Emission control strategies for short-chain chloroparaffins in two semi-hypothetical case cities

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Abstract

The short-chain chloroparaffins (SCCP), (C_{10-13} chloroalkanes) are identified in the European Water Framework Directive, as priority hazardous substances. Within the ScorePP project, the aim is to develop emission control strategies that can be employed to reduce emissions from urban areas into receiving waters. Six different scenarios for mitigating SCCP emissions in two different semi-hypothetical case cities representing eastern inland and northern coastal conditions have been evaluated. The analysis, associated with scenario uncertainty, indicates that the EU legislation, Best Available Technologies (BAT) and stormwater/CSO management were the most favorable in reducing emissions into the environment.

Introduction

The short-chain chloroparaffins (SCCP, CAS registry number 85535-84-8) have been identified as a priority hazardous substance by the European Union [1] and as such have been targeted to be phased-out [2] of discharges to surface waters. The SCCP group consists of an anthropogenic mixture of C_{10-13} chloroalkanes with varying chlorine content which are used as plasticizers, flame retardants and lubricants in various articles such as metal-working fluids; textiles and rubbers; paints, coating and sealants/adhesives; as well as in the leather and PVC industries [3].

Within the EU funded project "Source Control Options for Reducing Emissions of Priority Pollutants" (ScorePP), an important aim has been to develop comprehensive and appropriate emission control strategies (ECSs) that relevant stakeholders (such as governments, water utilities and industries) can employ to reduce emissions from urban areas into the receiving water environment. The ECSs are based on a “near to the source” approach limiting releases at the sources and “end-of-pipe treatment” to attenuate already released substances. This dual approach is based on findings within the ScorePP project revealing that all substances can neither be mitigated at the source [4] nor removed with conventional treatment to a sufficient extent [5]. The aim of the presented work was to evaluate the efficiencies of different ECSs for SCCP in two semi-hypothetical case city archetypes (SHCCA).

Approach

The semi-hypothetical case city archetypes

Working with selected case cities may hamper or bias the outcome of the study (e.g. due to the lack of key data, differing climatic or socio-economic conditions), hence the concept of SHCCA was developed, virtual cities which contain both generic and specific information to enhance robustness diversity, and facilitate completeness [6].

Table 1. Business-as-usual city indicators and characteristics

City indicators	EI	NC
Population (mio.)	1.2	0.51
Population growth (5 y; %)	2	0.5
City area (km^2)	500	450
Precipitation (mm/y)	530	650
Receiving water flow (m^3/s)	700	50
Industries		
-heavily polluting	70	30
-moderately polluting	279	119
Wastewater		
-treatment type	Secondary	Secondary
-dwellings connected (%)	90	99
-volume to overflows (%)	18	10
Stormwater		
-in combined sewer (%)	50	90
-in separate sewer (%)	50	10
--stormwater flow to BMPs (%)	20	20
--surface area for BMPs (m^2)	2500	721

Two SHCCA have been defined and are identified (in Table 1) as an Eastern European Inland (EI) city and a Northern European Coastal (NC) city. EI has a growing economy, an increasing population, many heavy industries and is situated by a large river. NC is a city with a consumer-oriented industry and is located on the coast by a brackish water body and at the mouth of a medium sized river.

Emission Control Strategies

Within the ScorePP project, six ECSs (Table 2) have been developed and used to evaluate a number of different priority substances. Since different substances have different properties and source patterns, different source control measures and different treatment processes can be the most feasible and appropriate for them. Therefore, specific ECS scenarios have been developed for each substance defining which source control and treatment options have been included. ECS1 is a business-as-usual strategy, i.e. the future scenario will not involve any deliberate changes, whereas ECS2 assumes that all relevant existing EU directives will be fully implemented. ECS3-6 build on ECS2 with the addition of voluntary options (ECS3), industrial onsite treatment by Best Available Technologies (BAT) (ECS4), stormwater and combined sewer overflow (CSO) management (ECS5) and advanced wastewater treatment plant (WWTP) (ECS6) (Table 2).

The ECSs are effective on different levels in the urban catchment: pre-application (source control e.g. substitution, legislation, and voluntary initiatives); pre-release (treatment before emissions to the environment, e.g. WWTP and CSO treatment); and post-release (attenuation after release into the environment such as stormwater Best Management Practices (BMPs) and dredging of contaminated sediments) (Figure 1). This means that various ECSs address the relevant actions of households, municipalities, governments and industries. For example ECS3, involves the introduction of voluntary initiatives aimed at ceasing the use of or substituting for articles containing SCCP. ECS3 Education campaign can promote the use of eco-labeled articles to industries, municipalities and households. ESC5 stormwater BMPs can be used on household properties, industrial sites, or public open spaces.

