites sampled could not be assessed.

The paper is published in a peer-reviewed journal using a method shown to be acceptable for the analysis of D4 and D5 in wastewater, surface water and sediment. The results of the study are therefore considered to be reliable although the GLP status is unknown.

B(iii).1.1.6 van Egmond *et al.* (2013), Monitoring and modelling of siloxanes in a STP in the UK

Monitoring of D4, D5 and D6 was performed at Broadholme STP, operated by Anglian Water, UK at various sampling locations including at the site influent and effluent discharges. The analysis of samples was performed by HS-GC/MS after the addition of an isotopically labelled cVMS, to allow for correction for activity. The performance characteristics of the study indicate that good recoveries from samples were achieved using either the internal standard for total concentrations (114 ± 4%, 76 ± 14%, and 110 ± 13% for D4, D5 and D6 respectively) or external standard for dissolved concentrations, although recoveries of D6 using the headspace analysis method were low (96 ± 5%, 87 ± 14% and 30 ± 2% for D4, D5 and D6, respectively). Concentrations in raw sewage, determined over a 24-hour period were in the ranges <0.2 − 0.3, 5.6 − 36 and 2.0 − 24 µg/L for D4, D5 and D6, respectively. The corresponding effluent concentrations were <0.01, 0.305 − 0.347 and 0.071 − 0.117 µg/L, respectively. The percentage of D5 in the dissolved form in the effluent was 73 ± 4% for D5, and 26 ± 3% for D6.

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[5] This study concerns Chinese locations so is considered less relevant for this dossier.

The estimated removal rates of D5 and D6 at Broadholme STP were 98.3 and 99.0%, respectively. From the results of monitoring at different parts of the WWTP, the authors concluded that adsorption and volatilisation are the key processes in the removal of cVMS, and that only changes in the removal efficiency of organic matter in the final clarifier are likely to influence cVMS removal. The authors also observed a diurnal fluctuation in the influent at Broadholme STP, with concentrations lowest during the night and highest during the late morning, with a secondary peak in concentration observed during the late evening; however, this fluctuation was not observed in the final effluent. In addition, the estimated consumption of D5 ($\sim$2.7 mg cap^{-1} d^{-1}) derived for the population served by this plant was lower than that derived in the Environment Agency (UK) risk assessment (11.6 mg cap^{-1}d^{-1}).

The paper is published in a peer-reviewed journal using a validated method shown to be acceptable for the analysis of D4, D5 and D6 in wastewater. The results of the study are therefore considered to be reliable although the GLP status is unknown.

B(iii).1.1.7 Kaj *et al*. (2005a), Results from the Swedish National Screening Programme 2004. Part 4 Siloxanes

The Swedish Environmental Protection Agency (SIVL) performed a screening study for D4, D5 and D6 with the aim of determining concentrations in a variety of media in the Swedish environment. The sampling programme was designed to account for identified possible emission sources and sites where the substances are used. The samples were collected mainly during 2004 but are included here as this is a well-reported study.

The sampling and analytical methods used were designed to avoid both loss of the substances from the sample by volatilisation and sample contamination. The samples were collected from sites both near to potential industrial point sources and more remote areas, and include both freshwater and coastal sites. However, few details of the potential point sources are given, and it is not clear if the substances were actually being used in the areas.

D4 was found to be present in 37 sediment samples out of 54 (68.5%), with a maximum concentration of 2,300 ng/g dw. However, no detectable D4 concentrations were observed in water samples (0 of 25), although it was detected in air samples, indicating that volatilisation may be a loss pathway for D4.

D5 was the dominant siloxane monitored in this survey, being found in most samples (62 of 105 water, sludge and sediment samples), with the highest concentration reported as 1.1 µg/L in WWTP influent, 54,000 ng/g dw in sewage sludge (mean: 11,000 ng/g dw) and 190 ng/g dw in sediment. The source of D5 in these samples is unclear. Overall, the levels of D5 in surface water found in this survey appear to be generally low, but relatively few surface water samples were included, and these were generally taken from industrial areas where it was not clear whether or not D5 was being used at the time.

The study used appropriate analysis and extraction techniques for the analysis of samples. The results are therefore considered to be reliable although the GLP status is unknown.

B(iii).1.1.8 Kaj *et al*. (2005b), Siloxanes in the Nordic environment

Kaj *et al*. (2005b) investigated the environmental occurrence and distribution of volatile methyl siloxanes (including D4 and D5) in six countries (Denmark, Faroe Islands, Finland, Iceland, Norway and Sweden) in the Nordic environment. The sampling and analytical methods used were designed to avoid both loss of the substances from the sample by volatilisation and sample contamination. The samples were collected during 2004 and 2005.

No detectable amounts (< 0.1 µg/L) of D4 or D5 were observed in water samples collected from urban sites or for the four samples assessed for background exposures sampled from the Outer Oslofjord, Lake Røgden and Lake Bergsjøen in Norway and the Kattegat in Denmark. The highest cVMS concentration reported in the influents to STPs was 26 µg/L for D5. Significant reductions were observed in the STP effluents, with a maximum effluent concentration of 5.2 µg/L for D5, reported for Sersjantvíkin STP in the Faroe Islands. Removal efficiencies can be calculated from the reported influent and effluent concentrations, and the results are summarised in Table B(III).1.1.

Table B(iii).1.1 Removal efficiencies of several Nordic STPs (data from Kaj *et al*., 2005b)

Site	Influent (µg/L)	Effluent (µg/L)	Removal (%)
D4			
Arendal STP, Norway	0.15	0.035	76.7
Nokia 1, Tyre Factory, Finland	3.7	0.03	99.2
Nokia 2, Floor Factory	0.25	0.11	56.0
Bjergmarken STP, Roskile, Denmark	0.6	0.03	95.0
Lynetten STP, Kopenhavn, Denmark	0.28	0.03	89.3
D5			
Arendal STP, Norway	5	0.72	85.6
Nokia 1, Tyre Factory, Finland	5.3	0.48	90.4
Nokia 2, Floor Factory	0.33	0.98	-197.0
Bjergmarken STP, Roskile, Denmark	24	0.092	99.6
Lynetten STP, Kopenhavn, Denmark	26	0.063	99.8

Note: Yellow highlighting indicates values below the LoD, which are therefore expressed as half the LoD

Grey highlighting indicates an increase in concentration in effluent compared to the influent

The results indicated that there is a widespread distribution of siloxanes in the Nordic environment with a wide variation in measured concentrations across environmental media. The cyclic siloxanes were noted to occur in all media at significantly higher concentrations than the linear siloxanes and D5 was the dominant siloxane in all matrices but air, where D4 dominated. The concentrations were generally elevated in urban areas and in areas close to sewage treatment plants.

From Table B(iii).1.1, it can be seen that the removal efficiencies of D4 and D5 are 56.0 – 99.2% and -197.0 – 99.8%, respectively (although values from sites where the influent/effluent concentrations were below the limit of detection should be treated with caution). These removal efficiencies are lower than observed for

previous studies, but no explanation is provided. In addition, no explanation is given for the increased D5 concentration in the effluent of the site Nokia 2, in comparison to the influent.

The authors state that great variation in siloxane concentration was observed for different samples, but that the relative distribution of D4, D5 and D6 in WWTP influent are similar to that in sludge, with D5 being the dominant cVMS present. However, for a tyre factory in Finland, this distribution did not hold, with D4 and D6 being the dominant cVMS.

cVMS were found in all the sludge samples analysed from throughout the Nordic countries, with D5 found to be dominant in sludge even though the consumption of D4 and D5 are approximately equal. There was greater variation in sediment concentrations. The average concentration of all cVMS of interest was 30 µg/g dw, excluding samples from Iceland. The samples from Iceland only undergo mechanical treatment, so are likely to be not directly comparable. The lowest concentrations of cVMS in sludge, apart from in Iceland, were observed at two small Swedish STP (Ellinge and Floda), and in the sample from Sersjantvíkin in Faroe Islands, with total concentrations of 5.6, 6.7 and 5.5 µg/g dw for D4, D5 and D6, respectively. No sludge samples from Norway were analysed. The authors conclude the results from these sludge samples are in good agreement with the Swedish screening study of siloxanes performed by the SLU in 2004 (Kaj *et al.*, 2005a).

Sediment and sludge were observed to have a great variation in cVMS concentrations, with the highest concentrations observed close to urban areas; no cVMS were detected in the background concentration samples taken from the Kattegat in Denmark, two samples each from Lake Bergsjøen and Lake Røgden in Norway and from Ö Gotlandsdjupet and Ö Landsortsdjupet, Sweden. The highest concentration reported for total cVMS was 2,300 ng/g dw in sediment from a site near Roskilde in Denmark, which is 14 times greater than the next highest concentration, found at Essingen in Stockholm, Sweden (160 ng/g dw). As was seen for water and sludge samples, D5 was the dominant cVMS present in sediment samples.

Data presented in the report indicate that D4 and D5 were consumed in approximately equal quantities (~80 tonnes/year) within the Nordic countries over the years 1999 – 2003, although whilst the quantity of D5 used was relatively constant the quantity of D4 used seemed to fluctuate considerably. It is acknowledged in the report that these figures may be an underestimate of the true use of D4/D5 in the Nordic countries (due to the fact that importers are not obliged to register the full content of chemicals in their products) and it should also be noted that quantities used and use patterns may have altered considerably in the ten years since these data were compiled.

Data from the study are considered to be reliable, as the extraction and analysis techniques were suitable for the analysis of water, sludge and sediment samples for D4, D5 and D6. The report has been reviewed and published by the Nordic Council of Ministers.

B(iii).1.1.9 Schlabach *et al.* (2007), Siloxanes in the Environment of the Inner Oslofjord.

Schlabach et al. (2007) investigated the levels of D4 and D5 in influent and effluent from two sewage treatment plants discharging to the Inner Oslofjord in Norway (Bekkelaget STP and VEAS STP), as well as the levels in water and sediment from the Inner Oslofjord itself. The sampling and analytical methods used were designed to avoid loss of the substances from the sample by volatilisation and sample contamination. The samples were collected in September and October 2006.

D4 was detected in the influent to both STPs, and in the effluent from one sewage treatment plant at very low concentrations, but it was not detectable in seawater or sediment. D5 was present in both the influent and effluent from the STPs, but was not detectable in seawater. D5 levels in sediment were highest in the samples from Bekkelagsbassenget (concentration 690–920 µg/kg dw), which is near to the Bekkelaget STP. These findings are similar to those of the Kaj *et al.* (2005b) survey.

B(iii).1.1.10 Joint Research Centre [JRC] (2012), EU Wide Monitoring Survey on Waste Water Treatment Plant Effluents.

In 2010, 77 effluent samples from WWTPs in 17 EU Member States (MS) were analysed for D4, D5 and D6 at the Federal Environmental Agency (Umweltbundesamt (UBA)) laboratories in Vienna, Austria as part of an EU-wide monitoring survey of chemical contaminants. Table B(III).1.2 summarises where the samples were collected.

Table B(iii).1.2 Number of WWTP effluent samples per MS for analysis of D4, D5 and D6 (data from JRC, 2012)

Member State	Number of Samples	Member State	Number of Samples
Austria	6	Ireland	2
Belgium	19	Italy	2
Cyprus	2	Lithuania	3
Czech Republic	7	Netherlands	11
Finland	6	Portugal	2
France	2	Slovenia	1
Germany	2	Spain	3
Greece	2	Switzerland	5
Hungary	2		

At each sampling site, a 24-hour composite sample was taken by either grab-sampler or using automated systems. It is stated that samples were stored at ~4 °C and transported to JRC and UBA in temperature-controlled boxes as fast as possible. The method used by UBA for the extraction and analysis of samples is not reported explicitly, but either an SPE or LLE method was utilised followed by analysis by either LC-MS/MS or GC-HRMS. The LoQs in this study for D4, D5 and D6 were 0.02, 0.055 and 0.035 µg/L, respectively.

D4, D5 and D6 were only detected at one site, at concentrations of 0.11, 0.28 and 0.68 µg/L, respectively. The site was industrial (Colortex, Sint-Niklaas, Belgium). All the other samples analysed for this project returned results below the LoQ, indicating

good agreement in reported D4, D5 and D6 concentrations in WWTP effluents throughout the EU, within the confines of current analytical capabilities. However, the D6 results for the samples from site Fate_Sees 143 (Undisclosed Site, Czech Republic) and Fate_Sees 256 (AVZ Hungerbachtal, Germany) were reported as <0.04 µg/L, an elevated LoQ compared to the other samples. This increased LoQ for these samples was due to an increase in the signal:noise ratio during analysis. The majority of samples were extracted within 2 months and had been previously held under temperature controlled conditions, so loss of D4, D5 or D6 prior to analysis is considered unlikely to be an issue

Although the data have been reviewed and published by the European Commission, they are considered to be of uncertain reliability, because although all analyses were performed in a single laboratory (the GLP status of which is unknown), the analytical method is not described explicitly, and there is no information about potential losses between sample collection and analysis. Given the small sample sizes, and lack of information about treatment type and daily or seasonal differences in concentrations, the results are of limited usefulness. No assessment can be made as to the removal efficiencies of the compounds in the WWTP or their ultimate fate.

B(iii).1.1.11 Xu *et al.* (2013), Occurrence and fate of volatile siloxanes in a municipal Wastewater Treatment Plant of Beijing, China

Xu *et al.* (2013) investigated the behaviour of cVMS in WWTPs utilising either traditional anaerobic-anoxic-oxic (traditional A^2/O) or reversed anoxic-anaerobic-oxic (reversed A^2/O) secondary sludge treatment in China over two sampling events. The study also investigated the removal of cVMS by sorption at secondary treatment processes and the target compound elimination along each unit of the secondary treatment process. Details of the WWTP are detailed below (the treatment capacity was 200,000 m^3/d in both cases).

Process	Retention Time	
	Traditional A^2/O	Reversed A^2/O
Anaerobic tank	1.5 h	2.5 h
Anoxic tank	3 h	1.5 h
Oxic tank	10.8 h	10 h
Solids	20 - 25 d	6 - 7 d

The authors state that secondary effluent samples generally had lower cVMS concentrations than primary effluent samples, with mean removal efficiencies over the two sampling events of 76.2 – 92.7% and 59.3 – 80.6% for the traditional A^2/O and the reversed A^2/O process, respectively. D4, D5 and D6 concentrations were observed at higher concentrations than in the primary effluent in both the anaerobic unit of the traditional A^2/O process and in the anoxic unit of the reversed A^2/O process. This suggests that the increased concentrations are due to the cVMS re-entering the aqueous phase from the return sludge (after settling in the secondary clarifier, a portion of the sludge was returned to the anaerobic tank, the rest was dehydrated) during agitation. Based on the mean results over the two sampling events, D4, D5 and D6 relative mass fraction loss by sorption during the traditional

A^2/O process was 29.4 ± 2.8%, 38.1 ± 7.2% and 53.0 ± 13.5%, respectively. In the reversed A^2/O process losses were 19.0 ± 1.3%, 32.0 ± 2.3% and 40.2 ± 6.0% for D4, D5 and D6, respectively. These results show that sorption to sludge can be used as an abatement technique with the greatest efficiencies observed for higher molecular weight cVMS. The mass removal was also calculated for each process at various locations during treatment, as indicated below:

Location	Mass Loss (%)[1]
Traditional A^2/O process; Anaerobic tank	44.4 - 84.3
Traditional A^2/O process; Anoxic and oxic tanks, and secondary clarifier	6.3 - 7.4
Reversed A^2/O process; Anaerobic tank	45.8 - 77.1
Reversed A^2/O process; Other units	12.7 - 22.9

Note: [1]Results reported as percentage mass loss of D3, D4, D5 and D6.

From these results, it can be seen that most elimination occurs in the anaerobic tanks. However in Figure B(iii).1, it can be seen that the removal rates of D4, D5 and D6 by adsorption to excess sludge were different in each secondary treatment unit and for each compound.
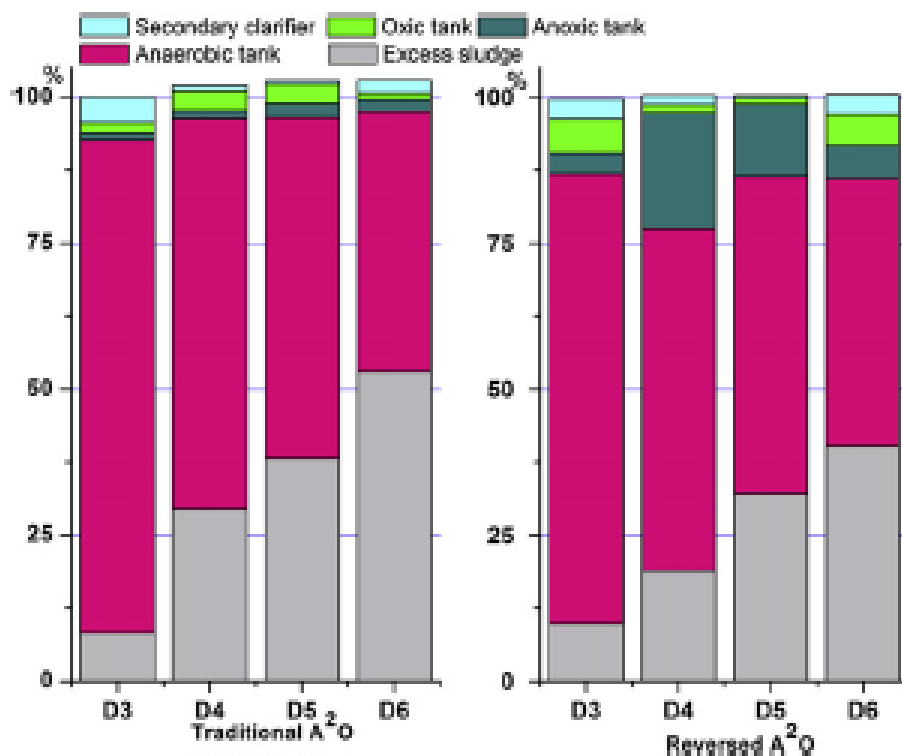

Figure B(iii).1   Mean relative fractions of mass loss (%) of D3, D4, D5 and D6 to excess sludge in both the traditional A^2/O and reversed A^2/O processes (Xu *et al.*, 2013)

The authors concluded that the compounds were ubiquitous in both wastewater and sludge samples for both the traditional A^2/O and reversed A^2/O processes, with removal efficiencies of up to 92.7% observed from the primary effluent. D4, D5 and D6 were all removed via adsorption to excess sludge and via volatilisation in the anaerobic units of both processes, with degradation via microbial-catalysed hydrolysis also observed for D5 and D6 in the anaerobic compartments. The authors observed significant differences in the partition coefficients of D4, D5 and D6 depending on organic matter distribution. They suggested that this was due to dissolved organic matter (DOM) entering the aqueous phase from the return sludge during agitation with wastewater. The DOM in the aqueous phase resulted in elevated dissolved concentrations by enhancing water solubility and aggravating their desorption from the activated sludge, hence reducing the partition coefficient. This had the effect of increasing the fractions of cVMS in the treated effluent, reducing removal efficiency.

B(iii).1.2 Comparison of modelled and measured concentrations in existing literature

B(iii).1.2.1 Whelan and Breivik (2013), Dynamic modelling of aquatic exposure and pelagic food chain transfer of cVMS in the Inner Oslofjord

Whelan and Breivik (2013) investigated the marine fate and pelagic food chain transfer of D4, D5 and D6 in Norway's Inner Oslofjord. The study used both modelled and measured influent, effluent and sludge concentrations of D4, D5 and D6. The Oslofjord POP (Persistent Organic Pollutants) model is a bespoke dynamic non-equilibrium multimedia fate and transport model specifically designed to take account of processes occurring in the three compartments of the Oslofjord. Emission rates of cVMS were based on per capita usage estimates in cosmetic products and the assumption that 10% is lost to the wastewater stream as reported by Environment Agency (2009a,b).

The degradation rates used in the POP model were adjusted bulk half-lives; these half lives needed to be adjusted for the dissolved fraction, as hydrolysis is the only degradation process considered in the model. There is some uncertainty associated with the food web part of the model due to assumptions made about the relative importance of different feeding relationships, and the herring and cod metabolism rate constants were adjusted for the difference between the Baltic Sea and the Inner Oslofjord. The seasonal distribution of temperature in the different compartments of the Inner Oslofjord were also taken into account by adjustment of the temperature dependent partition coefficients. All model input parameters were adjusted so that the model derives K_{OC} values which were consistent with the measured values since the default model input parameters tend to significantly over-estimate the K_{OC} for the cVMS of interest.

