MCCPs in Water-Miscible MWFs: Making The Case For Continued Use

John K. Howell, PhD
GHS Resources Inc.
http://www.ghsresources.com

"The times, they are a changin'…" - Bob Dylan

MCCPs in Water-Miscible MWFs: Making the Case - Outline

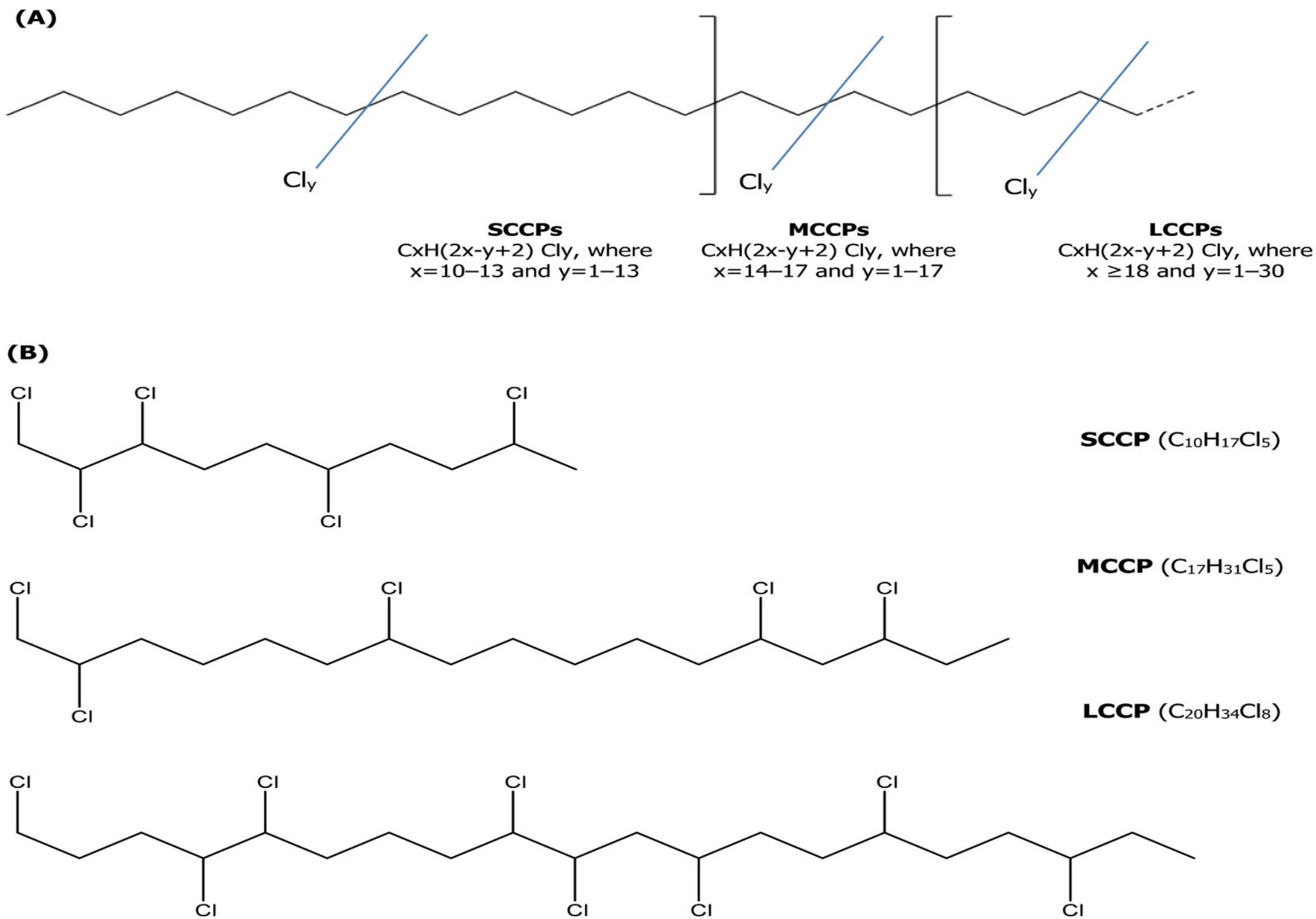
- Introduction
- MCCP PBT characteristics
- FOG effluent limits
- What else can we do in the plant?
- Call to action

Making the Case: Introduction

8. [By way of derogation, paragraph 1 shall not apply to substances if placed on the market for use as Extreme Pressure Additives in oil-based metalworking fluids - as defined in DIN 51385 -] [for 7 years after into force.