Table 2. Definition of ECS1-6 for SCCP. Percentages indicate efficiency of release reduction or removal.

ECS number	Description
ECS1: Business-as-usual	Not all dwellings connected to the sewer system, no BAT, composition based on article Material Safety Datasheets

	(MSDS) (e.g. 4-20%), limited management of stormwater.
ECS2: Full implementation of relevant EU directives	Generic BAT applied to heavily polluting industries by adsorption [5, 7], efficiency 59%, 100% of dwellings connected to a WWTP, article composition based on legislation, e.g. Directive 2002/45/EC with leather working and leather fat (article content max 1%).
ECS3: Household and municipality participation by voluntary options	ECS2 implemented. Article composition voluntary changed for paint and putty to max 1%. Industrial initiative to substitute SCCP by 50%. Choice of eco-labeled products (rubber, textiles and sealants) reduces the release by 25%. Education campaigns for painters and paint removers reduce societal releases by 50% and collection and recycling of PVC decreases the related emission by 50%. Loosely based on [4]*
ECS4: Industrial treatment by BAT and beyond	ECS2 implemented. Generic BAT (adsorption) applied to both heavily and moderately polluting industries. Heavily polluting industries applies also advanced oxidation processes (AOP; efficiency 24% [8]).
ECS5: Stormwater treatment and Combined Sewer Overflow (CSO) volume reduction and treatment	ECS2 implemented. 75% of the stormwater is treated in the most feasible BMPs; infiltration (25%) and retention ponds (75%) [9]. The volume of CSOs is halved due to storage in tanks and the remaining CSOs are treated by adsorption [5] by coagulation/flocculation (59%)
ECS6: Advanced WWTP end-of-pipe processes	ECS2 implemented. WWTP treatment is enhanced by coagulation/flocculation in dual tanks by 93% [10], the effluent is polished by AOP (24% [7]) and the sludge is subjected to anaerobic digestion (dechlorination, 35% [11]).

*Assumed data in tiers of 25/50/75

Substance flow analysis

The release, flow and environmental emissions of SCCP in each SHCCA have been evaluated though a substance flow analysis (SFA) approach. SFA is "a tool for analyzing the societal metabolism of substances" [12], i.e. for evaluating how substances are used and disposed of. The SFAs have been based on data extracted from an Emission String database (ES-DB) based on a comprehensive literature search [13], additional data from the relevant EU risk assessment reports (EU-RAR) [3]. The ES data is in the form of release per unit with the units originating from the definition of the SHCCA. For example, the EU data were extrapolated according to city size (e.g. population) or industry activities (Standard nomenclature for economic activities, NACE codes). The releases into different compartments can be seen in Table 3 and originate from the ES-DB and EU RAR [3,13]. The releases were divided into discharges to surface waters (if applicable), to water indirect (i.e. stormwater or wastewater systems), to air and to urban surfaces (mainly urban soils).

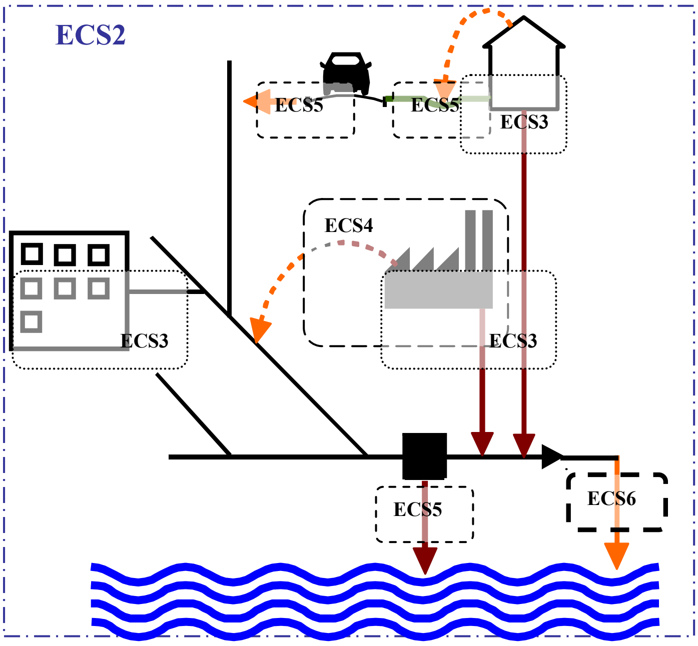

Fig. 1. Illustration of the location of the ECSs in the urban context, based on Eriksson et al. [6].

Table 3. Distribution of releases (%) based on literature data [3,13] or expert judgment (when independent information is not available).