The authors concluded that the concentrations of D4, D5 and D6 in the water column and concentrations of D4 in the Inner Oslofjord were all predicted to be less than the current limits of detection of 20-30 ng/L, and these predictions were supported by the measured cVMS data; the predicted concentrations of D5 and D6 in sediments were also in agreement with the monitoring of Schlabach *et al.* (2007). Measured

sediment concentrations of D5 and D6 were 93 – 920 and <17 – 100 ng/g dw, respectively, with the predicted concentrations being ≤ 250 ng/g dw for D5 and ≤ 80 ng/g dw for D6. The measured D4 concentrations were all less than the LoD (4 – 38 ng/g dw), as predicted by the model. However, for all three compounds the model estimates are much higher than the measured data for influent concentrations, by up to a factor of 8 for D4. The authors concluded that this over-estimation of cVMS influent concentrations was due to the 10% wash-off emission scenario being larger than the observed percentage wash-off. For D5 and D6 the major loss pathway in the water column is expected to be volatilisation with losses greater than 50% of the emissions, with peak losses occurring during the winter; for D4 hydrolysis is the dominant pathway for loss with losses expected to exceed 60% of emissions, and burial in the sediment accounting for ~10% of emissions, although volatilisation is still significant. Degradation by hydrolysis of D5 and D6 is expected to be slow. When the predicted model results are compared with measured biota concentrations, the model concentrations of D4 were under-estimated, and the concentrations of D5 and D6 were over-estimated, though when measured concentrations in the biota were used to predict D5 concentrations in herring and cod there was good agreement. For D4 and D6 the results were over-estimated and under-estimated, respectively.

The study authors also concluded that the lack of benthic organism data, both measured and from the food-web model, may be important as it has been shown that sediments can be an important repository of cVMS materials. Therefore, although the models can be used to assess the dominant loss processes and the importance of metabolism, there are uncertainties in some of the rate constant model parameters used, which are postulated to account for the differences observed between the predicted and measured concentrations. A reliable estimate of emission rates is also important, as it has been shown that this can cause large discrepancies between observed and predicted concentrations. The size of the discrepancy between actual and modelled emission rates may also have a significant impact on observed and predicted concentrations.

This study is published in a peer-reviewed journal. The model detailed in the paper was developed from previous POP and steady-state models and utilises measured environmental concentrations of cVMS from validated methods. Therefore, the results of this study are deemed to be reasonably robust.

B(iii).1.2.2 van Egmond *et al.* (2013), Monitoring and modelling of siloxanes in a STP in the UK

van Egmond *et al.* (2013) reproduced the SimpleTreat simulations reported by Environment Agency (2009a,b) in SimpleTreat 3.1 using default settings, for verification, comparison and further analysis of default parameters characterising total suspended solids [TSS] discharge to effluent to compare the result with the measured results obtained from a sampling survey performed at Anglian Water's Broadholme STP.

Measured concentrations were <0.01, 0.305-0.347 and 0.071 – 0.117 µg/L for D4, D5 and D6, respectively. The estimated removal rate of D5 was 98.3%. In addition, the estimated D5 emissions of 2.7 mg cap^{-1} d^{-1} were an order of magnitude lower than the predictions of Environment Agency (2009b). The study authors concluded that although their results are fairly representative of previous predictions, further

investigation into the specific uses of 'leave-on' and 'rinse-off' cVMS containing personnel care products should be performed.

This study is published in a peer-review journal using results from a validated method shown to be acceptable for the analysis of D4, D5 and D6 in wastewater. Therefore, the results are considered to be reasonably reliable.

B(iii).1.3 Polymer degradation in soil.

Lehmann *et al.* (1994) showed that ^{14}C-polydimethylsiloxane (PDMS) (200 cst viscosity, number average molecular weight 6642 g/mol) degraded slowly when incubated in a Londo sandy clay loam soil with a water content of 12 per cent. The radiolabel in the test substance was randomly distributed on the methyl groups. The soil was collected from an agricultural field in Michigan (top 5 cm), sieved (2 mm), and stored at 4 °C prior to use. It had an organic matter content of 2.4 per cent, a pH of 7, and a sand:silt:clay ratio of 50:28:22. The test system used consisted of 50 g of soil in biometer flasks to which 0.5 mL of a solution of PDMS in tetrahydrofuran was added to give an initial PDMS concentration of 100 mg/kg. The soil was left uncovered for three hours to allow the solvent to evaporate, and then carbon dioxide and volatiles traps were added. Next, the flasks were attached to an oxygen manifold and incubated at a constant moisture content at 25 °C for up to 25 weeks. A second set of experiments investigated the effect of soil drying on the degradation rate. These samples were prepared in a similar way, except that 5 g of soil in centrifuge tubes was used, a foam plug moistened with PDMS (350 cst viscosity) inserted into the neck of the tube (to trap volatiles), and the tubes set open to dry at 25 °C for up to 14 days.

In the experiments using moist soil (12.2–13.2 per cent moisture) the amount of water-extractable ^{14}C in the soil increased with time, which suggests that the polymer degraded to smaller, water-soluble compounds. After 25 weeks of incubation the yield of low molecular weight water-soluble products was around 2.9 per cent of the radioactivity initially applied. The soil-extractable degradation products were low molecular weight linear siloxanols of general formula $HO–[Si(CH_3)_2O]_n–H$. A small number of volatile ^{14}C compounds were also evident (collected in the trap). These compounds were not identified, but accounted for around only 0.5 per cent of the applied radioactivity after 25 weeks. In addition, a small amount of [14]CO_2 was found (around 0.19 per cent of the total ^{14}C applied). The overall mass balance from these experiments was generally very good (in the range 92.8–107.2 per cent), which indicates that all major degradation products are accounted for. When the soil was allowed to dry (from a moisture content of 12 per cent to around 3 per cent over the period of a week), degradation was much more rapid.

For the soil-drying experiments, the soil dried steadily from an initial water content of around 12 per cent to a water content of about 2–3 per cent by day four. After this time the water content remained relatively constant throughout the experiment. No degradation of PDMS was evident over the first three days of the experiment. On day four a decrease in the molecular weight distribution and a slight formation of water-soluble degradation products was evident. However, by day seven a significant breakdown of the PDMS to low molecular weight products had occurred and by day 14 the water-extractable and acid-extractable (0.1 M HCl) products

accounted for around 18.2 and 11.5 per cent, respectively, of the total radioactivity applied. No significant amounts of volatile products formed (<0.11 per cent of the amount of radioactivity applied). The mass balance from this experiment was very good (99.0–107.4 per cent).

Additional experiments on the microbial degradation of the low molecular weight products showed that dimethylsilanediol was the major ultimate degradation product. Lehmann *et al.* (1994) concluded that the degradation of PDMS is probably not biological in origin, as it is more rapid under lower soil moisture conditions that are less favourable to microbial populations.

A follow-on study that used seven soils from the USA of differing pH, percentage organic matter, texture, mineralogy, and geographic origin demonstrated the general applicability of this degradation route (Lehmann *et al.*, 1995). Moist soils (initial moisture between 8 and 31 per cent, depending on the soil) were amended with ^{14}C -PDMS (viscosity 350 cst and number average molecular weight 9440 g/mol) and maintained at 23°C for up to 14 days (during which the soils were allowed to dry naturally). In all soils, PDMS degraded to low molecular weight, water-soluble products over the 14 days of the experiment (for one soil the experiment was extended to 28 days). The main degradation product was dimethylsilanediol. Other small silanols or cyclic siloxanes were either not detected or formed in only trace amounts. Additional experiments were carried out to investigate the effects of the loading rate on the degradation products seen with one soil (Londo soil). At loadings of around 100 mg/kg, the dominant degradation product was dimethylsilanediol, using both moist and oven-dried soil. However, at very high PDMS loadings (1 per cent or 10,000 mg/kg), a higher proportion of cyclic products (i.e. D4 and D5) formed.

Another study by Lehmann *et al.* (2000) investigated the degradation of a commercially available PDMS (viscosity of 350 cst) emulsion in field soils under natural conditions. Aqueous emulsions of PDMS were sprayed onto four soil plots (each 2.44 m by 2.44 m) in Michigan in May 1997 to give concentrations of 0 mg/kg (control), 215 mg/kg (low treatment), 430 mg/kg (medium treatment), and 860 mg/kg (high treatment). Soil cores (0–5 and 5–10 cm) were collected every two weeks over the following summer and analysed for total soil PDMS and decreases in molecular weight of the PDMS that remained. The concentration of PDMS decreased by 50 per cent within 4.5, 5.3, and 9.6 weeks for the low, medium, and high treatments, respectively. Dimethylsilanediol was the main degradation product identified in the soil columns (found in most samples at <5 per cent of the original PDMS concentration). A further application of the medium treatment level was carried out in late August. This showed a slow degradation of PDMS during the cool, wet, autumn months followed by around 40 per cent degradation over the winter months, with further, extensive degradation in the summer of 1998. These findings are consistent with the results of the laboratory studies, but substances that volatilised from the soil were not collected in this study.

In summary, PDMS can break down in soil at ambient temperatures to form small amounts of D4 and D5 if the polymer is present at high loading rates (which might not be environmentally realistic). The emission to the (air) environment that results

from such processes is very difficult, if not impossible, to estimate as the yield depends on the specific conditions to which the polymers are exposed.

Annex 1: D4 concentrations in the aquatic environment

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
Wang *et al.* (2013a)	1 (Canada)	Secondary Activated Sludge	12/05/2010	0.77	0.02	ND	0.00	0.05
Wang *et al.* (2013a)	2 (Canada)	Lagoon	18/05/2010	6.69	0.02	ND	0.02	0.00
Wang *et al.* (2013a)	3 (Canada)	Lagoon	12/06/2010	1.27	0.04	ND	0.01	0.00
Wang *et al.* (2013a)	4 (Canada)	Lagoon	22/06/2010	0.28	0.00	ND	0.00	0.00
Wang *et al.* (2013a)	5 (Canada)	Lagoon	07/07/2010	0.73	0.00	ND	0.01	0.03
Wang *et al.* (2013a)	6 (Canada)	Secondary Activated Sludge	27/07/2010	1.04	0.02	ND	0.02	0.02
Wang *et al.* (2013a)	7 (Canada)	Secondary Activated Sludge	03/08/2010	0.55	0.02	ND	0.01	0.03
Wang *et al.* (2013a)	8 (Canada)	Lagoon	04/10/2010	4.23	0.03	ND	0.01	0.00
Wang *et al.* (2013a)	9 (Canada)	Chemically Assisted Primary	20/09/2010	1.92	0.05	ND	0.02	0.05
Wang *et al.* (2013a)	10 (Canada)	Lagoon	23/08/2010	0.84	0.02	ND	0.00	0.00
Wang *et al.* (2013a)	11 (Canada)	Lagoon	12/10/2010	0.73	0.00	ND	0.00	0.04
Bletsou *et al.* (2013)[1]	WWTP, Athens, Greece	Primary sedimentation, Activated sludge process with biological N and P removal, Secondary Sedimentation	04/2012	0.15	0.13	0.11	ND	ND
Whelan and Breivik (2013)[2]	Bekkelaget, Norway	Not Reported	2004	0.10	0.02	1.10	ND	ND
Whelan and Breivik (2013)[3]	Bekkelaget, Norway	Not Reported	2004	0.10	0.02	2.70	ND	ND
Whelan and Breivik (2013)[2]	VEAS, Norway	Not Reported	2004	0.20	0.10	90.00	ND	ND
Whelan and Breivik (2013)[3]	VEAS, Norway	Not Reported	2004	0.20	0.10	1.00	ND	ND
Kaj *et al.* (2005a,b)	Gislaveds, Sweden	Not Reported	NR	0.04	0.04	0.14	0.035	0.015
Kaj *et al.* (2005a)	Landsbro, Sweden	Not Reported	24/11/2004	0.03	0.03	0.34	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
Kaj *et al.* (2005a)	Hultsfred, Sweden	Not Reported	24/11/2004	0.04	ND	0.11	ND	ND
Kaj *et al.* (2005a)	Virserum STP, Sweden	Not Reported	24/11/2004	0.04	ND	0.38	ND	0.01
Kaj *et al.* (2005a)	SCA Ostrand, Sweden	Not Reported	NR	0.04*	ND	0.01	ND	ND
Kaj *et al.* (2005b)	Kobenhavn, Denmark	Not Reported	26/10/2004	0.28	0.03	0.47 – 0.74	ND	0.0025
Kaj *et al.* (2005b)	Roskilde, Denmark	Not Reported	19/10/2004	0.60	0.03	ND	0.02	84 ng
Kaj *et al.* (2005b)	Tyre factory, Finland	Not Reported	01/09/2004	3.70*	0.03	0.96	ND	ND
Kaj *et al.* (2005b)	Floor Factory, Finland	Not Reported	01/09/2004	0.25*	0.11		ND	ND
Kaj *et al.* (2005b)	Espoo, Finland	Not Reported	24/05/2005	ND	0.04	0.53	ND	0.01
Kaj *et al.* (2005b)	Helsinki, Finland	Not Reported	24/05/2005	ND	0.04	0.23	ND	0.01
Kaj *et al.* (2005b)	Arendal, Norway	Not Reported	NR	0.15	0.04	ND	ND	ND
Kaj *et al.* (2005b)	Lake Bergsjøen, Norway	NA	NR	NA	NA	NA	0.03	0.0325
Kaj *et al.* (2005b)	Lake Røgden, Norway	NA	NR	NA	NA	NA	0.045	0.025
Kaj *et al.* (2005b)	Pornainen STP, Finland	Not Reported	26/01/2005	ND	ND	0.74	ND	ND
Kaj *et al.* (2005b)	Kokonniemi STP, Finland	Not Reported	26/01/2005	ND	ND	0.66	ND	ND
Kaj *et al.* (2005b)	Klettegardar STP, Reykjavik, Iceland	Not Reported	26/01/2005	ND	ND	0.12	ND	ND
Kaj *et al.* (2005b)	Ananaust STP, Reykjavik, Iceland	Not Reported	26/01/2005	ND	ND	0.096	ND	ND
Kaj *et al.* (2005b)	Skellefteå STP, Skellefteå, Sweden	Not Reported	26/01/2005	ND	ND	0.37	ND	ND
Sparham *et al.* (2011)	Felmersham, River Great Ouse, UK	Not Reported	27/08/2008	ND	ND	ND	ND	0.02
Sparham *et al.* (2011)	Felmersham, River Great Ouse, UK	Not Reported	27/08/2008	ND	ND	ND	ND	0.02