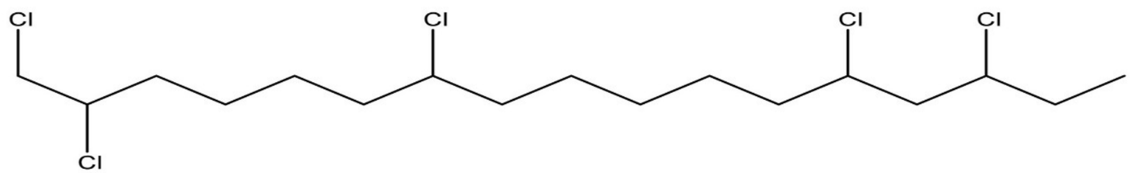
   By way of derogation, the concentration limit set under paragraph 1 shall not apply to mixtures placed on the market as oil-based metal working fluids referred to in paragraph 8 - [for 7 years after the EIF].

Making the Case: Introduction



Making the Case: Introduction

- With MCCP, do chlorination levels make a difference?



  - MCCP: $C_{17}H_{31}Cl_5$: 43% chlorine
  - MCCP: $C_{17}H_{30}Cl_6$: 47% chlorine
  - MCCP: $C_{17}H_{29}Cl_7$: 52% chlorine

GHS RESOURCES

MCCP PBT Characteristics

- Reviewed two articles:
  - Glüge, J. et al., *Environ Sci Technol.* 2018, 52, 6743-6760

    Environmental Risks of Medium-Chain Chlorinated Paraffins (MCCPs): A Review (acs.org)

  - ECHA MCCP registration dossier

    Registration Dossier - ECHA (europa.eu)

GHS RESOURCES

MCCP PBT Characteristics

Critical Review

Cite This: *Environ. Sci. Technol.* 2018, 52, 6743–6760

pubs.acs.org/est

Environmental Risks of Medium-Chain Chlorinated Paraffins (MCCPs): A Review

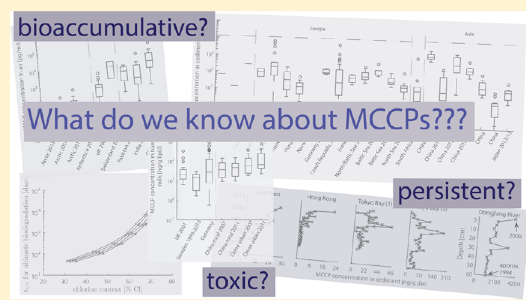
Juliane Glüge,*[†] Lena Schinkel,[‡] Konrad Hungerbühler,[†] Ronan Cariou,[§] and Christian Bogdal*[†]

[†]Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology, ETH Zurich, 8093 Zurich, Switzerland

[‡]Laboratory for Advanced Analytical Technologies, Empa Dübendorf, 8600 Dübendorf, Switzerland

[§]LABERCA, Oniris, INRA, Université Bretagne-Loire, 44307 Nantes, France

Supporting Information



ABSTRACT: Chlorinated paraffins are industrial chemicals that can be subdivided into short-chain (SCCP), medium-chain (MCCP), and long-chain (LCCP) chlorinated paraffins. The global production volumes of MCCPs are nowadays suspected to be much higher than those of S- and LCCPs, and the few available studies on the environmental occurrence of chlorinated paraffins report often higher MCCP concentrations than S- or LCCP concentrations in the environment. The present review focuses, therefore, on MCCPs specifically and provides a literature overview and a data analysis of the production volumes, PBT properties (persistence, bioaccumulation potential, and toxicity), and the worldwide measured concentrations of MCCP in environmental samples, biota, and humans. Furthermore, we include our own measurements of technical CP formulations from China, the major global producing country, to estimate the global production amounts of MCCPs. The key findings from this review are that (1) MCCPs are toxic to the aquatic environment, and the available data suggest that they are also persistent; (2) available time trends for MCCPs in soil, biota, and most of the sediment cores show increasing time trends over the last years to decades; and (3) MCCP concentrations in sediment close to local sources exceed toxicity thresholds (i.e., the PNEC). Our study shows that overall, MCCPs are of growing concern, and regulatory actions should be considered seriously.