ES-ID [13]	Description of ES	Storm-water	Waste water	Air	Urban surfac-es
10931	production of basic organic chemicals		97		3
10954	use in metal working -formulation		100		
10958	use in metal working -formulation		100		
10984	use in metal working and extreme pressure lubricating fluids		100		
10986	use in metal working and extreme pressure lubricating fluids		100		
10995	use in metal working and extreme pressure lubricating fluids		100		
10996	use as flame retardant in rubber formulations	25	75		
10997	leather formulations		99.5	0.5	

10999	leather formulations		100		
11001	Formulations		100		
11001	leather formulations		100		
	paint production		75	25	
	painted surfaces	25		75	
	Painting	50		50	
	putty in society	25	50	25	
	PVC in society	25	25	50	
	rubber in society	25	25	25	25
	sealants/adhesives	25	25	25	25

Results and discussion

City EI has several industrial sources for SCCP (SCCP production, leather and metal works) whereas city NC has only a few minor industrial sources (manufacturing of leather commodities) (Table 4). Articles containing SCCP such as textiles, putty, paint, rubber and plastic are considered for both cities as urban sources as they release SCCP during application, during use or when being discarded.

Loads and releases

For EI the minimum, maximum and average predicted loads are presented in Table 4 based on the ranges of article compositions (e.g. MSDS), the ranges in use applications and the ranges in releases. If no ranges have been found, the same value is presented in all three columns. For NC only the average values are shown as the ranges are relatively small compared to EI as fewer industrial sources are present.

Table 4. Total releases from industrial sources and emission from urban sources of SCCP in EI and NC (kg/year).

ES-ID	Description of ES	Min.	Average	Max.	Average
[13]		EI			NC
10931	production of basic organic chemicals	300	4650	9000	
10954	use in metal working -formulation	39	39	39	
10958	use in metal working -formulation	39	39	39	
10984	use in metal working and extreme pressure lubricating fluids				77
10986	use in metal working and extreme pressure lubricating fluids	12	582	1152	7.7
10995	use in metal working and extreme pressure lubricating fluids	12	582	1152	

10996	use as flame retardant in rubber formulations	1.3	1.3	1.3	
10997	leather formulations	5.3	9.3	13	
10999	leather formulations	5.3	9.3	13	2.4
11001	leather formulations	5.3	9.3	13	4.8
[3,14]	paint production	10	10	10	4.3
[3,14]	painted surfaces	97	97	97	43
[3,14]	painting	2.5	2.5	2.5	1.1
[3,14]	putty in society	8.7	8.7	8.7	26
[3,14]	PVC in society	2.2	2.2	2.2	22
[3,14]	rubber in society	23	23	23	2.1
[3,14]	sealant/adhesive				0.1
	Total	**562**	**6064**	**11566**	**189**

Distribution between urban and environmental compartments

The releases from the different sources have been divided into stormwater, wastewater, air and urban surface fractions (Table 3) but redistribution may occur following release. For example, in stormwater treated within a BMP, the SCCP could sorb to sediment or infiltrate, volatilize to air, be degraded (by removal of parent substance) or be emitted to surface water via the BMP effluent. In Figures 2 and 3 the emissions directly to surface water have been added to the load estimated in the effluents from BMPs, WWTPs and CSOs to provide the total load to surface water. Similarly, direct air emissions have been added to the loads volatilized from BMPs, WWTPs, and CSOs during treatment. As the SCCP substances have medium to high volatility [5] their distribution to air is substantial and for some scenarios, primarily ECS4 and 6, degradation can also be seen to make up a significant part of the mass balance. Industrial onsite treatments generate industrial waste either as sludge or solid waste.

In EI, the only two ECSs that substantially affected the total load being emitted were ECS2 and 4 as the legislation and industrial BAT affect the article composition and treatment onsite, and as the apparent reductions associated with ECS3, 5 and 6 are mainly due to the impact of ECS2. ECS5 was found to yield the lowest emission of SCCP to surface waters, and ECS4 and 6 were found to yield the highest total degradations.

In NC, ECS2 was again effective in reducing the total load being emitted. As very few industrial sources were present in NC, ECS3 consisted of the voluntary reduction in SCCP use by industries and education campaigns to mitigate SCCP during the article use or when the article was treated as waste, however, these appeared to have little impact on the emission of total SCCP loads. As for EI, the lowest loads to surface water in NC are associated with the use of ECS5 and the highest amount of degradation seen for ECS6. The least favorable ECS for both SHCCA was ECS1, i.e., business-as-usual and carrying on without taking any action to limit the release of SCCP.