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
Sparham *et al.* (2011)	Felmersham, River Great Ouse, UK	Not Reported	27/08/2008	ND	ND	ND	ND	0.01
Sparham *et al.* (2011)	Tyringham Bridge, River Great Ouse, UK	Not Reported	23/09/2008	ND	ND	ND	ND	0.10
Sparham *et al.* (2011)	Tyringham Bridge, River Great Ouse, UK	Not Reported	23/09/2008	ND	ND	ND	ND	0.10
Sparham *et al.* (2011)	Tyringham Bridge, River Great Ouse, UK	Not Reported	23/09/2008	ND	ND	ND	ND	0.10
Wang *et al.* (2013b)	Canada	Not Reported		ND	ND	ND	ND	0.03
Kaj *et al.* (2005b)	O Gotlandsdjupet, Sweden	Not Reported	NR	ND	ND	ND	ND	0.01
Kaj *et al.* (2005a)	O Oland, Sweden	Not Reported	NR	ND	ND	ND	ND	0.02
Kaj *et al.* (2005a)	Norrkopingsdjupet, Sweden	Not Reported	NR	ND	ND	ND	ND	0.01
Kaj *et al.* (2005a)	Stenungsund, Sweden	Not Reported	08/11/2012 - 09/11/2012	ND	ND	ND	0.03	0.01
Kaj *et al.* (2005a)	Akzo-Nobel Stockvik. STP, Sweden	Not Reported	22/10/2004	ND	0.03	ND	0.03	0.00
Kaj *et al.* (2005a)	Henriksdal STP, Sweden	Not Reported	16/11/2004	ND	ND	0.28	ND	ND
Kaj *et al.* (2005a)	Gasslosa STP, Sweden	Not Reported	24/11/2004	ND	ND	0.31	ND	ND
Kaj *et al.* (2005a)	Ryaverket STP, Sweden	Not Reported	15/12/2004	ND	ND	0.43	ND	ND
Kaj *et al.* (2005a)	Bay outside Stockvik 1 and 2, Sweden	NA	21/10/2004	ND	ND	ND	0.03	0.011
Kaj *et al.* (2005a)	Karlshamn STP, Sweden	Activated sludge, chemical and mechanical	28/09/2004	ND	ND	0.15	ND	ND
Kaj *et al.* (2005a)	Mörrum landfill, Sweden	NA	23/09/2004	ND	0.035⁻	ND	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
Kaj et al. (2005a)	Karlskrona STP, Sweden	Biological, chemical post suspensions mechanical	07/10/2004	ND	ND	0.30	ND	ND
Kaj et al. (2005a)	Volvo cars STP, Sweden	Not Reported	06/10/2004	ND	ND	0.06	ND	ND
Kaj et al. (2005a)	Angelskog landfill, Sweden	NA	06/10/2004	ND	0.035⁻	ND	0.035	ND
Kaj et al. (2005a)	Ronneby STP, Sweden	Biological, chemical and mechanical	06/10/2004	ND	ND	0.125	ND	ND
Kaj et al. (2005a)	Sölvesborg STP, Sweden	Activated sludge with N-elimination	29/09/2004	ND	ND	0.23	ND	ND
Kaj et al. (2005a)	Lake Bäsingen, Sweden	NA	04/10/2004	ND	ND	ND	ND	0.095
Kaj et al. (2005a)	Krylbo STP, Sweden	Suspension, activated sludge	29/09/2004	ND	ND	0.13	ND	ND
Kaj et al. (2005a)	Fagresta STP, Sweden	Suspension, activated sludge	12/10/2004	ND	ND	0.59	ND	ND
Kaj et al. (2005a)	Venjam STP, Sweden	Mechanical, chemical	06/10/2004	ND	ND	0.235	ND	ND
Kaj et al. (2005a)	Lake Venjan/Venjansjön, Sweden	NA	03/10/2004	ND	ND	ND	ND	0.0235
Kaj et al. (2005a)	Bollnäs STP, Sweden	Not Reported	20/10/2004	ND	ND	0.14	ND	ND
Kaj et al. (2005a)	Duvbacken STP, Sweden	Not Reported	12/10/2004	ND	ND	0.2	ND	ND
Kaj et al. (2005a)	Resselvans STP, Sweden	Not Reported	07/12/2004	ND	ND	0.49	ND	ND
Kaj et al. (2005a)	Sandviken STP, Sweden	Not Reported	13/10/2004	ND	ND	0.35	ND	ND
Kaj et al. (2005a)	Myrviken STP, Sweden	Mechanical, dehydration, compost	01/11/2004	ND	ND	0.075	ND	ND
Kaj et al. (2005a)	Bräcke STP, Sweden	Mechanical, biological	19/10/2004	ND	ND	0.43	ND	ND
Kaj et al. (2005a)	Björnrike STP, Sweden	Mechanical, chemical	21/06/2004	ND	ND	0.039	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
Kaj *et al.* (2005a)	Hissmofors STP, Sweden	Mechanical, chemical, biological	19/10/2004	ND	ND	0.37	ND	ND
Kaj *et al.* (2005a)	Ragunda STP/Överammer STP, Sweden	Dehydration	19/10/2004	ND	ND	0.21	ND	ND
Kaj *et al.* (2005a)	Strömsund STP, Sweden	Mechanical, chemical, biological	27/10/2004	ND	ND	0.26	ND	ND
Kaj *et al.* (2005a)	Åre STP, Sweden	Mechanical, chemical, biological	13/04/2004	ND	ND	0.31	ND	ND
Kaj *et al.* (2005a)	Östersund STP/ Göviken STP, Sweden	Mechanical, chemical, biological	29/09/2004	ND	ND	0.07	ND	ND
Kaj *et al.* (2005a)	Gröpplebäcken, Sweden	NA	24/11/2004	ND	ND	ND	ND	0.008
Kaj *et al.* (2005a)	Hulingen, Sweden	NA	24/11/2004	ND	ND	ND	ND	0.022
Kaj *et al.* (2005a)	Viserum, Sweden	NA	24/11/2004	ND	ND	ND	ND	0.00345
Kaj *et al.* (2005a)	Viserum STP, Sweden	Not Reported	24/11/2004	0.04	0.03	0.38	ND	ND
Kaj *et al.* (2005a)	Mouth of Emån, Sweden	NA	27/10/2004	ND	ND	ND	ND	0.006
Kaj *et al.* (2005a)	Bromölla STP, Sweden	Not Reported	28/09/2004	ND	ND	0.19	ND	ND
Kaj *et al.* (2005a)	Ivösjön, Sweden	NA	19/10/2004	ND	ND	ND	ND	0.03
Kaj *et al.* (2005a)	Öresunds STP/Helsingborg STP, Sweden	Not Reported	22/09/2004	ND	ND	0.45	ND	ND
Kaj *et al.* (2005a)	Helsingborg (coast), Sweden	NA	03/11/2004	ND	ND	ND	ND	0.008
Kaj *et al.* (2005a)	Hammarsjön, Sweden	NA	19/10/2004	ND	ND	ND	ND	0.01
Kaj *et al.* (2005a)	Kristianstad STP, Sweden	Not Reported	05/10/2004	ND	ND	2.3	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
Kaj *et al.* (2005a)	Lundåkrav STP, Sweden	Not Reported	29/09/2004	ND	ND	0.27	ND	ND
Kaj *et al.* (2005a)	Källby STP, Sweden	Not Reported	27/09/2004	ND	ND	0.13	ND	ND
Kaj *et al.* (2005a)	Sjölunda STP, Sweden	Not Reported	22/09/2004	ND	ND	0.3	ND	ND
Kaj *et al.* (2005a)	Perstorp STP, Sweden	Not Reported	26/10/2004	ND	ND	0.11	ND	ND
Kaj *et al.* (2005a)	Storarydsdammen, Sweden	NA	22/10/2004	ND	ND	ND	ND	0.014
Kaj *et al.* (2005a)	Ystad STP, Sweden	Not Reported	22/09/2004	ND	ND	0.33	ND	ND
Kaj *et al.* (2005a)	Himmerfjärdsverket, Sweden	Not Reported	28-30/09/2004	ND	0.03	0.14	ND	ND
Kaj *et al.* (2005a)	Himmerfjärden, Sweden	NA	01/09/2004	ND	ND	ND	ND	0.115
Kaj *et al.* (2005a)	St. Envättern, Sweden	NA	01/09/2004	ND	ND	ND	ND	0.0575
Kaj *et al.* (2005a)	Flen STP, Sweden	Mechanical, chemical, biological	11/10/2004	ND	ND	0.065	ND	ND
Kaj *et al.* (2005a)	Gnesta STO, Sweden	Mechanical and chemical	19/10/2004	ND	ND	1.1	ND	ND
Kaj *et al.* (2005a)	Eskilstuna STP, Sweden	Mechanical, chemical, biological and wetland	18/10/2004	ND	ND	0.28	ND	ND
Kaj *et al.* (2005a)	Katrineholm STP, Sweden	Mechanical, chemical, biological	20/10/2004	ND	ND	0.46	ND	ND
Kaj *et al.* (2005a)	Nyköping STP, Sweden	Mechanical, chemical, biological	NR	ND	ND	0.49	ND	ND
Kaj *et al.* (2005a)	Oxelösund STP, Sweden	Mechanical and wetland	27/10/2004	ND	ND	0.18	ND	ND
Kaj *et al.* (2005a)	Strängäs STP, Sweden	Mechanical, chemical, biological	NR	ND	ND	0.13	ND	ND
Kaj *et al.* (2005a)	Vagnhärad STP, Sweden	Mechanical, chemical and wetland	13/10/2004	ND	ND	0.37	ND	ND
Kaj *et al.* (2005a)	Vingåker STP, Sweden	Mechanical, chemical, biological and wetland	13/10/2004	ND	ND	0.41	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (μg/L)	Effluent (μg/L)	Sludge (μg/g dw)	Receiving Waters (μg/L)	Receiving Water Sediment (μg/g dw)
Kaj *et al.* (2005a)	Vik STP, Sweden	Mechanical, chemical, biological	02/11/2004	ND	0.03	0.15	ND	ND
Kaj *et al.* (2005a)	Vänern, Åsfjorden, Sweden	NA	30/09/2004	ND	ND	ND	ND	0.14
Kaj *et al.* (2005a)	Vänern, Kattfjorden, Sweden	NA	30/09/2004	ND	ND	ND	ND	0.115
Kaj *et al.* (2005a)	Skåre STP, Sweden	Mechanical, chemical, biological	19/10/2004	ND	0.03	0.34	ND	ND
Kaj *et al.* (2005a)	Fiskartorpet STP, Sweden	Mechanical, chemical, biological	26-28/10/2004	ND	0.03	0.13	ND	ND
Kaj *et al.* (2005a)	Tivoliverket, Sweden	Not reported	NR	ND	ND	0.135	ND	ND
Kaj *et al.* (2005a)	Bodum STP, Sweden	Not reported	10/11/2004	ND	ND	0.18	ND	ND
Kaj *et al.* (2005a)	Lidköping STP, Sweden	Not reported	NR	ND	0.03	1	ND	ND
Kaj *et al.* (2005a)	Vara STP, Sweden	Mechanical, chemical, biological	04/10/2004	ND	ND	0.35	ND	ND
Kaj *et al.* (2005a)	Åmål STP, Sweden	Mechanical and chemical	29/09/2004	ND	0.03	0.095	ND	ND
Kaj *et al.* (2005a)	Finspångs STP, Sweden	Not reported	26/10/2004	ND	0.035	0.42	ND	ND
Kaj *et al.* (2005a)	Skuten, Sweden	NA	29/10/2004	ND	ND	ND	ND	0.014
Kaj *et al.* (2005a)	Linköping STP, Sweden	Not reported	09/11/2004	ND	0.03	0.22	ND	ND
Kaj *et al.* (2005a)	Roxen, Sweden	NA	29/09/2004	ND	ND	ND	ND	0.225
Kaj *et al.* (2005b)	Sersjantvíkin STP, Faroe Islands	Not Reported	26/01/2005	ND	0.04	0.19	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
Kaj *et al.* (2005b)	Ellinge STP, Eslöv, Sweden	Not Reported	26/01/2005	ND	ND	0.20	ND	ND
Kaj *et al.* (2005b)	Floda STP, Lerum, Sweden	Not Reported	26/01/2005	ND	ND	0.12	ND	ND
van Egmond *et al.* (2013)	Broadholme STP, UK	Primary and secondary treatment	22/03/2010 - 23/03/2010	< 0.2 - 0.3	0.01	ND	ND	ND
van Egmond *et al.* (2013)	Broadholme STP, UK	Primary and secondary treatment	07/07/2010 - 08/07/2010	< 0.2	0.012**	ND	ND	ND
Sanchís *et al.* (2013)	WWTP-1; Discharge to Mediterranean Sea, Spain	Primary and Secondary. Biological treatment with nitrogen and phosphorus removal. Anaerobic digestion.	02/2011	0.351 ± 0.0052	0.125 ± 0.012	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-2; Discharge to Ter River, Spain	Secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion.	02/2011	0.0374 ± 0.012	0.00	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-3; Discharge to Besos River, Spain	Primary and Secondary. Biological treatment with phosphor removal. Anaerobic digestion.	02/2011	1.041 ± 0.0078	ND	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-4; Discharge to Mediterranean Sea, Spain	Primary and secondary. Biological treatment. Anaerobic digestion.	02/2011	1.089 ± 0.441	0.0662 ± 0.0066	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-5; Discharge to Besos River, Spain	Primary and secondary. Biological treatment, Anaerobic digestion.	02/2011	0.320 ± 0.0051	0.0175 ± 0.026	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-6; Discharge to Besos River, Spain	Primary and secondary. Biological treatment with nitrogen removal	02/2011	0.210 ± 0.0029	0.0791 ± 0.0018	NA	NA	NA

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
Sanchís et al. (2013)	WWTP-7; Discharge to Llobregat River, Spain	Primary, Secondary and Tertiary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion.	02/2011	0.289 ± 0.0045	0.476 ± 0.0023	NA	NA	NA
Sanchís et al. (2013)	WWTP-8; Discharge to Barranc de Mas Calbo, Spain	Primary and secondary. Biological treatment Anaerobic digestion.	02/2011	0.539 ± 0.014	ND	NA	NA	NA
Sanchís et al. (2013)	WWTP-9; Discharge to Besos River, Spain	Primary and secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion	02/2011	0.426 ± 0.016	0.0196 ± 0.0011	NA	NA	NA
Sanchís et al. (2013)	WWTP-10; Discharge to Riera de Rubí (Llobregat tributary), Spain	Primary and secondary. Biological treatment with nitrogen removal. Anaerobic digestion	02/2011	0.01	0.125 ± 0.0011	NA	NA	NA
Sanchís et al. (2013)	WWTP-11; Discharge to Mediterranean Sea, Spain	Primary and secondary. Biological treatment. Anaerobic digestion	02/2011	0.01	ND	NA	NA	NA
Sanchís et al. (2013)	WWTP-12; Discharge to Riera de Rubí (Llobregat tributary), Spain	Secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion.	02/2011	0.169 ± 0.0097	0.0842 ± 0.005	NA	NA	NA
Sanchís et al. (2013)	WWTP-13; Discharge to Riera de Rimentol Ter, Spain	Primary and secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion	02/2011	0.149 ± 0.0043	0.0182 ± 0.0018	NA	NA	NA

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
Sanchís *et al.* (2013)	WWTP-14; Discharge to Mediterranean Sea, Spain	Primary, Secondary and Tertiary. Biological treatment. Anaerobic digestion.	02/2011	0.0206 ± 0.0008	0.159 ± 0.0014	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-15; Discharge to Llera Riera Llitra, Spain	Primary and secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion	02/2011	0.203 ± 0.0036	ND	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-16; Discharge to Llobregat River, Spain	Primary and secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion	02/2011	ND	0.00989 ± 0.0005	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-17; Discharge to Segra River (Ebro tributary), Spain	Primary and secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion	02/2011	ND	0.0156 ± 0.0013	NA	NA	NA
Sanchís *et al.* (2013)	Llobregat River, Martorell, Spain	NA	02/2011	NA	NA	NA	0.07	0.00
Sanchís *et al.* (2013)	Llobregat River, El Papiol, Spain	NA	02/2011	NA	NA	NA	0.06	0.00
Sanchís *et al.* (2013)	Llobregat River, Pallejà, Spain	NA	02/2011	NA	NA	NA	0.10	0.01
Sanchís *et al.* (2013)	Rubí Brook (Llobregat tributary), Rubí, Spain	NA	02/2011	NA	NA	NA	0.42	0.05
Sanchís *et al.* (2013)	Rubí Brook (Llobregat tributary), Castellbisbal, Spain	NA	02/2011	NA	NA	NA	0.99	0.01

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
Sanchís *et al.* (2013)	Rubí Brook (Llobregat tributary), Castellbisbal, Spain	NA	02/2011	NA	NA	NA	0.25	0.20
JRC (2012)	Larnaka, Cyprus	Tertiary treatment with sand filtration; chlorination	12/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Limassol, Cyprus	Tertiary treatment with sand filtration; chlorination	04/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	France	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Givors (CA2), France	Not Reported	N,R,	ND	0.01	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	10/05/2010	ND	<0.040	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	10/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	09/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	09/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Location not disclosed, , Czech Republic	Not Reported	11/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	09/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	10/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Tankreiniging, Evergem (2406), Belgium	Not Reported	19/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Shanks Vlaanderen, Lokeren, Belgium	Not Reported	16/06/2010	ND	0.01	ND	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
JRC (2012)	Truck-en tankcleaning Tack, Oostrozebeke, Belgium	Not Reported	23/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Colortex, Sint-Niklaas, Belgium	Not Reported	16/06/2010	ND	0.11	ND	ND	ND
JRC (2012)	EOC Belgium, Oudenaarde, Belgium	Not Reported	15/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	3M Belgium, Zwijndrecht, Belgium	Not Reported	28/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Taminco Gent (69471), Belgium	Not Reported	16/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Ajjinomoto Ominichem, Wetteren, Belgium	Not Reported	23/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Bayer Antweroen, Zandvliet, Belgium	Not Reported	30/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Janssen Pharmaceutica, Geel, Belgium	Not Reported	16/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Claerebout Potatoes, Heuvelland, Belgium	Not Reported	17/06/210	ND	0.01	ND	ND	ND
JRC (2012)	Ardo, Ardooie (Expl. 84), Belgium	Not Reported	23/06/210	ND	0.01	ND	ND	ND
JRC (2012)	Agristo, Hulste (Expl. 369), Belgium	Not Reported	21/06/210	ND	0.01	ND	ND	ND
JRC (2012)	RWZI Ronse, Belgium	Not Reported	17/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	RWZI Waregem, Belgium	Not Reported	23/06/2010	ND	0.01	ND	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
JRC (2012)	RWZI Deurne, Antwerpen, Belgium	Not Reported	22/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	RWZI Hasselt, Kuringen, Belgium	Not Reported	22/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	RWZI Geel, Belgium	Not Reported	23/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Ljubljana, Slovenia	Not Reported	15/04/2010	ND	0.01	ND	ND	ND
JRC (2012)	Nummi-Pusula, Finland	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Lohja, Finland	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Alattyán Municipal WWTP, Hungary	Not Reported	08/07/2010	ND	0.01	ND	ND	ND
JRC (2012)	Martfû, Hungary	Not Reported	08/07/2010	ND	0.01	ND	ND	ND
JRC (2012)	Vihti, Finland	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Mäntsälä, Finland	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Helsinki, Finland	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Espoo, Finland	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Thessaloniki (WWTP – EELTH), Greece	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Thessaloniki (WWTP – EEL AINEIA), Greece	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Wenslingen, Switzerland	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Seuzach, Switzerland	Not Reported	17/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Konolfingen, Switzerland	Not Reported	04/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Affoltern a.A., Switzerland	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Zürich Werdhölzli, Switzerland	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Dublin, Ireland	Tertiary UV light treatment	24/05/2010	ND	0.01	ND	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
JRC (2012)	Osberstown, Ireland	Not Reported	24/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	WV Hofsteig, Austria	Not Reported	08/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	AWV Region Feldkirch, Austria	Not Reported	08/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	AWV Hall i.Tirol-Friztens, Austria	Not Reported	08/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Eisenstadt, Austria	Not Reported	18/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	AWV Wiener Neustadt – Sud, Austria	Not Reported	24/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Feldkirchen, Austria	Not Reported	19/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Tortosa, Spain	Not Reported	14/04/2010	ND	0.01	ND	ND	ND
JRC (2012)	Uldecona, Spain	Not Reported	14/04/2010	ND	0.01	ND	ND	ND
JRC (2012)	Godall, Spain	Not Reported	14/04/2010	ND	0.01	ND	ND	ND
JRC (2012)	WWTP Roma nord ACEA, Italy	Tertiary treatment; final disinfection step	25/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	WWTP Klaipedo vanduo, Lithuania	Not Reported	19/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Kaunas, Lithuania	Not Reported	18/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Panevezys regional, Lithuania	Not Reported	19/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	WWTP Harnaschpolder, The Netherlands	Not Reported	09/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	WWTP Zaandam Oost, The Netherlands	Not Reported	03/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Rotterdam Dokhaven, The Netherlands	Not Reported	19/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	WWTP Venlo, The Netherlands	Not Reported	22/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	WWTP Winterswijk, The Netherlands	Not Reported	N.R.	ND	0.01	ND	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
JRC (2012)	WWTP Nieuwgraaf, The Netherlands	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	WWTP Simpelveld, The Netherlands	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	WWTP Amstelveen, The Netherlands	Not Reported	14/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Almere, The Netherlands	Not Reported	18/05/2010	ND	0.01	ND	ND	ND
JRC (2012)	Klaranlage Seehausen, Bremen, Germany	Not Reported	17/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	Kläwerk Gut Marienhof (Muenchen), Germany	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	Depuratore 'Jugendwerk Brebbia', Italy	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	WWTP Parada, Portugal	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	AZV Hungerbachtal, Germany	Not Reported	28/06/2010	ND	0.01	ND	ND	ND
JRC (2012)	WWTP Leek (Noorderzijlvest), The Netherlands	Not Reported	N.R.	ND	<0.040	ND	ND	ND
JRC (2012)	WWTP Garmerwold (Noorderzijlvest), The Netherlands	Not Reported	N.R.	ND	0.01	ND	ND	ND
JRC (2012)	WWTP Viana do Castelo, Portugal	Not Reported	25/06/2010	ND	0.01	ND	ND	ND
Schlabach et al. (2007)	Bekkelaget STP, Norway	Not Reported	N.R.	0.1	<0.03	NA	<0.03	NA

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Waters (µg/L)	Receiving Water Sediment (µg/g dw)
Schlabach *et al.* (2007)	VEAS STP, Norway	Not Reported	N.R.	0.2	0.1	NA	NA	NA
Schlabach *et al.* (2007)	Seawater, Lysaker, Norway	NA	N.R.	NA	NA	NA	<0.03	<33
Schlabach *et al.* (2007)	Seawater, Vestfjord/Nesodden, Norway	NA	N.R.	NA	NA	NA	<0.03	<23
Schlabach *et al.* (2007)	Seawater, Færder, Norway	NA	N.R.	NA	NA	NA	<0.03	NA
Schlabach *et al.* (2007)	Bekkelagsbassenget, Norway	NA	N.R.	NA	NA	NA	NA	<4 - <38

Key:

Yellow highlighting indicates concentrations below the LoD; reported as 0.5 x LoD

[1] = Dissolved + Particulate Concentrations

[2] = Additional Sludge results from the paper Schlabach *et al.* (2007)

[3] = Sampled from Bekkelaget inlet

[4] = Sampled from Bekkelaget outlet

[5] = Sampled from VEAS inlet

[6] = Sampled from VEAS outlet

* = Industrial effluent sample

ND = Not determined

NR = Not reported

NA = not applicable

- = Not detected

** = Trickling filter channel post sand filter

[-] = Landfill leachate sample

Annex 2: D5 concentrations in the aquatic environment

Study Author	Site	Treatment Type	Sample Date	Influent (μg/L)	Effluent (μg/L)	Sludge (μg/g dw)	Receiving Water (μg/L)	Receiving Water Sediment (μg/g dw)
Wang *et al.* (2013a)	1 (Canada)	Secondary Activated Sludge	12/05/2010	25.20	0.06	ND	0.01	0.91
Wang *et al.* (2013a)	2 (Canada)	Lagoon	18/05/2010	9.63	0.10	ND	0.01	0.02
Wang *et al.* (2013a)	3 (Canada)	Lagoon	12/06/2010	41.90	0.01	ND	0.01	0.06
Wang *et al.* (2013a)	4 (Canada)	Lagoon	22/06/2010	7.75	0.07	ND	0.01	0.15
Wang *et al.* (2013a)	5 (Canada)	Lagoon	07/07/2010	51.00	0.01	ND	0.01	0.04
Wang *et al.* (2013a)	6 (Canada)	Secondary Activated Sludge	27/07/2010	18.60	0.34	ND	0.26	0.26
Wang *et al.* (2013a)	7 (Canada)	Secondary Activated Sludge	03/08/2010	21.50	0.39	ND	0.27	1.11
Wang *et al.* (2013a)	8 (Canada)	Lagoon	04/10/2010	691.00	135.00	ND	1.48	5.84
Wang *et al.* (2013a)	9 (Canada)	Chemically Assisted Primary	20/09/2010	17.80	1.31	ND	0.58	0.80
Wang *et al.* (2013a)	10 (Canada)	Lagoon	23/08/2010	20.40	0.05	ND	0.01	0.07
Wang *et al.* (2013a)	11 (Canada)	Lagoon	12/10/2010	17.30	0.25	ND	0.03	1.55
Bletsou *et al.* (2013)[1]	WWTP, Athens, Greece	Primary sedimentation, Activated sludge process with biological N and P removal, Secondary Sedimentation	04/2012	2.60	1.79	15.10	ND	ND
Whelan and Breivik (2013)[2]	Bekkelaget, Norway	Not Reported	2004	9.80	0.20	130.00	ND	ND
Whelan and Breivik (2013)[3]	Bekkelaget, Norway	Not Reported	2004	9.80	0.20	14.00	ND	ND
Whelan and Breivik (2013)[2]	VEAS, Norway	Not Reported	2004	12.00	1.00	25.00	ND	ND
Whelan and Breivik (2013)[3]	VEAS, Norway	Not Reported	2004	12.00	1.00	62.00	ND	ND
Kaj *et al.* (2005a,b)	Gislaveds, Sweden	Not Reported	NR	1.10	0.05	7.20	0.02	0.0015
Kaj *et al.* (2005a)	Landsbro, Sweden	Not Reported	24/11/2004	0.02	0.02	13.00	ND	0.02
Kaj *et al.* (2005a)	Hultsfred, Sweden	Not Reported	24/11/2004	0.21	ND	5.40	ND	0.01
Kaj *et al.* (2005a)	Virserum, Sweden	Not Reported	24/11/2004	0.10	ND	5.90	ND	0.00
Kaj *et al.* (2005a)	SCA Ostrand, Sweden	Not Reported	NR	0.06*	ND	ND	ND	ND
Kaj *et al.* (2005b)	Kobenhavn, Denmark	Not Reported	26/10/2004	26.00	0.06	27 - 50	0.01	0.0015
Kaj *et al.* (2005b)	Roskilde, Denmark	Not Reported	19/10/2004	24.00	0.09	ND	0.01	2