GHS RESOURCES

MCCP PBT Characteristics

mixtures with 30–55% chlorine ranged between 9.6 h (for C_{17-24}-CPs with 35% chlorine) and 12.8 h (for C_{12-18}-CPs with 52% chlorine). However, these half-lives are only relevant for chemicals in the uppermost water layer. MCCPs in deeper water layers cannot be photochemically degraded due to a lack of UV radiation.

Biodegradation. Ready biodegradation tests in secondary activated sludge reported by the MCCP manufacturer in the EU showed no biodegradation for C_{14-17}-CPs with 63.2% chlorine and C_{15}–CPs with 51% chlorine. Only substances and mixtures with a chlorine content below 46% were readily biodegradable.[48] According to these data, MCCP congeners with more than 46% chlorine have to be considered as persistent, which is in line with the estimated data from EPI Suite (Table S6). Reliable studies on the biodegradation of MCCPs in water, soil, or sediment are missing.

Transformation Pathways and Products. Bergman et al.[49] reported that synthetic CPs and commercial CP products are transformed into a large number of aromatic hydrocarbons as well as numerous polychlorinated aromatic compounds at temperatures above 300 °C. They stated that dehydrohalogenation of the aliphatic structure, followed by ring formation, is most

therefore, questionable.

Conclusions. It remains so far unclear whether or not MCCPs are bioaccumulative and there is, therefore, an urgent need for reliable studies that investigate the bioaccumulation and biomagnification potential of these chemicals. Studies on the BMF and TMF should pay attention to compare concentrations in similar tissues. Also, care should be taken that animals are representative of the same food web.

ECHA[62] considered C_{14}–CPs with 40% to 56% Cl by weight and C_{15}–CPs with 51% Cl by weight as potentially bioaccumulative and proposed that the bioaccumulation potential of MCCPs is decreasing with increasing carbon chain length and chlorine content. However, if we consider the available measured data for SCCPs and MCCPs (section S2.2 of the Supporting Information), no clear trends are visible. ECHA requested aqueous and dietary exposure tests from the registrant manufacturers for C_{14}–CPs with 50–52% and 55–60% chlorine until September 2018,[63] but tests for MCCPs with other carbon chain lengths and chlorination degrees will most probably be necessary to conclude whether or not MCCPs (or single-congener groups of the MCCPs) should finally be considered as bioaccumulative.

GHS RESOURCES

MCCP PBT Characteristics

Alkanes, C14-17, chloro

EC number: 287-477-0 | CAS number: 85535-85-9

General information
Classification & Labelling & PBT assessment
Manufacture, use & exposure
Physical & Chemical properties
Environmental fate & pathways
Ecotoxicological information
Toxicological information
Analytical methods

- Endpoint summary
- Stability
- Biodegradation
  - Endpoint summary
  - Biodegradation in water: screening tests
  - Biodegradation in water and sediment: simulation tests
  - Biodegradation in soil
  - Mode of degradation in actual use
- Bioaccumulation
- Transport and distribution
- Environmental data
- Additional information on environmental fate and behaviour

Endpoint summary

Administrative data | Description of key information | Additional information

Administrative data

Description of key information

[Note: See CSR for complete text, several figures could not be uploaded into IUCLID]

The biodegradation of MCCP has been evaluated by numerous studies on both commercial products and specifically identified components of interest, in particular different chlorinated version of C_{14}(tetradecane) and C_{15}(pentadecane). The ability to test the biodegradation of MCCP is high dependent upon the testing system set up given the very low water solubility of MCCP and its high potential to sorb onto organic matter and vessel walls in the test system. Studies that have taken this into account and made MCCP more bioavailable have demonstrated that MCCP up to 50% chlorination by weight is readily biodegradable and that MCCP in the 50-60% chlorination (by wt.) is inherently biodegradable.