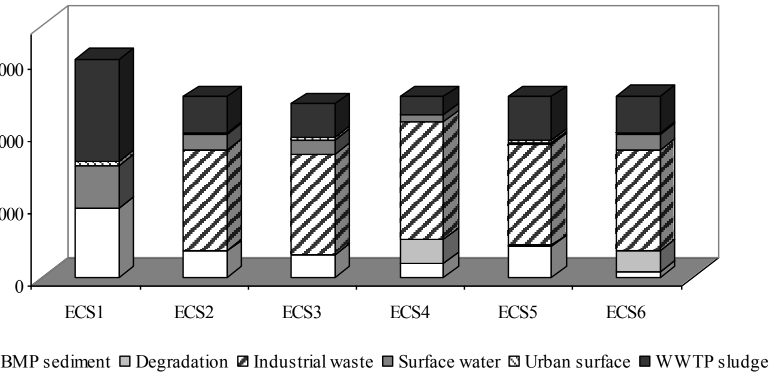

Fig. 2. Emissions of SCCP in EI (kg/year) using a SFA approach.

The total SCCP loads released for EI range from a minimum of 0.56 ton to a maximum of 11.6 tons (Table 4). For NC, the average value (0.189 tons) is considerably lower than the corresponding value predicted for EI (6.06 tons). The calculated loads are fairly good agreement with a SFA study performed for Stockholm (Sweden) [14]. The size of Stockholm (380 km^2) and the number of inhabitants (1.2 mio) are in the same order as EI and NC, and therefore the total load is in the same order of magnitude. The implementation of the SFA is of course associated with various kinds of uncertainty; statistical uncertainty as illustrated by the concentrations of SCCP varying from article to article as stated in the MSDS; scenario uncertainty associated with values allocated to the SHCCA, ECS and NACE codes. There will also be some level of ignorance as relevant NACE codes may have been overlooked. One flaw is that the release that occurs to air may be wrongly addressed and no data on distribution of SCCP in air/rain could be found.

In the SFA study for Stockholm an estimated annual use of 2.8-26 tons SCCP/year [14] was calculated and the associated annual releases to wastewater and air were calculated to be 3.24 and 0.25 tons. However, based on measurements of SCCP completed in these two compartments, actual loads of 0.036 and 0.75 tons/year were estimated. Hence there is a major difference between the outcome of the SFA and the results obtained from a monitoring campaign. Primarily, the release to air seems to be substantially underestimated and the release to wastewater overestimated. At the same time WWTP sludge were noted to accumulate SCCP (2300 ng/kg dry weight) [15] as also seen for the SHCCA.

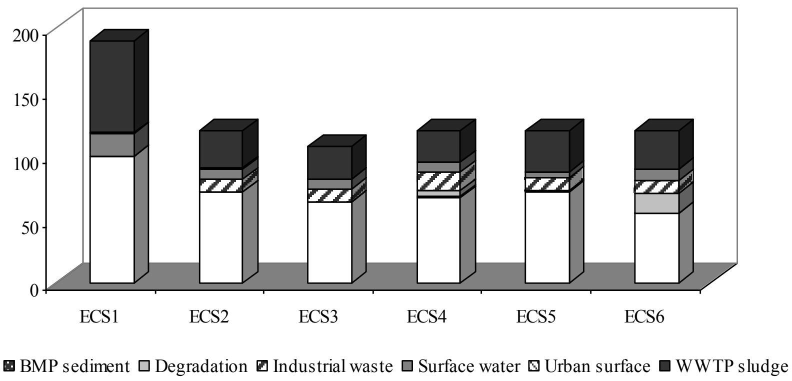

Fig. 3. Emissions of SCCP in NC (kg/year) using a SFA approach.

And in Stockholm as for NC there are no main industrial sources for SCCP. The recommendations in order to limit the releases of SCCP are green procurement in conjunction with information campaigns, efficient management of the SCCP containing articles in city (the stock) as well as implementation of BAT on smaller (modestly polluting) industries [14].

Conclusion

Implementation of the existing EU legislation involving article content limitations, wastewater treatment, and BAT should be encouraged. In EI, which is the more industrialized SHCCA, ECS4 with BAT and beyond was the most efficient strategy to reduce the overall emissions of SCCP but result in a industrial waste fraction, whereas ECS5 (stormwater and CSO treatment) was most successful for mitigating releases to surface waters. For NC, ECS2 produced the greatest reduction in the total SCCP load, ECS5 resulted in the lowest emissions to surface waters and ECS6 yielded the highest SCCP degradation. The total mass balance shows how the ECSs move the SCCP from one compartment to another. These results indicate that the selected ECS needs to be context specific and refer to the sources causing the releases and the pathways the substances take before being emitted into the environment.

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