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
Kaj *et al.* (2005b)	Tyre factory, Finland	Not Reported	01/09/2004	5.30*	0.48	30	ND	ND
Kaj *et al.* (2005b)	Floor Factory, Finland	Not Reported	01/09/2004	0.33*	0.98		ND	ND
Kaj *et al.* (2005b)	Espoo, Finland	Not Reported	24/05/2005	0.62	ND	89	ND	0.058
Kaj *et al.* (2005b)	Helsinki, Finland	Not Reported	24/05/2005	0.29	ND	21	ND	0.019
Kaj *et al.* (2005b)	Arendal, Norway	Not Reported	NR	5.00	0.72	ND	ND	ND
Kaj *et al.* (2005b)	Lake Bergsjøen, Norway	NA	NR	NA	NA	NA	0.02	0.015
Kaj *et al.* (2005b)	Lake Røgden, Norway	NA	NR	NA	NA	NA	0.025	0.015
Kaj *et al.* (2005b)	Pornainen STP, Finland	Not Reported	26/01/2005	ND	ND	31	ND	ND
Kaj *et al.* (2005b)	Kokonniemi STP, Finland	Not Reported	26/01/2005	ND	ND	25	ND	ND
Kaj *et al.* (2005b)	Klettegardar STP, Reykjavik, Iceland	Not Reported	26/01/2005	ND	ND	1.6	ND	ND
Kaj *et al.* (2005b)	Ananaust STP, Reykjavik, Iceland	Not Reported	26/01/2005	ND	ND	1.1	ND	ND
Kaj *et al.* (2005b)	Skellefteå STP, Skellefteå, Sweden	Not Reported	26/01/2005	ND	ND	21	ND	ND
Wang *et al.* (2013b)	China	Not Reported	NR	ND	ND	0.17 – 0.32	ND	0.08
Sparham *et al.* (2008)	Great Billing, UK	Activated Sludge	21/06/2006	ND	0.40	ND	0.02**; 0.07***	ND
Sparham *et al.* (2008)	Cotton Valley, UK	Tertiary treatment via large polishing ponds	16/10/2006	ND	0.03	ND	0.03	ND
Sparham *et al.* (2011)	Felmersham, River Great Ouse, UK	Not Reported	27/08/2008	ND	ND	ND	ND	1.41
Sparham *et al.* (2011)	Felmersham, River Great Ouse, UK	Not Reported	27/08/2008	ND	ND	ND	ND	1.45
Sparham *et al.* (2011)	Felmersham, River Great Ouse, UK	Not Reported	27/08/2008	ND	ND	ND	ND	0.82
Sparham *et al.* (2011)	Tyringham Bridge, River Great Ouse, UK	Not Reported	23/09/2008	ND	ND	ND	ND	0.19
Sparham *et al.* (2011)	Tyringham Bridge, River Great Ouse, UK	Not Reported	23/09/2008	ND	ND	ND	ND	0.70

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
Sparham et al. (2011)	Tyringham Bridge, River Great Ouse, UK	Not Reported	23/09/2008	ND	ND	ND	ND	0.49
Sparham et al. (2011)	Chowder Ness, Humber Estuary, UK	Not Reported	01/10/2009	ND	ND	ND	ND	0.26
Sparham et al. (2011)	Paull Holme, Humber Estuary, UK	Not Reported	24/09/2009	ND	ND	ND	ND	0.10
Sparham et al. (2011)	Stone creek, Humber Estuary, UK	Not Reported	15/10/2009	ND	ND	ND	ND	0.07
Sparham et al. (2011)	Welwick, Humber Estuary, UK	Not Reported	29/09/2009	ND	ND	ND	ND	0.07
Sparham et al. (2011)	Cleethorpes, Humber Estuary, UK	Not Reported	15/10/2009	ND	ND	ND	ND	0.05
Sparham et al. (2011)	Skeffling, Humber Estuary, UK	Not Reported	02/10/2009	ND	ND	ND	ND	0.07
Wang et al. (2013b)	Canada	Not Reported	NR	ND	ND	ND	ND	2.93
Kaj et al. (2005a)	O Gotlandsdjupet, Sweden	Not Reported	NR	ND	ND	ND	ND	0.00
Kaj et al. (2005a)	O Oland, Sweden	Not Reported	NR	ND	ND	ND	ND	0.01
Kaj et al. (2005a)	Norrkopingsdjupet, Sweden	Not Reported	NR	ND	ND	ND	ND	0.00
Kaj et al. (2005a)	Stenungsund, Sweden	Not Reported	08/11/2012 - 09/11/2012	ND	ND	ND	0.02	0.00
Kaj et al. (2005a)	Akzo-Nobel Stockvik. STP, Sweden	Not Reported	22/10/2004	ND	0.03	ND	0.02	0.01
Kaj et al. (2005a)	Henriksdal STP, Sweden	Not Reported	16/11/2004	ND	ND	22.00	ND	ND
Kaj et al. (2005a)	Gasslosa STP, Sweden	Not Reported	24/11/2004	ND	ND	10.00	ND	ND
Kaj et al. (2005a)	Ryaverket STP, Sweden	Not Reported	15/12/2004	ND	ND	19.00	ND	ND
Kaj et al. (2005a)	Bay outside Stockvik 1 and 2, Sweden	NA	21/10/2004	ND	ND	ND	0.015	0.055
Kaj et al. (2005a)	Karlshamn STP, Sweden	Activated sludge, chemical and mechanical	28/09/2004	ND	ND	5	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
Kaj *et al.* (2005a)	Mörrum landfill, Sweden	NA	23/09/2004	ND	0.02⁻	ND	ND	ND
Kaj *et al.* (2005a)	Karlskrona STP, Sweden	Biological, chemical post suspensions mechanical	07/10/2004	ND	ND	10	ND	ND
Kaj *et al.* (2005a)	Volvo cars STP, Sweden	Not Reported	06/10/2004	ND	ND	0.014	ND	ND
Kaj *et al.* (2005a)	Angelskog landfill, Sweden	NA	06/10/2004	ND	0.02⁻	ND	0.02	ND
Kaj *et al.* (2005a)	Ronneby STP, Sweden	Biological, chemical and mechanical	06/10/2004	ND	ND	7.6	ND	ND
Kaj *et al.* (2005a)	Sölvesborg STP, Sweden	Activated sludge with N-elimination	29/09/2004	ND	ND	7.8	ND	ND
Kaj *et al.* (2005a)	Lake Bäsingen, Sweden	NA	04/10/2004	ND	ND	ND	ND	0.0465
Kaj *et al.* (2005a)	Krylbo STP, Sweden	Suspension, activated sludge	29/09/2004	ND	ND	5.3	ND	ND
Kaj *et al.* (2005a)	Fagresta STP, Sweden	Suspension, activated sludge	12/10/2004	ND	ND	54	ND	ND
Kaj *et al.* (2005a)	Venjam STP, Sweden	Mechanical, chemical	06/10/20047	ND	ND	6.5	ND	ND
Kaj *et al.* (2005a)	Lake Venjan/Venjansjön, Sweden	NA	03/10/2004	ND	ND	ND	ND	0.0115
Kaj *et al.* (2005a)	Bollnäs STP, Sweden	Not Reported	20/10/2004	ND	ND	6.5	ND	ND
Kaj *et al.* (2005a)	Duvbacken STP, Sweden	Not Reported	12/10/2004	ND	ND	10	ND	ND
Kaj *et al.* (2005a)	Resselvans STP, Sweden	Not Reported	07/12/2004	ND	ND	19	ND	ND
Kaj *et al.* (2005a)	Sandviken STP, Sweden	Not Reported	13/10/2004	ND	ND	11	ND	ND
Kaj *et al.* (2005a)	Myrviken STP, Sweden	Mechanical, dehydration, compost	01/11/2004	ND	ND	2.3	ND	ND
Kaj *et al.* (2005a)	Bräcke STP, Sweden	Mechanical, biological	19/10/2004	ND	ND	23	ND	ND
Kaj *et al.* (2005a)	Björnrike STP, Sweden	Mechanical, chemical	21/06/2004	ND	ND	0.054	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
Kaj *et al.* (2005a)	Hissmofors STP, Sweden	Mechanical, chemical, biological	19/10/2004	ND	ND	14	ND	ND
Kaj *et al.* (2005a)	Ragunda STP/Överammer STP, Sweden	Dehydration	19/10/2004	ND	ND	3.1	ND	ND
Kaj *et al.* (2005a)	Strömsund STP, Sweden	Mechanical, chemical, biological	27/10/2004	ND	ND	12	ND	ND
Kaj *et al.* (2005a)	Åre STP, Sweden	Mechanical, chemical, biological	13/04/2004	ND	ND	6.5	ND	ND
Kaj *et al.* (2005a)	Östersund STP/ Göviken STP, Sweden	Mechanical, chemical, biological	29/09/2004	ND	ND	10	ND	ND
Kaj *et al.* (2005a)	Gröpplebäcken, Sweden	NA	24/11/2004	ND	ND	ND	ND	0.0172
Kaj *et al.* (2005a)	Hulingen, Sweden	NA	24/11/2004	ND	ND	ND	ND	0.011
Kaj *et al.* (2005a)	Viserum, Sweden	NA	24/11/2004	ND	ND	ND	ND	0.0017
Kaj *et al.* (2005a)	Viserum STP, Sweden	Not Reported	24/11/2004	0.099	0.02	59	ND	ND
Kaj *et al.* (2005a)	Mouth of Emån, Sweden	NA	27/10/2004	ND	ND	ND	ND	0.003
Kaj *et al.* (2005a)	Bromölla STP, Sweden	Not Reported	28/09/2004	ND	ND	14	ND	ND
Kaj *et al.* (2005a)	Ivösjön, Sweden	NA	19/10/2004	ND	ND	ND	ND	0.0145
Kaj *et al.* (2005a)	Öresunds, Sweden STP/Helsingborg STP, Sweden	Not Reported	22/09/2004	ND	ND	12	ND	ND
Kaj *et al.* (2005a)	Helsingborg (coast), Sweden	NA	03/11/2004	ND	ND	ND	ND	0.004
Kaj *et al.* (2005a)	Hammarsjön, Sweden	NA	19/10/2004	ND	ND	ND	ND	0.005
Kaj *et al.* (2005a)	Kristianstad STP, Sweden	Not Reported	05/10/2004	ND	ND	21.0	ND	ND
Kaj *et al.* (2005a)	Lundåkrav STP, Sweden	Not Reported	29/09/2004	ND	ND	6.7	ND	ND
Kaj *et al.* (2005a)	Källby STP, Sweden	Not Reported	27/09/2004	ND	ND	9.3	ND	ND
Kaj *et al.* (2005a)	Sjölunda STP, Sweden	Not Reported	22/09/2004	ND	ND	9.8	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
Kaj *et al.* (2005a)	Perstorp STP, Sweden	Not Reported	26/10/2004	ND	ND	12.0	ND	ND
Kaj *et al.* (2005a)	Storarydsdammen, Sweden	NA	22/10/2004	ND	ND	ND	ND	0.007
Kaj *et al.* (2005a)	Ystad STP, Sweden	Not Reported	22/09/2004	ND	ND	6.8	ND	ND
Kaj *et al.* (2005a)	Himmerfjärdsverket, Sweden	Not Reported	28-30/09/2004	ND	0.015	6.0	ND	ND
Kaj *et al.* (2005a)	Himmerfjärden, Sweden	NA	01/09/2004	ND	ND	ND	ND	0.19
Kaj *et al.* (2005a)	St. Envättern, Sweden	NA	01/09/2004	ND	ND	ND	ND	0.0285
Kaj *et al.* (2005a)	Flen STP, Sweden	Mechanical, chemical, biological	11/10/2004	ND	ND	0.57	ND	ND
Kaj *et al.* (2005a)	Gnesta STP, Sweden	Mechanical and chemical	19/10/2004	ND	ND	10.0	ND	ND
Kaj *et al.* (2005a)	Eskilstuna STP, Sweden	Mechanical, chemical, biological and wetland	18/10/2004	ND	ND	13.0	ND	ND
Kaj *et al.* (2005a)	Katrineholm STP, Sweden	Mechanical, chemical, biological	20/10/2004	ND	ND	23.0	ND	ND
Kaj *et al.* (2005a)	Nyköping STP, Sweden	Mechanical, chemical, biological	NR	ND	ND	15.0	ND	ND
Kaj *et al.* (2005a)	Oxelösund STP, Sweden	Mechanical and wetland	27/10/2004	ND	ND	5.8	ND	ND
Kaj *et al.* (2005a)	Strängäs STP, Sweden	Mechanical, chemical, biological	NR	ND	ND	9.9	ND	ND
Kaj *et al.* (2005a)	Vagnhärad STP, Sweden	Mechanical, chemical and wetland	13/10/2004	ND	ND	17.0	ND	ND
Kaj *et al.* (2005a)	Vingåker STP, Sweden	Mechanical, chemical, biological and wetland	13/10/2004	ND	ND	13.0	ND	ND
Kaj *et al.* (2005a)	Vik STP, Sweden	Mechanical, chemical, biological	02/11/2004	ND	0.02	5.5	ND	ND
Kaj *et al.* (2005a)	Vänern, Åsfjorden, Sweden	NA	30/09/2004	ND	ND	ND	ND	0.37
Kaj *et al.* (2005a)	Vänern, Kattfjorden, Sweden	NA	30/09/2004	ND	ND	ND	ND	0.0055
Kaj *et al.* (2005a)	Skåre STP, Sweden	Mechanical, chemical, biological	19/10/2004	ND	0.02	19.0	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
Kaj *et al.* (2005a)	Fiskartorpet STP, Sweden	Mechanical, chemical, biological	26-28/10/2004	ND	0.02	3.4	ND	ND
Kaj *et al.* (2005a)	Tivoliverket, Sweden	Not reported	NR	ND	ND	9.7	ND	ND
Kaj *et al.* (2005a)	Bodum STP, Sweden	Not reported	10/11/2004	ND	ND	7.4	ND	ND
Kaj *et al.* (2005a)	Lidköping STP, Sweden	Not reported	NR	ND	0.02	22.0	ND	ND
Kaj *et al.* (2005a)	Vara STP, Sweden	Mechanical, chemical, biological	04/10/2004	ND	ND	6.8	ND	ND
Kaj *et al.* (2005a)	Åmål STP, Sweden	Mechanical and chemical	29/09/2004	ND	0.02	9.3	ND	ND
Kaj *et al.* (2005a)	Finspångs STP, Sweden	Not reported	26/10/2004	ND	0.02	9.1	ND	ND
Kaj *et al.* (2005a)	Skuten, Sweden	NA	29/10/2004	ND	ND	ND	ND	0.026
Kaj *et al.* (2005a)	Linköping STP, Sweden	Not reported	09/11/2004	ND	0.015	10.0	ND	ND
Kaj *et al.* (2005a)	Roxen, Sweden	NA	29/09/2004	ND	ND	ND	ND	0.11
Kaj *et al.* (2005b)	Sersjantvíkin STP, Sweden, Faroe Islands	Not Reported	26/01/2005	ND	5.2	4.30	ND	ND
Kaj *et al.* (2005b)	Ellinge STP, Eslöv, Sweden	Not Reported	26/01/2005	ND	ND	4.50	ND	ND
Kaj *et al.* (2005b)	Floda STP, Lerum, Sweden	Not Reported	26/01/2005	ND	ND	5.80	ND	ND
van Egmond *et al.* (2013)	Broadholme STP, UK	Primary and secondary treatment	22/03/2010 - 23/03/2010	5.6 - 36	0.305 - 0.347	ND	ND	ND
van Egmond *et al.* (2013)	Broadholme STP, UK	Primary and secondary treatment	07/07/2010 - 08/07/2010	9.26 – 10.8	0.141 – 0.187⁻	ND	ND	ND
Sanchís *et al.* (2013)	WWTP-1; Discharge to Mediterranean Sea, Spain	Primary and Secondary. Biological treatment with nitrogen and phosphorus removal. Anaerobic digestion.	02/2011	24.484 ± 0.049	1.020 ± 0.0055	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-2; Discharge to Ter River, Spain	Secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion.	02/2011	13.077 ± 0.069	0.161 ± 0.0013	NA	NA	NA

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
Sanchís *et al.* (2013)	WWTP-3; Discharge to Besos River, Spain	Primary and Secondary. Biological treatment with phosphor removal. Anaerobic digestion.	02/2011	1.960 ± 0.022	0.202 ± 0.0024	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-4; Discharge to Mediterranean Sea, Spain	Primary and secondary. Biological treatment. Anaerobic digestion.	02/2011	ND	0.211 ± 0.0032	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-5; Discharge to Besos River, Spain	Primary and secondary. Biological treatment, Anaerobic digestion.	02/2011	12.379 ± 0.01	0.451 ± 0.0036	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-6; Discharge to Besos River, Spain	Primary and secondary. Biological treatment with nitrogen removal	02/2011	8.914 ± 0.066	0.507 ± 0.009	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-7; Discharge to Llobregat River, Spain	Primary, Secondary and Tertiary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion.	02/2011	13.716 ± 0.014	0.684 ± 0.004	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-8; Discharge to Barranc de Mas Calbo, Spain	Primary and secondary. Biological treatment Anaerobic digestion.	02/2011	14.601 ± 0.015	0.294 ± 0.020	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-9; Discharge to Besos River, Spain	Primary and secondary. Biological treatmentwith nitrogen and phosphor removal. Anaerobic digestion	02/2011	8.918 ± 0.049	0.134 ± 0.0034	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-10; Discharge to Riera de Rubí (Llobregat tributary) , Spain	Primary and secondary. Biological treatment with nitrogen removal. Anaerobic digestion	02/2011	5.296 ± 0.234	0.684 ± 0.0077	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-11; Discharge to Mediterranean Sea, Spain	Primary and secondary. Biological treatment. Anaerobic digestion	02/2011	3.368 ± 0.0131	0.299 ± 0.0037	NA	NA	NA

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
Sanchís *et al.* (2013)	WWTP-12; Discharge to Riera de Rubí (Llobregat tributary) , Spain	Secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion.	02/2011	5.048 ± 0.092	3.587 ± 0.0015	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-13; Discharge to Riera de Rimentol Ter, Spain	Primary and secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion	02/2011	3.220 ± 0.359	0.0421 ± 0.0040	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-14; Discharge to Mediterranean Sea, Spain	Primary, Secondary and Tertiary. Biological treatment. Anaerobic digestion.	02/2011	3.594 ± 0.024	0.251 ± 0.0066	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-15; Discharge to Llera Riera Llitra, Spain	Primary and secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion	02/2011	13.795 ± 0.012	ND	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-16; Discharge to Llobregat River, Spain	Primary and secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion	02/2011	ND	0.149 ± 0.0029	NA	NA	NA
Sanchís *et al.* (2013)	WWTP-17; Discharge to Segra River (Ebro tributary) , Spain	Primary and secondary. Biological treatment with nitrogen and phosphor removal. Anaerobic digestion	02/2011	ND	0.0472 ± 0.0043	NA	NA	NA
Sanchís *et al.* (2013)	Llobregat River, Martorell, Spain	NA	02/2011	NA	NA	NA	0.09	0.00
Sanchís *et al.* (2013)	Llobregat River El Papiol, Spain	NA	02/2011	NA	NA	NA	0.09	0.01
Sanchís *et al.* (2013)	Llobregat River, Pallejà, Spain	NA	02/2011	NA	NA	NA	0.11	0.01

