Chlorinated Paraffins

CHLORINATED PARAFFINS INDUSTRY ASSOCIATION

6TH INTERNATIONAL METALWORKING FLUIDS CONFERENCE

9 JANUARY 2024

Introduction to CP Groups

North America

- Chlorinated Paraffins Industry Association
  - Members Dover Chemical, INOVYN
  - Andrew Jaques, Executive Director

Europe

- Chloroalkane Sector Group (CASG, under Cefic, Belgium)
  - Richy Mariner, CASG Manager
- MCCP and LCCP REACH Consortia (administratively under the CPIA umbrella)
  - Andrew Jaques, Consortium manager

Global

- International Chloroalkane Industry Association (ICAIA; ad hoc affiliation of CAPG, CPIA, Indian and Chinese producers)

What is a Chlorinated Paraffin (CP)?

1. Straight-chain hydrocarbon feedstock
   - n-alkane/paraffin (oil/wax) or 1-alkene (alpha olefin)
   - Chain length of feedstock determines CP chain length
2. Chlorine
   - Chlorination is a bulk reaction carried out to an 'average weight of chlorine' (e.g. 50% Cl wt.)
   - Reaction is non-specific so result is a highly complex substance (UVCB)
   - Final ration of carbon to chlorine typically ranges from 3:1 to 2:1, though it can approach 1:1 in solid CPs

CP Nomenclature

- In countries with formal chemical inventories, CPs have generally been defined by the carbon chain length of the starting hydrocarbon
  - Short = SCCP = $C_{10\text{-}13}$
  - Medium = MCCP = $C_{14\text{-}17}$
  - Long = LCCP = C_{18+}
  - Very Long =vLCCP = C_{21+}
- Attempts to further define CPs have created many more CAS numbers

Global CP Situation

- China is largest global producing (and consuming) nation
  - ~900 kT/Y in 2020 (which was lower than recent years)
  - Chinese products focus on chlorination level not carbon-chain length (e.g. 42, 45, 52, 70% Cl-wt.)
    - CP-52 is largest product (~90% in 2020)
- India second largest (recent estimates in the 500-700 kT/Y)
- Europe (including UK) ~ 50-100 kT/Y
- USA ~20-25 kT/Y
- Uses vary somewhat from region to region
  - Polymer (PVC, PU, etc.) largest
  - MWF not common outside of N.A.

CPIA Presentations

- Understanding the Environmental Science of Chlorinated Paraffin– A Scientific Review of Recent Environmental Testing, Environmental Field Work
  - Dr. Tom Federle, Consultant to CPIA
- Regulatory Landscape – Overview of Recent Changes in U.S, EU, Canada, and Globally
  - Andrew Jaques, CPIA Executive Director
- Industry Perspectives on Chlorinated Paraffin use in Metalworking Fluids
  - Mike Pearce, Dodge Oil

Understanding the Environmental Science of Chlorinated Paraffin– A Scientific Review of Recent Environmental Testing and Field Work

THOMAS W FEDERLE
ANDREW JAQUES

ILMA 6th MWF Conf
9 January
2024

Medium Chain Chlorinated Paraffins (MCCP)

- Chain lengths range from C_{14} – C_{17}
- Chlorine content by weight range from 40 – 65%
- Type Specimen – C_{14}- C_{17} 52% Cl (by weight)
- Complex substance
  - Number of chlorines per molecule range from 3 to 13 (average 6 – 7)
  - 11 Congeners (based on the number of chlorines/molecule)
  - 44 Molecular Formulas
  - 100s of Isomers (2 stable isomers of chlorine)
  - 1000s of Homologues

Classified as UVCBs = Unknown or variable composition, complex reaction products or biological materials