A series of GLP Closed Bottle Test (CBT), OECD 301D guideline, studies were conducted in 2009 and 2010 to evaluate the ready biodegradation of MCCP and its constituents (van Ginkel 2010 a,b,c,d,e). In these CBT studies 2 mg/L of the test material was incubated in the dark with either river water or secondary activated sludge derived from a plant treating predominantly domestic wastewater and oxygen consumption was measured by analyzing for dissolved oxygen content. These studies were conducted using procedures to improve the bioavailability of the test material to the inoculum, in accordance with the guideline. In the first study, a chlorinated tetradecane (C14) at 45% Cl (wt.) showed biodegradation on days 0, 7, 14, 21, 28 and 42 of 0, 3, 14, 32, 64, and 67%, respectively. Therefore, this test material is considered "readily biodegradable" (van Ginkel, 2010a). Subsequently, three MCCP commercial products (46.5, 51.7% and 63.2% Cl wt.) were assessed in the CBT (van Ginkel, 2010b,c,d). Lastly, a comparative study of the biodegradation rates of chlorinated paraffins by chlorination levels was conducted using tetradecane chlorinated across the range from approximately 40% to 60% Cl (wt.) (van Ginkel 2010e). Table 1 below summarizes the results of these studies.

Table 1: Percent Degradation by Test Material from van Ginkel 2010 CBT Studies

GHS RESOURCES

MCCP PBT Characteristics

Overall Bioaccumulation Assessment

Figure 1 is from Arnot 2014 (full report attached in the dossier) and illustrates the application of a bioaccumulation (B) assessment framework proposed in Burkhard et al. (2012). The measured B data for MCCP constituents are from various aquatic species (plankton, invertebrates, fish) from laboratory testing (BCF, BMF) and environmental monitoring (BMF, BAF, TMF). A total of 97 measured data points are compared against the B assessment criterion of 1 (red horizontal line) proposed by Burkhard et al. (2012). Data derived from field studies, and in particular TMF values, are considered to be the ultimate indicator of a compound's potential to bioaccumulate in the natural environment (Gobas 2009). A total of 93% of the data in Figure 1 are from environmental (field) studies and are thus considered highly relevant ("real world") B assessment data. Of these 97 measured data points, 7 (7.2%) met or exceeded the threshold criterion and 93 (92.8%) were lower than the threshold criterion. The median value (central tendency) is 0.27 (black dashed line). The SETAC POP/PBT expert workshop experts considered that a TMF >1 represented the most conclusive evidence of the bioaccumulative nature of a chemical (Gobas 2009). Figure 1 shows that all of the TMFs for the MCCP constituents < 1. The current weight of evidence indicates that MCCP constituents are not likely to biomagnify in fish and in aquatic food webs.

GHS RESOURCES

MCCP PBT Characteristics

Table 1: Percent Degradation by Test Material from van Ginkel 2010 CBT Studies

Test Material	C14, 45% Cl[a]	MCCP, 45.6% Cl[b]	MCCP, 51.7% Cl[d]	MCCP, 63.2% Cl[c]	C14, 41.4% Cl[e]	C14, 45.4% Cl[e]	C14, 50.0% Cl[e]	C14, 55.0% Cl[e]	C14, 60.2% Cl[e]
Sampling Day									
7	3	0	7	0	3	5	1	0	4
14	14	9	10	5	34	28	13	4	11
21	32	31	17	14	56	64	46	18	22
28	64	51	27	5	62	73	54	30	28
42	67	63	47	5	74	75	71	50	39
56					83	73	78	57	49
60			57	10					