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
Sanchís *et al.* (2013)	Rubí Brook (Llobregat tributary), Rubí, Spain	NA	02/2011	NA	NA	NA	0.12	0.01
Sanchís *et al.* (2013)	Rubí Brook (Llobregat tributary), Castellbisbal, Spain	NA	02/2011	NA	NA	NA	0.47	0.02
Sanchís *et al.* (2013)	Rubí Brook (Llobregat tributary), Castellbisbal, Spain	NA	02/2011	NA	NA	NA	0.39	0.37
JRC (2012)	Larnaka, Cyprus	Tertiary treatment with sand filtration; chlorination	12/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Limassol, Cyprus	Tertiary treatment with sand filtration; chlorination	04/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	France	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Givors (CA2), France	Not Reported	N,R,	ND	0.0275	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	10/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	10/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	09/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	09/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	11/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	09/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Location not disclosed, Czech Republic	Not Reported	10/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Tankreiniging, Evergem (2406), Belgium	Not Reported	19/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Shanks Vlaanderen, Lokeren, Belgium	Not Reported	16/06/2010	ND	0.0275	ND	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
JRC (2012)	Truck-en tankcleaning Tack, Oostrozebeke, Belgium	Not Reported	23/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Colortex, Sint-Niklaas, Belgium	Not Reported	16/06/2010	ND	0.28	ND	ND	ND
JRC (2012)	EOC Belgium, Oudenaarde, Belgium	Not Reported	15/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	3M Belgium, Zwijndrecht, Belgium	Not Reported	28/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Taminco Gent (69471), Belgium	Not Reported	16/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Ajjinomoto Ominichem, Wetteren, Belgium	Not Reported	23/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Bayer Antweroen, Zandvliet, Belgium	Not Reported	30/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Janssen Pharmaceutica, Geel, Belgium	Not Reported	16/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Claerebout Potatoes, Heuvelland, Belgium	Not Reported	17/06/210	ND	0.0275	ND	ND	ND
JRC (2012)	Ardo, Ardooie (Expl. 84), Belgium	Not Reported	23/06/210	ND	0.0275	ND	ND	ND
JRC (2012)	Agristo, Hulste (Expl. 369), Belgium	Not Reported	21/06/210	ND	0.0275	ND	ND	ND
JRC (2012)	RWZI Ronse, Belgium	Not Reported	17/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	RWZI Waregem, Belgium	Not Reported	23/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	RWZI Deurne, Antwerpen, Belgium	Not Reported	22/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	RWZI Hasselt, Kuringen, Belgium	Not Reported	22/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	RWZI Geel, Belgium	Not Reported	23/06/2010	ND	0.0275	ND	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
JRC (2012)	Ljubljana, Slovenia	Not Reported	15/04/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Nummi-Pusula, Finland	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Lohja, Finland	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Alattyán Municipal WWTP, Hungary	Not Reported	08/07/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Martfû, Hungary	Not Reported	08/07/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Vihti, Finland	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Mäntsälä, Finland	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Helsinki, Finland	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Espoo, Finland	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Thessaloniki (WWTP – EELTH), Greece	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Thessaloniki (WWTP – EEL AINEIA), Greece	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Wenslingen, Switzerland	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Seuzach, Switzerland	Not Reported	17/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Konolfingen, Switzerland	Not Reported	04/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Affoltern a.A., Switzerland	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Zürich Werdhölzli, Switzerland	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Dublin, Ireland	Tertiary UV light treatment	24/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Osberstown, Ireland	Not Reported	24/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	WV Hofsteig, Austria	Not Reported	08/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	AWV Region Feldkirch, Austria	Not Reported	08/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	AWV Hall i.Tirol-Friztens, Austria	Not Reported	08/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Eisenstadt, Austria	Not Reported	18/05/2010	ND	0.0275	ND	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
JRC (2012)	AWV Wiener Neustadt – Sud, Austria	Not Reported	24/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Feldkirchen, Austroa	Not Reported	19/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Tortosa, Spain	Not Reported	14/04/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Uldecona, Spain	Not Reported	14/04/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Godall, Spain	Not Reported	14/04/2010	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Roma nord ACEA, Italy	Tertiary treatment; final disinfection step	25/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Klaipedo vanduo, Lithuania	Not Reported	19/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Kaunas, Lithuania	Not Reported	18/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Panevezys regional, Lithuania	Not Reported	19/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Harnaschpolder, The Netherlands	Not Reported	09/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Zaandam Oost, The Netherlands	Not Reported	03/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Rotterdam Dokhaven, The Netherlands	Not Reported	19/05/2010	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Venlo, The Netherlands	Not Reported	22/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Winterswijk, The Netherlands	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Nieuwgraaf, The Netherlands	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Simpelveld, The Netherlands	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Amstelveen, The Netherlands	Not Reported	14/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Almere, The Netherlands	Not Reported	18/05/2010	ND	0.0275	ND	ND	ND

Study Author	Site	Treatment Type	Sample Date	Influent (µg/L)	Effluent (µg/L)	Sludge (µg/g dw)	Receiving Water (µg/L)	Receiving Water Sediment (µg/g dw)
JRC (2012)	Klaranlage Seehausen, Bremen, Germany	Not Reported	17/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	Kläwerk Gut Marienhof (Muenchen), Germany	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	Depuratore 'Jugendwerk Brebbia', Italy	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Parada, Portugal	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	AZV Hungerbachtal, Germany	Not Reported	28/06/2010	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Leek (Noorderzijlvest), The Netherlands	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Garmerwold (Noorderzijlvest), The Netherlands	Not Reported	N.R.	ND	0.0275	ND	ND	ND
JRC (2012)	WWTP Viana do Castelo, Portugal	Not Reported	25/06/2010	ND	0.0275	ND	ND	ND
Schlabach *et al.* (2007)	Bekkelaget STP, Norway	Not Reported	N.R.	9.8	0.2	NA	<0.02	NA
Schlabach *et al.* (2007)	VEAS STP, Norway	Not Reported	N.R.	12.0	1.0	NA	NA	NA
Schlabach *et al.* (2007)	Seawater, Lysaker, Norway	NA	N.R.	NA	NA	NA	<0.02	93 - 200
Schlabach *et al.* (2007)	Seawater, Vestfjord/Nesodden, Norway	NA	N.R.	NA	NA	NA	<0.02	250 - 280
Schlabach *et al.* (2007)	Seawater, Færder, Norway	NA	N.R.	NA	NA	NA	<0.02	NA
Schlabach *et al.* (2007)	Bekkelagsbassenget, Norway	NA	N.R.	NA	NA	NA	NA	690 - 920

Key:

Yellow highlighting indicates concentrations below the LoD; reported as 0.5 x LoD

[1] = Dissolved + Particulate Concentrations

[2] = Additional Sludge results from the paper Schlabach *et al.* (2007)

[3] = Sampled from Bekkelaget inlet

[4] = Sampled from Bekkelaget outlet

[5] = Sampled from VEAS inlet

[6] = Sampled from VEAS outlet

* = Industrial effluent sample

** = Sample taken 1.2 km D/S of Great Biling STW

***= Sample taken 5 km D/S of Cotton Valley STW

ND = Not determined

NR = Not reported

NA = not applicable

‾ = Trickling filter channel post sand filter

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ANNEX C Available information on alternatives

Several sources of information on alternatives are available, including a review by the Danish Ministry of the Environment (2005), a survey performed by Cosmetics Europe (AMEC, 2013), publicly available literature (e.g. Woodruff, 2012) and a variety of information on the Internet (e.g. patents). The DS has also looked for information on alternatives for D4 on the Environment Canada website, as this substance is subject to regulatory controls in Canada.

The main source of stakeholder input for this dossier was the Cosmetics Europe survey of potential alternatives for D4 and D5 carried out during spring 2013. AMEC (2013) produced an assessment of the data from the survey, which addressed 'direct' uses of D4 and D5, by themselves or in blends/mixtures such as cyclomethicone and cyclodimethicone. It did not attempt to collect data on the uses of D4 and D5 related to presence as impurities in silicone polymers such as dimethicone and other derivatives (i.e. 'indirect uses'), due to a lack of information from raw material suppliers on their concentration in these products, as well as the very large number of products involved.

The survey included an indicative (i.e. incomplete) list of possible alternatives to D4 and D5 that have been suggested in the literature or the marketing materials of raw material suppliers (see Table A.C1). The stakeholders were asked to provide information about whether any of these alternatives may or may not be suitable for different product types in terms of the following:

• Technical performance of the final product relative to D4 and D5;

• Environmental, health and safety implications of using the alternative, in regards to the manufacturing of the finished products and the use of the finished products by consumers;

• Availability of the alternative substance in the market in the quantities required to substitute D4 and D5; and

• Cost implications, in terms of price and quantity required in finished product relative to D4 and D5, and impacts on consumers.

AMEC's evaluation is marked as confidential. Although no company-specific information, prices or tonnage data are provided, it is understood that some companies did not want to reveal their pursuit of alternatives to competitors. In addition, with few exceptions the survey correspondents discuss alternatives for leave-on products, which is not the focus of this restriction proposal. The data have therefore been reviewed for relevance and some non-confidential information from this source is included in this analysis.

In total, 38 companies provided information related to the use of D5, and five of these companies also provided information related to the use of D4. This represents a relatively small proportion of the total number of PCP companies in the EU, but the total sales turnover of the 38 survey respondents represents nearly two thirds of the EU PCP market in 2012 (i.e. it provides a reasonable response rate in terms of the overall quantity of the market covered). The share of the respondents' sales turnover related to products containing D5 and D4 was just over 30% and 5%, respectively.

These survey results therefore provide a partial sample in terms of the total use of D4 and D5 in wash-off PCPs, and companies that did not respond might have no current use of D4 and D5.

Table A.C1: Indicative list of possible substitutes for D4 and D5 as claimed by raw material suppliers (AMEC, 2013)

Substance
Coco-caprylate
Mixture of coco caprylate/caprate and coconut alkanes
Dicaprylyl carbonate
Mixture of dicaprylyl carbonate, stearalkonium hectorite and propylene carbonate)
Dicaprylyl ether
Mixture of microemulsion dicaprylyl ether, decyl glucoside and glyceryl oleate
Hydrogenated polyisobutene
Mixture of hydrogenated polyisobutylene, hydrogenated polydecene, hydrogenatated C16 olefin polymers
Ethyl macadamiate
Ethyl methicone
Octyldodecyl olivate
Mixture of isodecyl isononoate and ethylhexyl isononoate
Isodecyl neopentanoate
Isododecane
Mixture of isododecane, hydrogenated polydecene, bis-behenyl/isostearyl/phytostearyl dimerdilnoleyl dimer dilinoate
Mixture of isododecane plus PPG-3 myristyl ether neoheptanoate
Isostearyl neopentanoate
Linear volatile siloxanes (e.g. hexamethyldisiloxane)
Mixture of C11-13 isoparaffin, isohexadecane, dimethiconol and dimethicone
Neopentyl glycol diethylhexanoate
Mixture of neopentyl glycol diheptanoate and isododecane
Mixture of polyquaternium-37, dicaprylyl carbonate lauryl glucoside
PPG-3 Benzyl ether ethylhexanoate
PPG-3 Benzyl ether myristate
Propanediol dicaprylate
Propylheptyl caprylate
Speciality alkanes
Wax dispersion of PEG-4 distearyl ether, sodium laureth sulphate, distearyl ether and dicaprylyl ether

Some further information about selected substances is available for the Danish market (Danish Ministry of the Environment, 2005). Woodruff (2012) described a wide range of potential alternatives to silicones, many of which were not included in

the Cosmetics Europe survey. The DS was unable to find any relevant information on the Environment Canada website (it seems likely that most of the replacement of D4 in Canada will be by D5, as no regulatory action is being pursued there for that substance).

Due to the high uncertainty of knowing which combination of substances can be used in place of D4 and D5 in any particular PCP type, the DS has decided to present information on a representative range of potential alternatives rather than every substance that has been mentioned in the literature or the Cosmetics Europe survey.

C.1 Assessment of potential alternatives

The assessment is presented in sections C.2.1 to C.2.8 and each one comprises four sub-sections:
1. Human health information
2. Environmental information
3. Technical and economic feasibility
4. Conclusions on suitability

The information on human health and environment is presented according to the following structure:
- Information from regulatory authorities[6]
- Hazard information reported by Industry[7]
- Conclusions for Human Health *or* Conclusions for Environment

The assessment of net reduction of risk is limited to an assessment of environmental hazard (including PBT/vPvB properties). This is because information on human health effects of PCP ingredients for consumers is addressed under other EU legislation. In addition, D4 and D5 have PBT/vPvB properties that cannot be assessed using conventional risk assessment approaches, and exposures associated with the use of substances as an alternative to D4 and D5 are not available.

The assessment of technical feasibility focuses on the identification of PCP applications in which the substance has been reported to be used. This does not necessarily mean that the alternative can be used as a replacement for D4 or D5, but it is considered to be technically feasible in one or more PCP types.

The assessment of economic feasibility is limited by lack of information on relative prices and required loading rates of the alternatives, and the variability of the loading rate even within one type of PCP (e.g. for hair care). The assessment therefore

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[6] Using the Commission's CosIng database
(http://ec.europa.eu/consumers/cosmetics/cosing/index.cfm?fuseaction=search.simple) and the OECD eChemPortal (http://www.echemportal.org/echemportal/page.action?pageID=9). Where information is from outside the EU, it should be considered indicative since it might not be directly applicable to the EU.
[7] This information is taken directly from industry submissions on the ECHA website (in REACH registrations and in the C&L Inventory) and has not been assessed for its quality.

considers the current supply volume as an indicator of potential availability compared to D4 and D5.

No information is available on the potential need to change a production process to adopt any particular alternative substance, but physical hazards are mentioned where relevant.

C2 Alternative 1: Linear volatile methylsiloxanes, including polydimethylsiloxane (PDMS), dimethicone, L2, L3, L4 and L5

The term 'linear volatile methylsiloxanes' covers a range of different substances. For example, polydimethylsiloxane (PDMS) (CAS no. 63148-62-9) consists of fully methylated linear siloxane polymers containing repeating units of the formula $[(CH_3)_2SiO]$ with trimethylsiloxy end-blocking units of the formula $(CH_3)_3SiO$-. They generally have the following chemical structure:
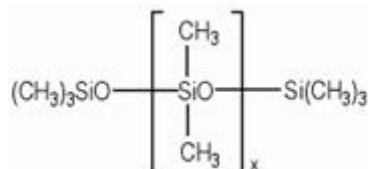
The term "PDMS" therefore covers a range of discrete linear siloxane substances (e.g. where x = 0-4), as well as polymers with average molecular weights up to approximately 30,000 Da[8]. The exact composition depends on the desired use (e.g. relating to volatility or viscosity), and consequently this type of substance can be described in a number of different ways and even with different CAS numbers (e.g. 9006-65-9 & 9016-00-6). Synonyms include poly(dimethylsiloxane), dimethyl-polysiloxane, dimethylsilicone fluid, dimethylsilicone oil, dimethicone and linear volatile methyl siloxanes. Other Voluntary Cosmetic Registration Program (VCRP) reported names include "dimethyl siloxanes and silicones".

The formal International Nomenclature of Cosmetic Ingredients (INCI) definition of "dimethicone" in the Personal Care Products Council (PCPC) database is "a mixture of fully methylated linear siloxane polymers end blocked with trimethylsiloxy units". One industry source considered that since there are separate monographs for hexamethyldisiloxane (L2, CAS no. 107-46-0) and octamethyltrisiloxane (L3, CAS no. 107-51-7), the term 'dimethicone' would cover the viscosities of PDMS beginning with decamethyltetrasiloxane (L4, CAS no. 141-62-8) and presumably including dodecamethylpentasiloxane (L5, CAS no. 141-63-9)[9].

Given the range of possible properties covered by the term 'linear volatile methylsiloxanes', this assessment will focus on the discrete substances L2, L3, L4 and L5 because polymers are not registered under REACH, and these shorter chain length substances are included in the CoRAP list for Substance Evaluation under REACH (rapporteur: UK). Hexamethyldisiloxane (L2) was evaluated in 2013 and the other three will be assessed during 2015. The concern is related to potential PBT properties and environmental exposure.

Higher molecular weight polymers would not be expected to have similar concerns due to their lower bioavailability. However, linear siloxanes are usually made by a catalytic polymerization reaction involving the equilibration of a short chain linear methylsiloxane with a cyclic methylsiloxane. The reaction products always include the starting materials. However, the reaction is reversible, so even if the cyclic starting material has been stripped out, there is potential for its reformation in the

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[8] http://www.fao.org/ag/agn/jecfa-additives/specs/monograph5/additive-315-m5.pdf

[9] The DS understands that tetradecamethylhexasiloxane (L6, CAS no. 107-52-8) is planned for registration under REACH by the 2018 deadline due to its low supply volume.

presence of acid, base or other catalysts. It also appears possible that the longer chain length polymers might degrade to the shorter chain length substances under some conditions in the environment.

C.2.1 Human health information

C.2.1.1 Information from regulatory authorities

The draft REACH Substance Evaluation Report for L2 (UK REACH CA, 2014) concludes that based on the available data, there is no concern for carcinogenicity, and it does not meet the classification criteria for any human health hazard end points. There are no EU reviews available for the other substances yet.

L2, L3, L4 and L5 (and dimethicone) do not meet the Canadian Government's Human Health Categorization Criteria. However, OECD Screening Initial Data Set assessments concluded that L2 and L3 possess properties indicating a hazard for human health (repeated-dose toxicity and/or developmental toxicity at high concentrations).[10] There are no OECD assessments for L4, L5 or dimethicone.

C.2.1.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classifications in the lead registrant's CSR	Self-notified classifications in the C&L Inventory
L2	-	Flam. Liquid 2 (H225: Highly flammable liquid and vapour)	Flam. Sol. 1 (H228) Flam. Liq. 2 (H225) Flam. Liq. 3 (H226) Water-react. 1 (H260) Asp. Tox. 1 (H304) Acute Tox. 3 (H301) Acute Tox. 4 (H332) Skin Irrit. 2 (H315) Eye Irrit. 2 (H319) Carc. 2 (H351)
L3	-	Flam. Liquid 3 (H226: Flammable liquid and vapour)	Flam. Liq. 3 (H226) May be fatal if swallowed and enters airways (H304) Causes skin irritation (H315) Causes serious eye irritation (H319) May cause respiratory irritation (H335)
L4	-	Flam. Liquid 3 (H226: Flammable liquid and vapour)	Flam. Liquid 3 (H226)
L5	-	-	Skin Irrit. 2 (H315) Eye Irrit. 2 (H319) STOT SE 3 (H335)

The validity of the self-classifications notified to the C&L Inventory is unknown. In the absence of other information, it is assumed that the lead registrant's self-classification is more appropriate.

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[10] L2: http://webnet.oecd.org/Hpv/UI/handler.axd?id=98264d1f-2476-42fb-ade8-0fc8485bae4c;
L3: http://webnet.oecd.org/Hpv/UI/handler.axd?id=83c0a20e-ecb8-4667-8f2d-7a06aaf70e91

C.2.1.3 Conclusions for human health

The main concern appears to relate to flammability hazards for L2 to L4 (but not L5). The human health classifications for L2 and L3 would appear to deserve harmonisation given the variety of entries in the C&L Inventory.

C2.2 Environmental information

C.2.2.1 Information from regulatory authorities

The draft Substance Evaluation Report for L2 (UK REACH CA, 2014) concludes that the substance potentially meets the Annex XIII PBT criteria, and further data are required to confirm the level of environmental persistence, bioaccumulation and long-term aquatic toxicity.

Draft PBT fact sheets have been prepared by the UK REACH CA for the other substances as part of preparations for CoRAP listing. The draft conclusions are as follows[11]:

- L3: Based on the available data it was concluded that the substance meets the Annex XIII criteria for B and vB and may have vPvB properties. Further information is needed to definitively confirm the persistence of L3 in sediment and/or soil.

- L4: Based on the available data it was concluded that the substance meets the Annex XIII criteria for B and vB and may have vPvB properties. Further information is needed to definitively confirm the persistence of L4 in sediment and/or soil.

- L5: Based on the available data it was concluded that the substance meets the Annex XIII criteria for B and potentially meets the criteria for P and vP. There are insufficient long-term aquatic toxicity data to conclude whether or not the Annex XIII criterion for T is met. The substance may therefore have PBT properties, but further information is needed to definitively confirm the persistence of L5 in sediment and/or soil, and potentially aquatic toxicity.

In addition, some of these substances can contain D4 and D5 as impurities at concentrations above 0.1% w/w, making them a PBT- or vPvB-containing substance. However, it is possible that some producers can make a purer product, and if they are diluted in the final PCP product, the concentration of D4 and D5 may be below 0.1% w/w.

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[11] The CoRAP justification documents can be viewed at http://echa.europa.eu/en/information-on-chemicals/evaluation/community-rolling-action-plan/corap-list-of-substances.

C.2.2.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classifications in the lead registrants' CSRs	Self-notified classifications in the C&L Inventory
L2	-	Aquatic Acute 1 (H400)	Aquatic Acute 1 (H400) Aquatic Chronic 1 (H410) Aquatic Chronic 2 (H411)
L3	-	-	Aquatic Chronic 4 (H413)
L4	-	-	Aquatic Chronic 4 (H413)
L5	-	-	-

The C&L Inventory includes chronic aquatic toxicity hazards for this L2, L3 and L4. This may be linked to the use of available chronic NOEC data in accordance with the 2nd ATP of the CLP Regulation, or application of the safety net criteria based on lack of ready biodegradation and a log K_{OW} > 4. The validity of the self-classifications notified to the C&L Inventory is unknown. In the absence of other information, it is assumed that the lead registrant's self-classification is more appropriate.

C.2.2.3 Conclusions for Environment

L2 is self-classified for acute aquatic toxicity by the REACH registrants.

Based on preliminary evaluations performed by the DS, all of the substances potentially meet the PBT or vPvB criteria (based on screening information). Further data are needed to clarify these properties.

C.2.3 Technical and economic feasibility

C.2.3.1 Technical feasibility - relevant applications

"PDMS fluids" were the only substance specifically highlighted as an alternative in wash-off PCPs by AMEC (2013), specifically for hair treatments. Compared to D5, they were said to have lower volatility so are not as fast drying, and may have a thicker feeling. However, for some types of PCP, they were said to have the same physical properties as D5 (i.e. fast drying and acting as a solvent) so this information is confusing in the context of *wash-off* products, presumably reflecting the variety of fluids available. The CosIng database mentions antifoaming use (alongside skin conditioning).

From the REACH registration data, linear volatile methylsiloxanes such as L4 and L5 are commercially available and could potentially replace D4 and D5 in PCPs. The lower molecular weight substances are more flammable than D4 or D5 so may be more of a problem in a factory environment and in use. Flash point can be increased by removing the lower molecular weight constituents (L3 and L4). L5 is not classified for flammable hazards.

C.2.3.2 Economic feasibility

AMEC (2013) indicates that a similar quantity of "PDMS fluid" is required to replace the intended function of D4 or D5.

AMEC (2013) indicates that "PDMS fluids" were readily available. L2 is registered in the 1,000 – 10,000 tonnes per annum band. L3 and L4 are registered in the 100 – 1,000 tonnes per annum band. L5 is registered in the 10 – 100 tonnes per annum band. These linear volatile methyl siloxanes are therefore available in much smaller amounts than D4 or D5.

AMEC (2013), supplemented by internet market place data, indicates that the unit cost of some types of "PDMS fluid" may be up to ten times higher than D5, although for other types the price is apparently similar, presumably reflecting the wide range of PDMS products available (as well as different prices for different volumes). Processing to remove L3 and L4 to increase the flash point, or reduce the concentration of D4 and D5 below 0.1% w/w, is possible but may be expensive and require significant energy input.

C.2.4 Conclusions

The following table summarises the conclusions from the above information on the feasibility and suitability of linear volatile methyl siloxanes as a replacement for D4 and D5.

Table: Conclusions on suitability and feasibility of linear volatile methylsiloxanes

Category	Conclusion
Hazard	Some linear volatile methylsiloxanes potentially have PBT or vPvB properties, although a final decision cannot be made without more definitive data. They also appear to possess some chronic aquatic toxicity, based on self-classifications. Four substances are listed on the CoRAP for REACH Evaluation, based on the potential PBT/vPvB concern.
Technical feasibility	Can feasibly be used in PCP applications, although some may have a thicker feeling; additional precautions may be needed to avoid risks arising from the flammability of some constituents.
Economic feasibility	May be more expensive than D4 and D5 in some cases. They are supplied in smaller quantities than D4 or D5, although polymers are typically supplied in much higher amounts.
Overall conclusion	**Some linear volatile methylsiloxanes appear to be a technically feasible alternative to D4 and D5 in wash-off PCPs, although some may be more expensive and supply tonnages may be lower. They have potential PBT/vPvB concerns, although these have not yet been confirmed. This type of substance may contain D4 or D5 as impurities.**

C.3 Alternative 2: Dodecamethylcyclohexasiloxane (D6), CAS no. 540-97-6

D6 is close analogue of D4 and D5, with the following chemical structure:
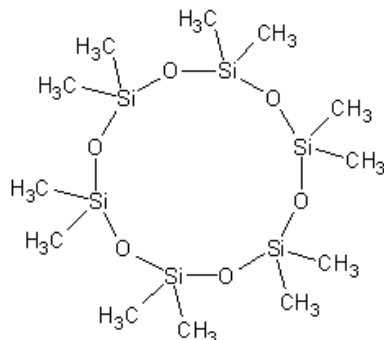
It is made using the same manufacturing process as for D4 and D5, and is separated from them by distillation. Consequently, it can contain small amounts of these two substances as impurities. It is also present together with both D4 and D5 in commercial products called "cyclomethicone" or "cyclodimethicone". This substance was not included in the Cosmetics Europe survey of alternatives (AMEC, 2013).

C.3.1 Human health information

C.3.1.1 Information from regulatory authorities

A national UK environmental risk evaluation report is available (EA, 2009). D6 is of low acute toxicity via the oral and dermal routes, and it is anticipated that acute toxicity after inhalation exposure is also likely to be low. D6 is not a skin or eye irritant and is not predicted to irritate the respiratory tract. Also, D6 is not a skin sensitiser and is not predicted to have asthmagenic potential. The only information on the effects of repeated exposure comes from a 28-day oral dosing study in rats in which the only effect seen was liver enlargement of up to 20 per cent above controls at 1000 mg/kg/day. This was not observed in another 28-day study in which rats were treated with up to 1500 mg/kg/day. As the magnitude of liver enlargement was relatively small (compared to those for D4 and D5), and only occurred after treatment with high doses in the absence of any other effects, this observation is not considered a concern for human health.

D6 has been investigated for mutagenicity in one bacterial reverse mutation assay, with negative results. On the basis of this finding and the lack of evidence for mutagenic properties with D4 and D5, there are no concerns for mutagenicity with D6. There are no data on the carcinogenic potential of D6. It is possible that D6 might cause endometrial tumours (as does D5), but the mechanism for tumour formation is not relevant to human health. On this basis, no concerns are identified for carcinogenicity in relation to D6.

No adverse effects on fertility or development are reported from a combined repeated dose–reproductive and developmental toxicity screening study in which rats were treated orally with up to 1000 mg/kg/day for up to 45 consecutive days. Overall, no toxicological hazards are identified for D6, and it does not meet the classification criteria for any human health hazard end points. It is understood that

ECHA has requested a repeated dose inhalation study using rats, but the timing of this study is not known.

It does not meet the Canadian Government's Human Health Categorization Criteria. However, an OECD Screening Initial Data Set assessment concluded that D6 possesses properties indicating a hazard for human health (repeated-dose toxicity).[12]

C.3.1.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrant's CSR	Self-notified classifications in the C&L Inventory
D6	-	-	Eye Irrit. 2 (H319)

The validity of the self-classifications notified to the C&L Inventory is unknown. In the absence of other information, it is assumed that the lead registrant's self-classification is more appropriate.

C.3.1.3 Conclusions for human health

There are potential concerns relating to human health hazards for D6, although it does not appear to require classification for this hazard in the EU.

C.3.2 Environmental information

C.3.2.1 Information from regulatory authorities

A national UK environmental risk evaluation report is available (EA, 2009) along with a draft PBT fact sheet prepared by the UK REACH CA at the same time as work was completed for D4 and D5. Based on the available data it was concluded that D6 meets the Annex XIII criteria for P/vP and B, but not vB or T. Uncertainties remain for a fish bioconcentration study that appears to indicate a high level of bioconcentration but a test report is not available for evaluation by the DS. If the fish grew significantly during the study, growth correction is likely to confirm that the substance meets the vB criterion. In addition, a recent field study from Norway suggests that D6 may undergo trophic magnification in a pelagic food web, although other studies suggest that biodilution occurs in other food webs. The results of the Japanese BCF study require full evaluation before a final decision can be made.

In addition, D6 as commercially supplied can contain D4 and D5 at concentrations above 0.1% w/w, making it a PBT- or vPvB-containing substance. However, it is possible that some producers can make a purer product, and if D6 is diluted in the final PCP product, the concentration of D4 and D5 may be below 0.1% w/w.

C.3.2.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrants' CSRs	Self-notified classifications in the C&L Inventory
D6	-	-	Aquatic Chronic 4 (H413)

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[12] http://webnet.oecd.org/Hpv/UI/handler.axd?id=bdbde485-8087-4034-83d9-cd0c9af7e4de

Since D5 is not classified for aquatic toxicity, the notified self-classification appears to be in error since D6 is less bioaccumulative and more insoluble (it may be based on the application of the safety net approach based on a lack of ready biodegradation and high K_{OW} value).

C.3.2.3 Conclusions for Environment

D6 is not classified for acute or chronic aquatic toxicity by the REACH registrants. Based on the evaluation performed by the DS, D6 potentially meets the vPvB criteria; further evaluation of a fish BCF study is needed to clarify these properties.

C.3.3 Technical and economic feasibility

C.3.3.1 Technical feasibility - relevant applications

D6 is already used for PCPs, and it therefore appears likely that it could be used as a replacement for D4 and D5 in some PCPs. It is less volatile, and differences in its surface tension and heat of evaporation may limit its application in some types of PCP although this might be less relevant for wash-off products. The CosIng database mentions use as an emollient and solvent, and in hair conditioning.

C.3.3.2 Economic feasibility

No information is available on the relative loading amounts required to (partially) replace the intended function of D4 or D5, although they might be expected to be similar (and this is suggested by internet market place prices).

D6 is a registered in the 10,000 - 100,000 tonnes per annum band, with around 2,000 tonnes supplied for use in PCPs in the EU in 2004 (EA, 2009). The relative price of D6 compared to D4 and D5 is not known, but given the high tonnage, might be expected to be similar.

Processing to improve the purity of D6 (i.e. to reduce the concentration of D4 and D5 below 0.1% w/w) is possible but may be expensive and require significant energy input.

C.3.4 Conclusions

The following table summarises the conclusions from the above information on the feasibility and suitability of D6 as a replacement for D4 and D5.

Table : Conclusions on suitability and feasibility of D6

Category	Conclusion
Hazard	Potentially meets the vPvB criteria, and further evaluation is required. It also contains D4 and D5 as impurities above 0.1% w/w.
Technical feasibility	Can feasibly be used in some types of wash-off PCP.
Economic feasibility	No information is available on economic feasibility, although its overall production volume is similar to D4 and D5.
Overall conclusion	**D6 is a technically feasible alternative to D4 and D5 in wash-off PCPs. Although its relative price is unknown, it is likely to be similar to D4 and D5 given the large amounts that are produced. It has potential vPvB concerns, although these have not yet been confirmed. It contains D4 and D5 as impurities.**

C.4 Alternative 3: Ethyl methicone, CAS no. 63148-54-9

This substance was mentioned in the questionnaire that formed the basis for the Cosmetics Europe survey of alternatives, but none of the respondents highlighted it in their reply (AMEC, 2013). It has been advertised as a replacement for both D4 and D5 in PCPs (e.g. under the trade name Silwax D-02[13]), formulated with esters. It has a polymeric structure, with the general molecular formula:

$$CH_3\text{-}Si\text{-}O\text{-} (\text{-} Si\text{-} O)_b\text{-}O\text{-} Si\text{-} CH_3$$
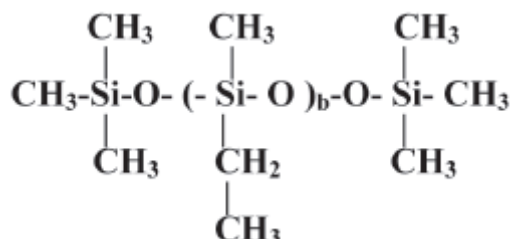
The number of repeating units is not described on the SILTECH LLC website, so it could contain a variety of chain lengths. It appears that several other types of silicone polymers might be available for use in PCPs, e.g. amodimethicone, methyl trimethicone and phenyl trimethicone (none of which were included in the Cosmetics Europe survey). The above substance has been included in this assessment as a representative of this group, although the DS recognises that their properties could be very different.

C.4.1 Human health information

C.4.1.1 Information from regulatory authorities

No regulatory reviews have been identified.

C.4.1.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrant's CSR	Self-notified classifications in the C&L Inventory
Ethyl methicone	-	-	

This substance has not been registered and there is no entry on the C&L Inventory.

C.4.1.3 Conclusions for human health

There is insufficient information to establish whether there are any concerns relating to human health hazards for ethyl methicone.

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13 http://www.siltechpersonalcare.com/products_page.html.

C.4.2 Environmental information

C.4.2.1 Information from regulatory authorities

No regulatory reviews have been identified. The chemical structure suggests that ethyl methicone will be more hydrophobic and less volatile than analogous linear methylsilicones with the same number of repeating units (PDMS). The technical data sheet on the SILTECH LLC website says that the substance is insoluble in water but soluble in triglycerides and mineral oil. This suggests that there may be some potential for bioaccumulation. In the absence of other information, it would appear that this substance could have similar properties to L2 – L5, if it is supplied as similar chain lengths. The properties of any degradation products from depolymerisation reactions are unknown for the time being.

C.4.2.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrants' CSRs	Self-notified classifications in the C&L Inventory
Ethyl methicone	-	-	-

This substance has not been registered (and presumably will not be if it is considered to be a polymer) and there is no entry on the C&L Inventory.

C.4.2.3 Conclusions for Environment

There is insufficient information to establish whether there are any concerns relating to environmental hazards for ethyl methicone, although by analogy with the dimethicones, it could potentially have PBT-related concerns.

C.4.3 Technical and economic feasibility

C.4.3.1 Technical feasibility - relevant applications

Ethyl methicone is advertised (in the USA at least) as a replacement for D4 and D5 in PCP applications including, but not limited to, antiperspirants, hair glossers, resins, moisturizers, lotions and pigmented products. The CosIng database mentions use as an emollient. It therefore appears likely that it could be used as a replacement for D4 and D5 in some wash-off PCPs.

C.4.3.2 Economic feasibility

No information is available on the relative loading amounts required to (partially) replace the intended function of D4 or D5.

Ethyl methicone is not registered under REACH (presumably because it is a polymeric substance). The relative price compared to D4 and D5 is not known, although the SILTECH LLC website states that it is a "cost effective" replacement.

C.4.4 Conclusions

The following table summarises the conclusions from the above information on the feasibility and suitability of ethyl methicone as a replacement for D4 and D5.

Table : Conclusions on suitability and feasibility of ethyl methicone

Category	Conclusion
Hazard	Insufficient data for a conclusion, although potentially has PBT-related concerns by analogy with the dimethicones.
Technical feasibility	Appears to be a feasible alternative for some types of wash-off PCP.
Economic feasibility	No information is available on economic feasibility, although one source claims that it is a cost-effective replacement for D4 and D5.
Overall conclusion	**Ethyl methicone appears to be a technically feasible alternative to D4 and D5 in some wash-off PCPs, although its relative price and level of supply is unknown. It might have potential PBT-related concerns, although these have not yet been confirmed.**

C.5 Alternative 4: Neopentylglycol diheptanoate, CAS no. 68855-18-5

Neopentylglycol diheptanoate (also known as neopentylglycol heptanoate and heptanoic acid, ester with 2,2-dimethyl-1,3-propanediol) has the following chemical structure:
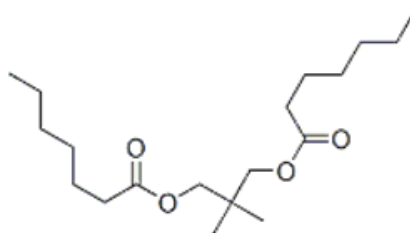
C.5.1 Human health information

C.5.1.1 Information from regulatory authorities

No regulatory reviews have been identified.

C.5.1.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrant's CSR	Self-notified classifications in the C&L Inventory
Neopentylglycol diheptanoate	-	Not classified	-

C.5.1.3 Conclusions for human health

There are currently no concerns relating to human health hazards for this substance.

C.5.2 Environmental information

C.5.2.1 Information from regulatory authorities

No regulatory reviews have been identified.

C.5.2.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrants' CSRs	Self-notified classifications in the C&L Inventory
Neopentylglycol diheptanoate	-	Not classified	-

According to the REACH registration, neopentylglycol diheptanoate is readily biodegradable, so it is does not meet the screening criteria for either a PBT or vPvB substance.

C.5.2.3 Conclusions for Environment

Neopentylglycol diheptanoate is not classified for acute or chronic aquatic toxicity by the REACH registrants.

Based on the REACH registration, it does not screen as either PBT or vPvB.

C.5.3 Technical and economic feasibility

C.5.3.1 Technical feasibility - relevant applications

It has been suggested that neopentylglycol diheptanoate can be used as an alternative to dimethicone (and therefore potentially D4 and D5) in conditioners and leave-on PCPs (Danish Ministry of the Environment, 2005). This substance has also been named in a patent for "personal care products that do not contain tetramer and/or pentamer cyclomethicones"[14]. The CosIng database mentions use as an emollient. The DS does not know if it can be used in wash-off PCP applications (AMEC (2013) only discussed its use for leave-on PCPs).

The Danish Ministry of the Environment (2005) stated that the use of neopentylglycol diheptanoate should not result in changes in PCP production equipment.

C.5.3.2 Economic feasibility

No information is available on the relative loading amounts required to (partially) replace the intended function of D4 or D5.

Neopentylglycol diheptanoate is registered in the 100 – 1,000 tonnes per annum band. The Danish Ministry of the Environment (2005) stated that it was just over twice the price of dimethicone - its relative price compared to D4 and D5 was not stated.

C.5.4 Conclusions

The following table summarises the conclusions from the above information on the feasibility and suitability of neopentylglycol diheptanoate as a replacement for D4 and D5.

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14 http://www.google.com/patents/WO2004103308A2?cl=en

Table: Conclusions on suitability and feasibility of neopentylglycol diheptanoate

Category	Conclusion
Hazard	Neopentylglycol diheptanoate has no human health or environmental hazards and does not meet the PBT/vPvB criteria.
Technical feasibility	Can feasibly be used in some types of PCPs, but this might not apply to wash-off PCPs.
Economic feasibility	No information is available on economic feasibility, although it is currently supplied in smaller amounts than D5.
Overall conclusion	**Neopentylglycol diheptanoate is possibly a technically feasible alternative to D4 and D5 in some wash-off PCPs, although its relative price is unknown and supply tonnages are lower. It has no relevant hazards.**

C.6 Alternative 5: PPG-3 benzyl ether ethylhexanoate, CAS no. 1073606-36-6

PPG-3 benzyl ether ethylhexanoate is an alkoxylated derivative of benzyl alcohol, with the molecular formula $C_{15}H_{22}O_2(C_3H_6O)_n$.

Note: Another potential alternative is PPG-3 benzyl ether myristate (CAS no. 642443-86-5), which differs from this substance by having a linear C_{14} (rather than C_8) alkyl chain. It is likely to have similar data availability issues.

C.6.1 Human health information

C.6.1.1 Information from regulatory authorities

No regulatory reviews have been identified.

C.6.1.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrant's CSR	Self-notified classifications in the C&L Inventory
PPG-3 benzyl ether ethylhexanoate	-	Not applicable	No entry

As a polymer, this substance does not require registration under REACH.

Information from a product safety data sheet[15] indicates that the substance did not cause skin irritation in an *in vitro* study or skin sensitization in a patch test, and is practically non-irritating to eyes. An Ames test was negative. No other data appear to be publicly available.

C.6.1.3 Conclusions for human health

There currently appear to be no concerns relating to human health hazards for PPG-3 benzyl ether ethylhexanoate, although this may reflect a lack of data.

C.6.2 Environmental information

C.6.2.1 Information from regulatory authorities

No regulatory reviews have been identified.

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[15] Crodamol™ SFX-LQ-(MH); Version 1.0; Revision Date 24/07/2012. Croda Europe Ltd., Cowick Hall, Snaith, Goole, East Yorkshire, DN14 9AA, UK.

C.6.2.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrants' CSRs	Self-notified classifications in the C&L Inventory
PPG-3 benzyl ether ethylhexanoate	-	Not applicable	No entry

As a polymer, this substance does not require registration under REACH.
The presence of a long alkoxylated chain implies that the substance may be rapidly degraded in the environment (by analogy with alkylphenol ethoxylates), although this might be limited by bioavailability if the water solubility is low.

C.6.2.3 Conclusions for Environment

Environmental hazards are expected to be low but there is a lack of data.

C.6.3 Technical and economic feasibility

C.6.3.1 Technical feasibility - relevant applications

PPG-3 benzyl ether ethylhexanoate is an emollient and solvent, marketed as a D5 replacement in a variety of PCPs including wash-off products such as hair conditioners (e.g. under the trade name Crodamol™ SFX (Croda, 2014); this information is also mentioned on the Commission's CosIng database).

C.6.3.2 Economic feasibility

No information is available on the relative loading amounts required to (partially) replace the intended function of D4 or D5.
As no registration data are available, the supply tonnage is unknown. The relative price of PPG-3 benzyl ether ethylhexanoate compared to D4 and D5 is not known.

C.6.4 Conclusions

The following table summarises the conclusions from the above information on the feasibility and suitability of PPG-3 benzyl ether ethylhexanoate as a replacement for D4 and D5.