a: van Ginkel 2010a

b: van Ginkel 2010b

c: van Ginkel 2010c

d: van Ginkel 2010d

e: van Ginkel 2010d

MCCP PBT Characteristics

Additional OECD guideline 301D CBT studies (van Ginkel 2014a,b and van Ginkel 2018a,b,c, d) were conducted on polychlorinated tetradecane (C14, 50, 55, 60% Cl by wt.) and pentadecane (C15, 51% Cl by wt.) as these test substances were identified by ECHA and the U.K. Environment Agency for additional evaluation as a part of an overall substance evaluation of MCCP. The 2014 studies on C15 (51% Cl wt.) found that the test material degraded up to 63% on day 60, indicating that the test material is inherently biodegradable and not persistence. The 2018 CBT studies included additional chemical analysis of the test materials beyond the standard biodegradation parameter, oxygen consumption in the case of the OECD 301D, and were conducted over an extended period of 120 days. The chemical analysis portion of this testing, conducted by Vrije Universitat (VU) Amsterdam, compared two different high-resolution methods of chemical analysis – GCxGC-ECD and APCI-TOFMS - to determine their abilities to measure and distinguish chloroalkane congener groups (e.g. $C_{14}H_{26}Cl_4$) within the test materials. Both methods performed well and were able to quantify C_{14}congener groups from $Cl_4$to Cl_{11}, which represent a range of approximately 35-68% chlorine by weight. This is the first time that such a congener group analysis has been applied to the biodegradation testing of MCCP. It should be noted that whilst the test materials are chlorinated to specific

MCCP PBT Characteristics

A recent analysis of the likely biochemical biodegradation pathways was conducted on a series of theoretical constituents in MCCP (Federle 2017). This assessment identified multiple biodegradation pathway options that may exist for a chlorinated paraffin (CP) molecule and that all of these pathway options involve conversion of the CP to a chlorinated fatty acid, shortening of the carbon chain and dechlorination. Each CP isomer will be degraded by a somewhat different pathway but overall these pathways lead to increasingly polar and less toxic metabolites. Pathway options decline as chlorination levels and occurrence of vicinal chlorine substitutions increase (Federle 2017 – attached in Section 13.2 of the dossier). One important conclusion from this work is that MCCP constituents cannot degrade into SCCP constituents as the chain-shortening reaction will involve oxidation of the molecule to a fatty acid.

GHS RESOURCES

MCCP PBT Characteristics

- CPIA has more data, but I conclude:
  - The lower the % chlorine, the more biodegradable MCCP is (is below 45% the sweet spot?)
  - Does the data already show that lower % chlorine MCCP is not bioaccumulative?

Oil & Grease Effluent Limits

- Oil & grease discharge limit under NPDES permits is 46 mg/l, as hexane extractables:
  - [Metal Products and Machinery Effluent Guidelines | US EPA]

Section 8. Additional Contaminants

The following levels of contaminants shall not be exceeded by any discharge of sewage, industrial wastes or other wastes to waters under the jurisdiction of the District.

Waste or Chemical	Concentration (mg/L)
Arsenic (total)	0.25
Barium (total)	2.0
Cadmium (total)	0.15
Chromium (total hexavalent)*	0.1
Chromium (total)	1.0
Copper (total)	0.5
Cyanide	0.10
Fats, oils and greases**	15.0
Fluoride (total)	15.0
Iron (total)	2.0
Lead (total)	0.2
Manganese (total)	1.0
Mercury (total)***	0.0005
Nickel (total)	1.0
Phenols	0.3
Silver	0.1
Zinc (total)	1.0
pH range (must be met at all times)	6.0 - 9.0

* Discharge of hexavalent chromium shall be subject to the averaging rule of Section 1c of this Appendix, modified as follows: monthly averages shall not exceed 0.1 mg/L; daily composites shall not exceed 0.3 mg/L; and grab samples shall not exceed 1.0 mg/L.

** Oil may be analytically separated into polar and nonpolar components. If such separation is done, neither of the components may exceed 15 mg/L (i.e., 15 mg/L polar materials and 15 mg/L nonpolar materials).

GHS RESOURCES

What Else Can We Do In The Plant?

- Isolate central systems that utilize MCCPs in their formulations?
- Apply additional equipment to remove oil & grease from washers?

GHS RESOURCES

Call to Action

- If we put our heads together, can we not:
  - Partner with CPIA and producers to better understand MCCP PTB data?
  - Focus on MCCPs in formulations that cause the fewest environmental issues?
  - Work with ILMA Member customers to demonstrate zero discharge of MCCPs?

GHS RESOURCES

Call to Action

- Anyone willing to help?

Call to Action

- Anyone willing to help?