Table : Conclusions on suitability and feasibility of PPG-3 benzyl ether ethylhexanoate

Category	Conclusion
Hazard	Does not currently appear to have any relevant hazards.
Technical feasibility	Technically feasible for at least some types of wash-off PCP.
Economic feasibility	No information is available on economic feasibility, and supply levels are unknown.
Overall conclusion	**PPG-3 benzyl ether ethylhexanoate is a technically feasible alternative to D4 and D5 in some wash-off PCPs, although its relative price and supply levels are unknown. It has no relevant hazards but publicly data available are very limited.**

C.7 Alternative 6: Isodecyl neopentanoate, CAS no. 60209-82-7

Isodecyl neopentanoate (also known as isodecyl pivalate or propanoic acid, 2,2-dimethyl-, isodecyl ester) has the following molecular structure:
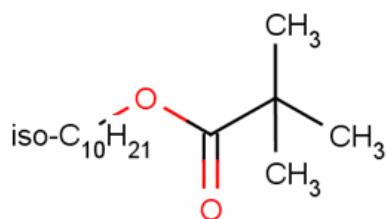
C.7.1 Human health information

C.7.1.1 Information from regulatory authorities

No regulatory reviews have been identified. It does not meet the Canadian Government's Human Health Categorization Criteria.

C.7.1.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrant's CSR	Self-notified classifications in the C&L Inventory
Isodecyl neopentanoate	-	Not classified	Not classified

C.7.1.3 Conclusions for human health

There currently appear to be no concerns relating to human health hazards.

C.7.2 Environmental information

C.7.2.1 Information from regulatory authorities

No regulatory reviews have been identified. It does not meet the Canadian Government's Envrionmental Categorization Criteria.

C.7.2.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrants' CSRs	Self-notified classifications in the C&L Inventory
Isodecyl neopentanoate	-	Aquatic Chronic 1 (H410)	Aquatic Chronic 1 (H410) Aquatic Chronic 3 (H412) Aquatic Chronic 4 (H413)

The validity of the self-classifications notified to the C&L Inventory is unknown. In the absence of other information, it is assumed that the lead registrant's self-classification is more appropriate.

According to the REACH registration, the substance screens as potentially P but has a log K_{OW} below 4 so does not meet the screening PBT or vPvB criteria.

C.7.2.3 Conclusions for Environment

The substance is self-classified for aquatic chronic hazard. It is not a PBT or vPvB substance.

C.7.3 Technical and economic feasibility

C.7.3.1 Technical feasibility - relevant applications

Isodecyl neopentanoate is an alternative to D4 and D5 with emulsifying and solvent properties, mainly used in conditioners and leave-on PCPs, but with a possible use in shampoos and cream soaps (Danish Ministry of the Environment, 2005). The CosIng database mentions use as an emollient. AMEC (2013) only discussed its use for leave-on PCPs. It might therefore provide some of the functionality of D4 and D5 in some types of wash-off PCP. The Danish Ministry of the Environment (2005) stated that the use of isodecyl neopentanoate should not result in changes in PCP production equipment.

C.7.3.2 Economic feasibility

No information is available on the relative loading amounts required to (partially) replace the intended function of D4 or D5.

Isodecyl neopentanoate is registered in the 100 – 1,000 tonnes per annum band. The Danish Ministry of the Environment (2005) stated that it was just over twice the price of D4 and D5.

C.7.4 Conclusions

The following table summarises the conclusions from the above information on the feasibility and suitability of isodecyl neopentanoate as a replacement for D4 and D5.

Table : Conclusions on suitability and feasibility of isodecyl neopentanoate

Category	Conclusion
Hazard	Not PBT or vPvB. Does not currently have any relevant human health hazards, but it appears to be classifiable for aquatic chronic hazards.
Technical feasibility	Can feasibly be used in some types of PCPs, including some wash-off products.
Economic feasibility	No information is available on economic feasibility, although it is currently supplied in smaller amounts than D5.
Overall conclusion	**Isodecyl neopentanoate appears to be a technically feasible alternative to D4 and D5 in some wash-off PCPs, although it is more expensive and supply levels are lower than D5. It potentially poses an aquatic chronic hazard but is not PBT or vPvB.**

C.8 Alternative 7: Dicaprylyl carbonate, CAS no. 1680-31-5

Dicaprylyl carbonate (also known as carbonic acid, dioctyl ester) has the following molecular structure:
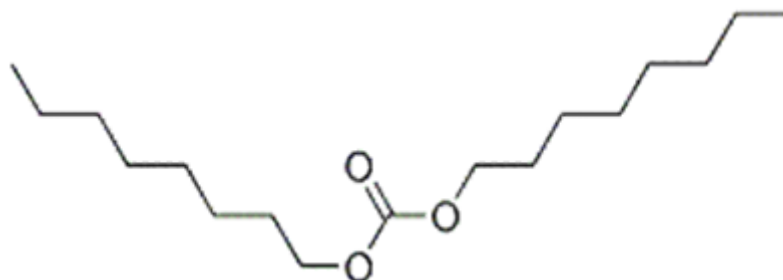
A related substance is diethylhexyl carbonate, which is similar to the above structure but would have a limited amount of branching.

C.8.1 Human health information

C.8.1.1 Information from regulatory authorities

No regulatory reviews have been identified.

C.8.1.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrant's CSR	Self-notified classifications in the C&L Inventory
Dicaprylyl carbonate	-	Not applicable	No entry

This substance is not yet registered under REACH.

C.8.1.3 Conclusions for human health

There currently appear to be no concerns relating to human health hazards for dicaprylyl carbonate, although this may reflect a lack of data.

C.8.2 Environmental information

C.8.2.1 Information from regulatory authorities

No regulatory reviews have been identified.

C.8.2.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrants' CSRs	Self-notified classifications in the C&L Inventory
Dicaprylyl carbonate	-	Not applicable	No entry

This substance is not yet registered under REACH.

The straight alkyl chains in the chemical structure suggests that the substance will be rapidly degraded in the environment, and it is predicted to be readily biodegradable by the DS using BIOWIN v4.10. In addition, the predicted acute $L(E)C_{50}$ is in the range 0.005 – 0.008 mg/L (ECOSAR v0.99), so it might meet the criteria for classification as Aquatic Acute 1 and Aquatic Chronic 1.

C.8.2.3 Conclusions for Environment

There currently appear to be no concerns relating to environmental hazards for dicaprylyl carbonate, although this may reflect a lack of data.

C.8.3 Technical and economic feasibility

C.8.3.1 Technical feasibility - relevant applications

Dicaprylyl carbonate has uses in creams and lotions, although it does not have the foam-reducing effect that some siloxanes have (Danish Ministry of the Environment, 2005). The CosIng database mentions use as an emollient. It might therefore provide some of the functionality of D4 and D5 in some types of PCP, but it is not known whether this includes wash-off products. AMEC (2013) only discussed its use for leave-on PCPs, but mentions that it is not suitable for haircare products due to volatile organic carbon legislation. The Danish Ministry of the Environment (2005) stated that the use of dicaprylyl carbonate probably will not result in changes in PCP production equipment.

C.8.3.2 Economic feasibility

No information is available on the relative loading amounts required to (partially) replace the intended function of D4 or D5, although it apparently has to be used with other substances to achieve a similar effect.

As no registration data are available, the supply tonnage is unknown but it is clearly lower than 10 tonnes/year. The relative price of this substance compared to D4 and D5 is not known. Confidential information in AMEC (2013) is conflicting, varying from a comparable price to D5 up to several times higher depending on the respondent. The Danish Ministry of the Environment (2005) stated that it was perhaps similar to but slightly higher in price than D4 and D5 (whereas the related substance diethylhexyl carbonate was cheaper).

C.8.4 Conclusions

The following table summarises the conclusions from the above information on the feasibility and suitability of dicaprylyl carbonate as a replacement for D4 and D5.

Table : Conclusions on suitability and feasibility of dicaprylyl carbonate

Category	Conclusion
Hazard	No data – QSAR predictions by the DS suggest that it is rapidly degradable, but might meet the criteria for classification as Aquatic Acute 1 and Aquatic Chronic 1.
Technical feasibility	Can feasibly be used in some types of PCPs. It is not known whether it can be used in wash-off PCPs.
Economic feasibility	Appears to be slightly more expensive than D5, and supplied in smaller amounts.
Overall conclusion	**Dicaprylyl carbonate is possibly a technically feasible alternative to D4 and D5 in some types of wash-off PCPs, although it appears to be more expensive than D5 and supply levels are lower. It may require classification for aquatic hazards but publicly data available are very limited.**

C.9 Alternative 8: Dicaprylyl ether, CAS no. 629-82-3

Dicaprylyl ether (also known as dioctyl ether) has the following molecular structure:
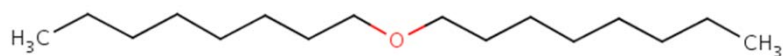
C.9.1 Human health information

C.9.1.1 Information from regulatory authorities

No regulatory reviews have been identified.

C.9.1.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrant's CSR	Self-notified classifications in the C&L Inventory
Dicaprylyl ether	-	Not classified	Not classified

C.9.1.2 Conclusions for human health

There currently appear to be no concerns relating to human health hazards for dicaprylyl ether.

C.9.2 Environmental information

C.9.2.1 Information from regulatory authorities

No regulatory reviews have been identified.

C.9.2.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrants' CSRs	Self-notified classifications in the C&L Inventory
Dicaprylyl ether	-	Not classified	Not classified

According to the REACH registration, this substance is readily biodegradable so does not meet the PBT or vPvB criteria.

C.9.2.3 Conclusions for Environment

There currently appear to be no concerns relating to environmental hazards for dicaprylyl ether.

C.9.3 Technical and economic feasibility

C.9.3.1 Technical feasibility - relevant applications

Dicaprylyl ether may be used with other substances (e.g. decyl glucoside and glyceryl oleate) as an alternative conditioner system to silicone polymers (Colipa-CTPA, 2011b). The CosIng database mentions use as an emollient and solvent. It might therefore provide some of the functionality of D4 and D5 in some types of wash-off PCPs. AMEC (2013) only discussed its use for leave-on PCPs.

C.9.3.2 Economic feasibility

No information is available on the relative loading amounts required to (partially) replace the intended function of D4 or D5.
Dicaprylyl ether is registered under REACH in the 1,000 – 10,000 tonnes per annum band. The relative price compared to D4 and D5 is not known.

C.9.4 Conclusions

The following table summarises the conclusions from the above information on the feasibility and suitability of dicaprylyl ether as a replacement for D4 and D5.

Table: Conclusions on suitability and feasibility of dicaprylyl ether

Category	Conclusion
Hazard	Does not currently appear to have any relevant hazards.
Technical feasibility	Can feasibly be used in some types of PCPs where conditioning properties are important, mixed with other substances.
Economic feasibility	No information is available on economic feasibility, although supplied in lower amounts than D5.
Overall conclusion	**Dicaprylyl ether in combination with other substances is a technically feasible alternative to D4 and D5 in some wash-off PCPs, although its relative price is unknown and it is supplied in smaller amounts than D5. It has no relevant hazards.**

C.10 Alternative 9: Hydrogenated polydecene, CAS no. 68037-01-4

Hydrogenated polydecene (also known as dec-1-ene, homopolymer, hydrogenated) is a synthetic polymer. Its molecular structure is approximated as follows:
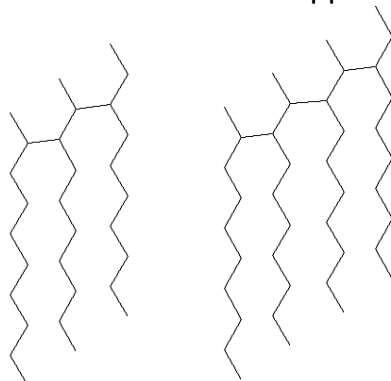
Other types of alkane (e.g. coconut alkanes) might also be used.

C.10.1 Human health information

C.10.1.1 Information from regulatory authorities

No regulatory reviews have been identified.

C.10.1.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrant's CSR	Self-notified classifications in the C&L Inventory
Hydrogenated polydecene	-	Not classified if kinematic viscosity >20.5 cSt 40 °C Asp. Tox. 1 (H304: May be fatal if swallowed and enters airways) if kinematic viscosity >20.5 cSt 40 °C	No entry

The self-classification for human health depends on the viscosity of the product.

C.10.1.3 Conclusions for human health

There currently appear to be no concerns relating to human health hazards for hydrogenated polydecene provided the viscosity exceeds a certain threshold.

C.10.2 Environmental information

C.10.2.1 Information from regulatory authorities

No regulatory reviews have been identified.

C.10.2.2 Hazard information reported by industry

Substance	Harmonised classification (Annex VI, CLP Regulation)	Self-classification in the lead registrants' CSRs	Self-notified classifications in the C&L Inventory
Hydrogenated polydecene	-	Not classified	No entry

According to the REACH registration, C_{6-24} constituents are readily biodegradable so do not meet the criteria for P or vP. Higher molecular weight constituents are potentially P or vP. C_{8-18} constituents are potentially B or vB based on their log K_{OW} values. None of the category members are considered to meet the T criterion.

C.10.2.3 Conclusions for Environment

Environmental hazards are expected to be low but as this is a complex substance, a more in depth analysis is needed.

C.10.3 Technical and economic feasibility

C.10.3.1 Technical feasibility - relevant applications

Hydrogenated polydecene is used as a non-sticky emollient and skin moisturizer for leave-on PCPs (Danish Ministry of the Environment, 2005) The CosIng database also mentions use as a solvent and hair conditioning. It might therefore provide some of the functionality of D4 and D5 in some types of PCP, although it is not known if it can be used in wash-off PCPs. AMEC (2013) only discussed its use for leave-on PCPs.

C.10.3.2 Economic feasibility

No information is available on the relative loading amounts required to (partially) replace the intended function of D4 or D5.
Hydrogenated polydecene is registered under REACH in the 100,000 - 1,000,000 tonnes per annum band. The relative price compared to D4 and D5 is not known.

C.10.4 Conclusions

The following table summarises the conclusions from the above information on the feasibility and suitability of hydrogenated polydecene as a replacement for D4 and D5.

Table: Conclusions on suitability and feasibility of hydrogenated polydecene

Category	Conclusion
Hazard	Does not currently appear to have any relevant hazards provided the viscosity exceeds a certain threshold, although further analysis may be needed for the environment as some constituents are potentially vPvB.
Technical feasibility	Can feasibly be used in some types of PCPs, but it is not known if this includes wash-off PCPs.
Economic feasibility	No information is available on economic feasibility, but supply levels are high.
Overall conclusion	**Hydrogenated polydecene is possibly a technically feasible alternative to D4 and D5 in wash-off PCPs; although its relative price is unknown, it is supplied in large amounts. It is unlikely that the substance used in PCPs would have relevant hazards but further analysis may be required for the environment.**

C.11 Conclusions on the analysis of alternatives

Different considerations are relevant when selecting a replacement for D4 and D5. An alternative substance needs to be both technically and economically feasible (including both cost and availability). In addition, users of D4 or D5 are unlikely to choose a replacement which may become the target of regulatory risk management in the future.

From the analysis presented in the preceding section, several substances appear to be potentially technically feasible alternatives to D4 and D5 in at least some wash-off PCP types. Some of the substances have potential PBT/vPvB concerns, although this is based on screening information only and further data are needed before a conclusion can be drawn. Other substances do not appear to have relevant hazards, so nominally will have a lower environmental impact than D4 or D5.

It is difficult to assess the economic feasibility of the alternatives. It is clear that several potential alternatives are currently supplied in smaller volumes than either D4 or D5. They may therefore currently have a lower availability and/or higher price. However, the cost of reformulation itself might be more important than the price differential.

Responses to the Cosmetics Europe survey are confidential, but were analysed by AMEC (2013). Unfortunately, the respondents chose to focus on leave-on PCPs, so there is very little direct information on alternatives for wash-off products. AMEC's analysis indicated the following:

- Many of the potential alternatives have emollient properties but cannot be used on their own to replace D4 or D5 due, for example, to differences in texture or volatility, skin irritation, odour, flammability, etc.

- It was also noted that the environmental fate and (eco)toxicology of some of the identified alternatives have not been studied in detail (although this is a generic issue rather than specific to alternatives for D4 and D5).

- Most of the potential alternatives are already supplied to the market, but it is not known whether they can be made available in sufficient quantities to completely replace D5.

- Cost implications of using the alternatives were considered in terms of unit price of the alternative substances and the required amount for a given product type (substitution factor), as well as how the cost implications for the manufacturers of the PCPs may affect the consumers. In the majority of cases, the unit price of the alternative substances was more than that of D5. Unit prices of a few alternative substances were considered similar to that of D5, and no alternative substance was considered to be cheaper than D5.

- As reformulation may require more than one alternative substance to replace D4/D5, the resulting production costs could be high, especially if there are additional costs associated with changes in manufacturing equipment and product packaging.

- For all potential alternatives, there would be an (unquantified) increase in product prices and/or products would provide a lower performance.

It is not known whether the survey included input from companies that do not routinely use D4 or D5 in their PCPs, or only elicited responses from companies that had an interest in retaining them in their product portfolio. The representivity of the responses is therefore unclear in the context of this restriction, which targets wash-off products only.

The DS notes that although many of the survey respondents believed that alternative substances are not suitable, a few PCP manufacturers considered that some may be suitable but cautioned that more research and development was needed and/or the availability and price of the alternatives needed to improve.

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Appendix E   Methods for the Extraction and Analysis of cVMS

E1   Pre-treatment and extraction methods

Numerous methods have been developed for the extraction of cVMS from waters and sediment. The extraction procedures used in the studies assessed during the literature review described in Appendix B are detailed below. The analytical methods for the analysis of extracted samples are detailed in Section E2 of this Appendix.

E1.1   Waters

Typically water samples are extracted following the method of Sparham *et al.* (2008), where headspace extraction is used due to the volatility of the cVMS. The method of Sparham *et al.* (2008) was used for the analysis of cVMS by Wang *et al.* (2013a) with minor deviations, Montemayor *et al.* (2013), and van Egmond *et al.* (2013). van Egmond *et al.* (2013) also validated the extraction method for 1:20 diluted raw sewage and effluent samples. Other methods use a thermal desorptive system, for example Kaj *et al.* (2005a,b), where a trapping agent is used in conjunction with a thermal desorber for extraction. This method has been shown to be suitable for the analyses of air, water, sediment and biota samples.

Membrane assisted solvent extraction (as described in Hauser and Popp (2001) and Hauser *et al.* (2002)) was used for aqueous phase sample extraction by Wang *et al.* (2013a), with the extraction being performed on whole-water samples without filtration. Prior to extraction $^{13}C_4$-D4, $^{13}C_5$-D5 and $^{13}C_6$-D6 are added as internal standards.

Bletsou *et al.* (2013) added an internal standard to the wastewater samples, leaving them to equilibrate, before extracting by liquid-liquid extraction (LLE) with hexane, a 1:1 v/v hexane:dichloromethane mix, and then a 1:1 hexane:ethyl acetate mixture. After each addition, the organic layer is removed and concentrated by rotary evaporator, before the addition of 0.5 mL of iso-octane, and evaporated under nitrogen. The extract is then transferred to a vial containing 0.5 mL of hexane prior to analysis. LLE was also utilised by Sanchís *et al.* (2013) with unfiltered samples spiked with the surrogate standard Si(OTMS)$_4$, homogenised and left undisturbed for 20 minutes. The siloxanes were extracted using three aliquots of hexane. These aliquots were then combined and concentrated to minimise volatile compound losses, and d10-anthracene internal standard added.

E1.2   Sediments and biological matrices

An ASE (Accelerated Solvent Extraction) method was developed by Sparham *et al.* (2011) for the extraction of river sediments (and also used by van Egmond *et al.*, 2013). Diatomaceous earth, pre-extracted with ethyl acetate by ASE was added to samples centrifuged at 1,500 rpm for 10 minutes with the overlying water removed, followed by thorough mixing and transfer to ASE cells containing a solvent-rinsed

cellulose filter at the bottom. Internal standard solution ($^{13}C_4$-D_4 and $^{13}C_5$-D_5) in acetone was spiked below the surface of the solid mixture and extracted with ethyl acetate. In the method conducted by van Egmond *et al.* (2013) no internal standard was added to the samples. After extraction, the extracts were dried using anhydrous sodium sulphate, if required, and the volume made up with ethyl acetate, a 1.5 mL aliquot was then used for analysis by GC-MS. All sample preparation was performed in a clean-air cabinet to minimise the potential for contamination.

A liquid-solid extraction rolling method used for the extraction of estuarine sediments was also developed by Sparham *et al.* (2011). The sample was centrifuged and homogenised as described for the ASE method, and 1.0 ± 0.2 g aliquots of sediment were weighed, followed by the addition of 5 mL acetonitrile and 5 mL hexane. To this $^{13}C_5$-D_5 internal standard was added, and then the sample was rolled for 60 minutes then centrifuged at 1,000 rpm for 10 minutes, an aliquot was removed and transferred to a chromatographic vial for analysis by GC/MS.

For extraction of the sludge and particulate matter samples, Bletsou *et al.* (2013) dried and homogenised samples with anhydrous sodium sulphate, internal standard was then applied and left to equilibrate. Following equilibration hexane was added and the samples were shaken and centrifuged. Samples were extracted with a 1:1 v/v hexane:dichloromethane mixture, and a 1:1 v/v hexane: ethyl acetate mixture. This was repeated, and extracts combined before undergoing concentration. The particulate matter samples were extracted in a similar manner, however the extraction was performed with 10 mL hexane, then 10 mL of a 1:1 hexane:dichloromethane mixture, and finally 10 mL of a 1:1 hexane: ethyl acetate mixture.

The LLE method used by Sanchís *et al.* (2013) was based on the method of Horii and Kannan (2008), where Si(OTMS)$_4$ was applied to the decanted and homogenized sediment and left for three hours at room temperature before extraction with a 1:1 v/v ethyl acetate:hexane mix in a ultrasonic bath. After extraction, the sample was spiked with d10-anthracene and analysed by GC-MS/MS.

Wang *et al.* (2013a) performed sediment and soil extraction according to the method of Sparham *et al.* (2011), with the deviation that pentane was used as one of the extraction solvents rather than hexane as detailed in the original method. For influent samples, whole samples, 1:10 dilutions and 1:100 dilutions were all analysed in triplicate, effluent samples were only analysed as whole samples and 1:10 dilutions, with analysis also being performed in triplicate. After extraction, but prior to analysis deuterium-labelled naphthalene was added to all samples to calculate recoveries and to compensate for inter-sample variability in the analysis.

E2   Analysis of siloxanes in personal care products

If restriction measures are implemented for the use of D4 and D5, then the analysis of siloxanes within products and industrial effluent will have increasing importance to ensure that products and emissions are meeting any proposed restriction measures.

- A study by Montemayor *et al.* (2013) examined rinsates and some products from three product groups: antiperspirants, skin care and hair care products. Chemical analysis for D5 followed the method developed by Sparham *et al.* (2008) with a limit of detection and limit of quantification of 0.07 and 0.023 µg/L, respectively; the extraction method for each product type is detailed in Section E1.

- Horii and Kannan (2008) developed a liquid-liquid extraction (LLE) method for the extraction of organosilicone compounds, including D4, D5 and D6, from both solid and liquid samples of personal-care and household products. Prior to extraction, liquid samples were mixed and solid samples were cut into pieces of approximately a few square millimetres using solvent-cleaned scissors. A 0.1 – 0.3 g aliquot of either liquid or solid sample was added to a polypropylene tube, prior to the addition of 500 ng of tetrakis(trimethylsiloxy)silane (M4Q), the surrogate standard. The tubes were then weighed and 3 mL of a 1:1 ethyl acetate/*n*-hexane mixture was added, followed by shaking for 15 minutes, then centrifugation at 3,500 rpm for 5 minutes. After centrifugation, the solvent layer was transferred to a separate polypropylene tube. The samples were then re-extracted twice more, resulting in 12 mL of total solvent, termed the first extract. After the first extraction, samples were allowed to soak overnight in 5 mL of 1:1 ethyl acetate/*n*-hexane. These samples were then re-extracted by shaking for 30 minutes and removal of the solvent layer to a polypropylene tube following centrifugation. This extract is termed the second extract. The first and second extracts were then concentrated to 2-3 mL, individually, using a gentle nitrogen stream. Following concentration the samples were passed through anhydrous sodium sulphate and a nylon filter (0.22 µm pore size, 30 mm diameter), with the rubber parts removed from the syringe to avoid contamination. The final sample volume was set to 10 mL and 1 mL for the first and second extract, respectively.

  The cVMS in the extracted samples were quantified by GC-MS, with separation achieved using a 30m fused silica capillary column (Rxi-5MS) and a 1 µL splitless injection with an initial inlet temperature of 200 °C. The MS was operated in SIM mode with the ions at *m/z* 281, *m/z* 355 and 267, *m/z* 341 and 429 and *m/z* 281 and 369 monitored for, D4, D5, D6 and M4Q, respectively. If after analysis of the second extract, target chemicals were detected at >10% of the amount in the first extract then the second extraction procedure was repeated resulting in a third extract.

A pacifier, shampoo, body wash and skin lotion sample were spiked with a mixture of D4, D5 and D6 at concentrations from 0.5 to 10 µg, and extracted as described above; the mean recoveries were 87 ± 5.4%, 87 ± 9.4% and 90 ± 10% for D4, D5 and D6, respectively. The limit of quantification (LoQ) was set as three times the level found in the procedure blanks, which was equal to 351 ng/g, 387 ng/g and 333 ng/g for D4, D5 and D6, respectively. Therefore, although losses via volatilisation are expected to be a significant loss pathway for cVMS, the concentration of the sample under nitrogen did not have a significant effect on the recoveries obtained, and therefore can be considered suitable for use.

- During the investigation conducted by Gouin *et al.* (2012), D5 was extracted from a variety of antiperspirant (AP) products, including soft solids, sticks and aerosol APs, and were analysed by GC/MS.

  For the extraction of soft solid and stick APs, 0.4 g (for soft solid) or 0.6 g (for stick APs) of AP product was weighed into a polypropylene centrifuge tube, and mixed with 40 mL of hexane on an orbital shaker for 15 minutes, followed by centrifugation at 2,000 rpm for 15 minutes. A clear layer is formed after centrifugation, this is collected and diluted 1,000 times before analysis; however, the diluent has not been reported.

  For the determination of D5 in an aerosol AP, as percentage of the total product sprayed, the spray adaptor was removed from the top of each test aerosol can, then tubing and a needle were attached to the exposed nozzle. The can was then shaken and the tubing purged, before the weight of the can, including the needle and tubing, was recorded. The needle was then used to pierce a septum of a 100 mL Duran flask containing 100 mL hexane. The can was then shaken again, and sprayed for ~2 seconds directly into the hexane. Using a second needle, the septum was pierced again, to relieve the pressure, and allow for the tubing contents to drain into the hexane. The can, tubing and needle ensemble were then re-weighed to determine the amount of aerosol sprayed. The hexane extract was then diluted by a factor of 200 with hexane, an aliquot was then transferred to a GC-vial.

  To allow for assessment of the recovery of D5 from the soft solid AP product, a sample was spiked with 400 µL neat D5 into hexane prior to the orbital shaker mixing. The soft-solid AP extraction procedure was then followed as above, except that, a 2,000-times dilution was used prior to analysis. To assess the recovery of D5 from stick and aerosol APs, a 1 mL aliquot of the final extracts were spiked with D5 at an appropriate level.

  The GC/MS method used for the analysis of D5 within products utilised a 30m x 0.25 mm i.d. x 0.25 µm film thickness DB-5MS column, and a 1 µL

injection. The MS was operated full scan mode, with the ion m/z 355 used for quantifying D5, and a 5 point calibration curve (47.9 to 9580 ng mL^{-1}) used for quantification. The limit of detection (LoD) or LoQ for this analytical method has not been reported.

E3   Analytical techniques

cVMS are generally separated by gas chromatography (GC) before entering the analyser. Usually analysis is performed using a mass spectrometer [MS] in selective ion monitoring [SIM] mode for *m/z* 281 (D4), 355 (D5) and 341 (D6) using electron capture. However, use of other analysers has also been reported including:

- Thermal couple detectors (TCDs)
- Flame Ionization detectors (FIDs)
- Electron Capture detectors (ECDs)

The analysis of samples extracted by Wang *et al.* (2013a) by membrane assisted solvent extraction was performed using a GC-MS technique for all samples with the LoDs for D4 being 0.009, 0.003 and 0.008 µg/L for water, sediment and soil, respectively. For D5 and D6 the LoDs were 0.027, 0.011, 0.007 and 0.022, 0.004 and 0.009 µg/L for water, sediment and soil, respectively with water, sediment and soil extraction recoveries ranging from 100 – 107%, 69 – 74%, and 70 – 78% respectively. The variability of recoveries between different mediums is to be expected due to the interactions of the cVMS with suspended particulate matter.

In the study performed by Olofsson *et al.* (2013), the siloxane concentrations measured in the sewage sludge were performed by Automated Thermal Desorption-GC-MS (ATD-GC-MS) using the method developed by the Swedish Environmental Research Institute (Kaj *et al.*, 2005a) and following strict quality guidelines. This method has an LoD of < 2 µg/L and an uncertainty factor associated with it of ± 40%. Additionally, an internal standard solution was used to compensate for any losses of siloxanes during analysis..

All samples extracted by Bletsou *et al.* (2013) were analysed by GC-MS, SIM mode. For confirmation of D3 – D6 responses relative to an internal standard, tetrakis(trimethylsiloxy)-silane was used, for all other siloxanes investigated. Quantification was performed in comparison to external calibration standards. The LoDs for D4, D5 and D6 ranged from 0.00003 – 0.0002 µg/L in water and 0.002 – 0.005 µg/L for sludge, the LoQs for D4, D5 and D6 were 0.00011, 0.00018 and 0.00060 µg/L, respectively in water and 0.006, 0.0075 and 0.015 µg/L, respectively, for sludge. It is important to note that the concentrations of siloxane reported in this study are the total siloxane concentration, i.e. dissolved and particulate concentrations.

For the HS-GC/MS method developed by Sparham *et al.* (2008), prior to analysis all samples and calibration standards were spiked with [13]C5-D5 internal standard to achieve a final concentration of 95.8 ng/L. Samples for head-space analysis taken in the field where immediately prepared for analysis after sampling as a precaution against possible contamination from laboratory air. In addition, all blank samples and their internal standard addition where performed in the field. The concentration of D5 in the samples was determined by comparing the MS response for the D5 quantification ion with that of the $^{13}C_5$-D5 for concentrations up to and including 1×10^4 ng/L. This method was then further developed by Unilever, who used multi-purpose samplers and gas-tight syringes in place of the pressurised sample loop, and some of the analysis parameters were altered. The authors concluded that, the method provides a straight-forward method for analysing D5 in water and treated sewage effluent samples and has an appropriate LoD for the concentrations expected in the environment. The internal standard recoveries were generally excellent for all sample types, and the addition of the internal standard to samples in the field allows for increased confidence in the reported concentrations. Additionally, the authors believe that any variation in the recovery of samples is most likely due to instrumental drift during the analysis rather than any matrix effects. This method was also used for the analysis of diluted raw sewage by van Egmond *et al.* (2013).

Sparham *et al.* (2011) also developed a GC/MS analysis method for D5 in extracted river and estuarine sediments using a 5 µL injection in pseudo on-column mode via an adapted programmed temperature vaporisation [PTV] inlet. From the results of the river sediment samples it was shown that the ASE (Accelerated Solvent Extraction) GC-MS analysis is suitable for the extraction and analysis of D4, D5 and linear alkylbenzenes [LAB], with LoDs of 7, 37 and 27 ng/g dry weight (dw), respectively, for the one set of samples (and LoQs of 22, 110 and 82 ng/g dw) and 19, 19 and 65 ng/g dw, respectively, for a second set of samples (with LoQs of 57, 57 and 195 ng/g dw). The results from the Humber estuary show that the liquid-solid extraction procedure is suitable for use for the extraction of D5 and LAB, but this method has not been validated for D4 extraction and analysis. The LoDs from the Humber estuary samples were reported as 1 ng/g dw for D5 and 7 ng/g dw for total LAB, with the LoQs reported as 4 and 21 ng/g dw, respectively. The authors concluded from the QC and validation data that greater precision is obtained using the ASE method rather than the liquid-solid extraction method for D5 analysis. However, the liquid-solid extraction tended to have a better LoQ due to the lower dilution of sediment to the final sample volume and the lower blank control contamination. In addition, the ASE method was also shown to be suitable for the simultaneous extraction of D4 and LAB. Even though the D4 concentrations are between the LoD and LoQ for the study of Sparham *et al.* (2011) they can be reported due to the lower risk of ambient contamination (Sparham *et al.* 2011). The reason for the lower risk of D4 contamination was not reported..

An optimised and validated GC-MS/MS method using a triple quadrupole analyser (QqQ) was developed by Sanchís *et al.* (2013) for the analysis of LLE wastewater, natural water and sediment samples. The method was validated with both spiked samples and blank samples for both cVMS and lVMS including both D4 and D5. The LoD for D4 and D5 in wastewater was 13 ± 4.8 and 3.2 ± 0.38 ng/L, respectively, and the LoQ was 26 ± 11 and 6.3 ± 0.8 ng/L for D4 and D5, respectively. For freshwater sediment samples the D4 and D5 LoDs were determined as 0.9 ± 0.1 and 0.3 ± 0.0 ng/g, and the LoQs were 1.8 ± 0.3 and 0.5 ± 0.0 ng/g, respectively. Residual contamination was identified in the procedural blanks performed in artificial wastewater and blank sediment, so a procedural blank was analysed after both the wastewater and blank sediment, with the residual concentration subtracted from the samples. In addition, two spiked control samples, two solvent injections and two procedural blanks were also analysed in each analytical run to conform to internal quality control procedures. The authors concluded that the method is suitable for environmental analysis based on the LoQs, and that good instrument linearity and intra- and inter-day linearity was observed for all analytes of interest.

E4   Potential contamination Issues

The cVMS investigated are ubiquitous in the environment, and Sparham *et al.* (2008 and 2011) stated that extreme care must be undertaken to minimise the sources of potential D5 contamination when analysing environmental samples. Therefore care was taken to reduce the risk of contamination via direct contact with laboratory staff and equipment used for sample storage, preparation and extraction. Contamination from cVMS may occur during the extraction and analysis of environmental samples and of PCP samples (e.g. giving false positive results), so attention must be paid to minimise this.

Laboratory staff abstained from use of products containing D5 for 24 hours prior to the start of the experiment and through-out the experiment in the study conducted by Montemayor *et al.* (2013). Analysts in the Bletsou *et al.* (2013) and Sparham *et al.* (2008 and 2011) studies also refrained from the use of products containing siloxanes. Other controls undertaken by Montemayor *et al.* (2013) included the separation of application and wash-off rooms, with dedicated staff in each room, to minimise the potential of cross-contamination. All sample bottles used were pre-cleaned with a detergent and had foil-lined caps to minimise loss of D5 after sampling and prior to analysis, and to minimise the potential for cross-contamination. Additionally, placebo controls and laboratory bottle blanks were also analysed at each time interval of interest to assess background concentrations. Also, to minimise the effect of background D5 concentrations, the 95% upper confidence limit of the mean was used for the average background concentration of D5 in calculations by Montemayor *et al.* (2013).

To minimise background levels of siloxanes in the study conducted by Bletsou *et al.* (2013), the vials were capped with aluminium foil. Hexane was injected into the GC-

MS prior to any experimental run until the background concentrations of siloxanes became stable. Hexane was injected after every 10 samples to assess background concentrations and whether carry-over had occurred between samples. Wang *et al.* (2013a,b) and Sanchís *et al.* (2013) also followed similar precautions to minimise the potential for contamination of samples.

Based on the observations of Varaprath *et al.* (2006), contamination has been seen to arise from vial caps, septa, GC columns, and the use of personal care products by laboratory staff. The initial investigations performed by the Sparham *et al.* (2008 and 2011) also showed that blank sample concentrations were lower when using a nitroterephthalic acid modified polyethylene glycol column instead of the siloxane-based stationary phase columns usually used by industry. Sparham *et al.* (2011), reported that a lesser degree of field blank contamination was measured when all preparations were prepared in a clear-air cabinet with the air previously filtered through a carbon containing filter, compared to direct preparation in the laboratory (10 - 42 ng/g compared to 37 – 114 ng/g for D5), due to measured D5 concentrations in the air being 10 – 100 fold lower in the clean-air cabinet than in the surrounding laboratory air. Therefore, the laboratory air was assessed as the most critical location for the contamination of samples with D5. Furthermore, to avoid evaporation and reduce contamination risk, a very short sample preparation method was followed (Kaj *et al.* 2005a and Wang *et al.* 2013a,b).

Horii and Kannan (2008) also tested the release of siloxanes from several types of inlet septum at various inlet temperatures, as this can introduce contamination. They found that the Restek BTO septum at an inlet temperature of 200 °C had the lowest release of siloxanes of the septums tested, and therefore was used for analyses of all samples. The authors also state that the release of organosiloxanes from a conditioned low-bleed column is minor in comparison to release from the septa, as the amount of cVMS introduced from one inlet septum particle into the sample extract can equate to almost half the total amount of silicones present in the entire stationary-phase.

Horii and Kannan (2008) also analysed a quality control standard mixture of organosiloxanes and *n*-hexane after every 5 samples run on the instrument to assess instrumental background, carry-over and stability. If a significant amount of a target compound was detected in the *n*-hexane, all of the samples in that batch were re-analysed.

The ASE method developed by Sparham *et al.* (2011) can be used to simultaneously extract LAB, which can be used as a control check of D5 contamination during sampling or the analytical procedures. This is because sewage-related samples containing D5 are also expected to contain LAB, so any sample containing D5 but not LAB may have been contaminated. This clearly is not relevant to PCP samples. Resins enclosed in heat-sealed nylon pouches and pre-cleaned by ASE in sampling

jars were also exposed during the sampling of sediments to assess any possible significant contamination via the atmosphere of the samples.

E5 Recommendations for siloxane analysis

The type of extraction method performed is dependent on the media for extraction. Headspace (as per Sparham *et al.*, 2008), membrane assisted solvent (as used by Wang *et al.*, 2013a) and LLE (as per Bletsou *et al.*, 2013)) extraction techniques are typically used for the extraction of siloxanes from natural waters. For the extraction of sediments and biological matrices ASE and LLE methods are routinely used (e.g. see Sparham *et al.* (2011) and Bletsou *et al.* (2013), respectively).

For the analysis of extracted samples, GC/MS techniques are most frequently used (e.g. Sparham *et al.* (2008) and Wang *et al.* (2013a)), with LoDs typically in the range of 0.00003 – 0.0062 µg/L in water and 0.002 – 0.005 µg/kg dw in sludge or sediment. Techniques have also been developed using other analysers coupled with GC including QqQ (Sanchís *et al.*, 2013). From the reviewed studies, the LLE and GC/MS analysis method performed by Bletsou *et al.* (2013) produced the lowest LoQs and LoDs for the analysis of D4, D5 and D6, so it is recommended that these methods are used to assess the environmental levels of cVMS. The head-space method of Sparham *et al.* (2008) would also be acceptable .

Numerous potential contamination issues have been identified for the analysis of siloxanes, due to the ubiquitous nature of siloxanes in the natural environment. Siloxane contamination has been shown to arise from vial caps, septa, GC columns, use of PCPs containing siloxanes by laboratory staff and D5 contamination in laboratory air. A variety of measures have been implemented in the published studies to minimise the potential for contamination including:

- abstaining from the use of siloxane containing PCPs;
- use of a very short sample preparation method;
- use of foil-lined caps to minimise losses and to reduce potential for cross-contamination;
- use of a non-siloxane based stationary phase column in the GC;
- running blank hexane injections until background concentrations become stable, this includes when drift of contamination in an analysis sequence is observed;
- preparation of samples in clean-air cabinets.

The use of the ASE method of Sparham *et al.* (2008), also allows LABs to be simultaneously extracted with D5, which can be used as an indicator of sample contamination from sampling or analytical procedures.

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Annex G Stakeholder Consultation

Member State Committee Call for Evidence

A call for evidence was advertised on the ECHA website from 15 October 2014 until 29 November 2014 on the persistence and bioaccumulation properties of D4 and D5.
The background notes for the calls for evidence gives more information:
http://echa.europa.eu/addressing-chemicals-of-concern/restriction/previous-calls-for-comments-and-evidence/-/substance-rev/2276/term
http://echa.europa.eu/addressing-chemicals-of-concern/restriction/previous-calls-for-comments-and-evidence/-/substance-rev/2275/term

Consultation with the affected industry

Extensive consultation with the REACH Registrants of D4 and D5 and the cosmetics industry in the UK and EU was carried out for a national risk assessment (EA, 2009a&b) and a follow-up risk management options analysis project, which was completed in November 2013. Meetings were held with the Registrants and representatives of the UK and EU trade associations for PCPs on several occasions for these two pieces of work.
The information requested from the industry groups covered the following topics:

- Uses and related tonnages.

- Releases and exposure in the EU.

- Technical and economic feasibility and market availability of alternatives.

- Reformulation practicalities and costs for affected products

Both groups of companies provided a large amount of information, some of which was specifically generated from member surveys (covering information on use volumes, breakdown of uses, alternatives and reformulation). The Registrants provided full socio-economic analyses for their main uses (although these focussed on polymer applications). The information was used in several sections of the restriction report, including uses of D4 and D5, information on alternatives and cost calculations.
Further targeted consultation with Registrants and Cosmetics Europe was carried out during 2014 as the restriction dossier was being prepared, to clarify specific details from the earlier submissions, and provide the stakeholders with an opportunity to comment on the accuracy of the draft report. Producers and users of silicone anti-foam polymers were also contacted in 2014 to gather additional information to refine the exposure assessment for this application.

Consultation with non-EU authorities

Environment Canada provided further information on their national regulations related to D4.