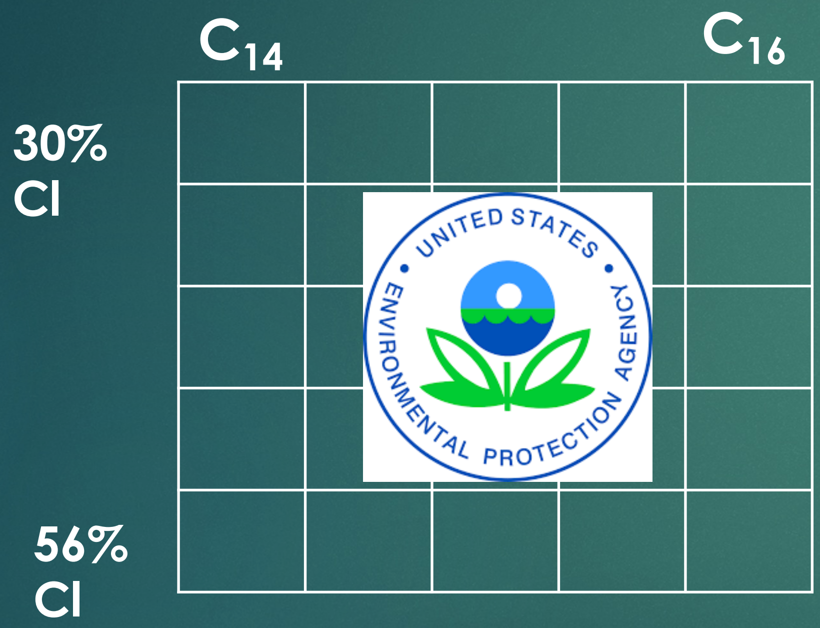
MCCP Physical Chemical Properties

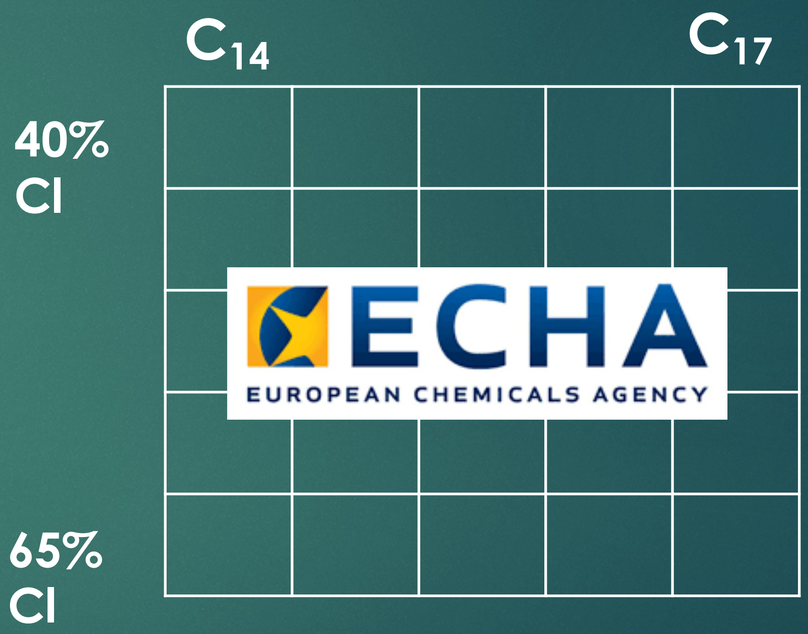
- Vapor Pressure 1.3 – 2.4 X 10^{-4} Pa at 20°C
- Octanol Water Coefficients (Log Kow or Log P)
  - C_{16} 35%Cl 7.2
  - C_{16} 69% Cl 7.4
  - C_{14-17} 45% Cl 5.5 - 8.2
  - C_{14-17} 52%Cl 5.47 - 8.0
  - C_{14} 50% Cl 6.6 ± 0.1 (6.0 -6.9) [Congener Analysis ACPI-TOF-HRMS]
- Water Solubility
  - C_{15} 51% Cl 5µg/L (parent) 27 µg/L (radioactivity)
  - C_{16} 52%Cl 10 µg/L
  - C_{14} 50% C 6.1 µg/L (<0.1 – 2.3 µg/L) [Congener Analysis ACPI-TOF-HRMS]

Difficult to Test Substance

OECD Guidance Document on Aquatic Toxicity Testing of Difficult Substances and Mixtures

Defining the Corners of the MCCP Box





Environmental Risk Assessment

Comparing Exposure to Potential for Adverse Effects

PEC = Predicted Environmental Concentration

PNEC = Predicted No Effect Concentration

Calculated From a Toxicity Term (NOEC, EC_{50})
Application Factor (Adjusts for Uncertainty)

$$\frac{PEC}{PNEC} \leq 1$$?????

PNEC & Effects Data

Low Level

QSAR

>1000

Acute Studies

Certainty & Cost

Application Factor

Chronic Studies

High Level

1-3

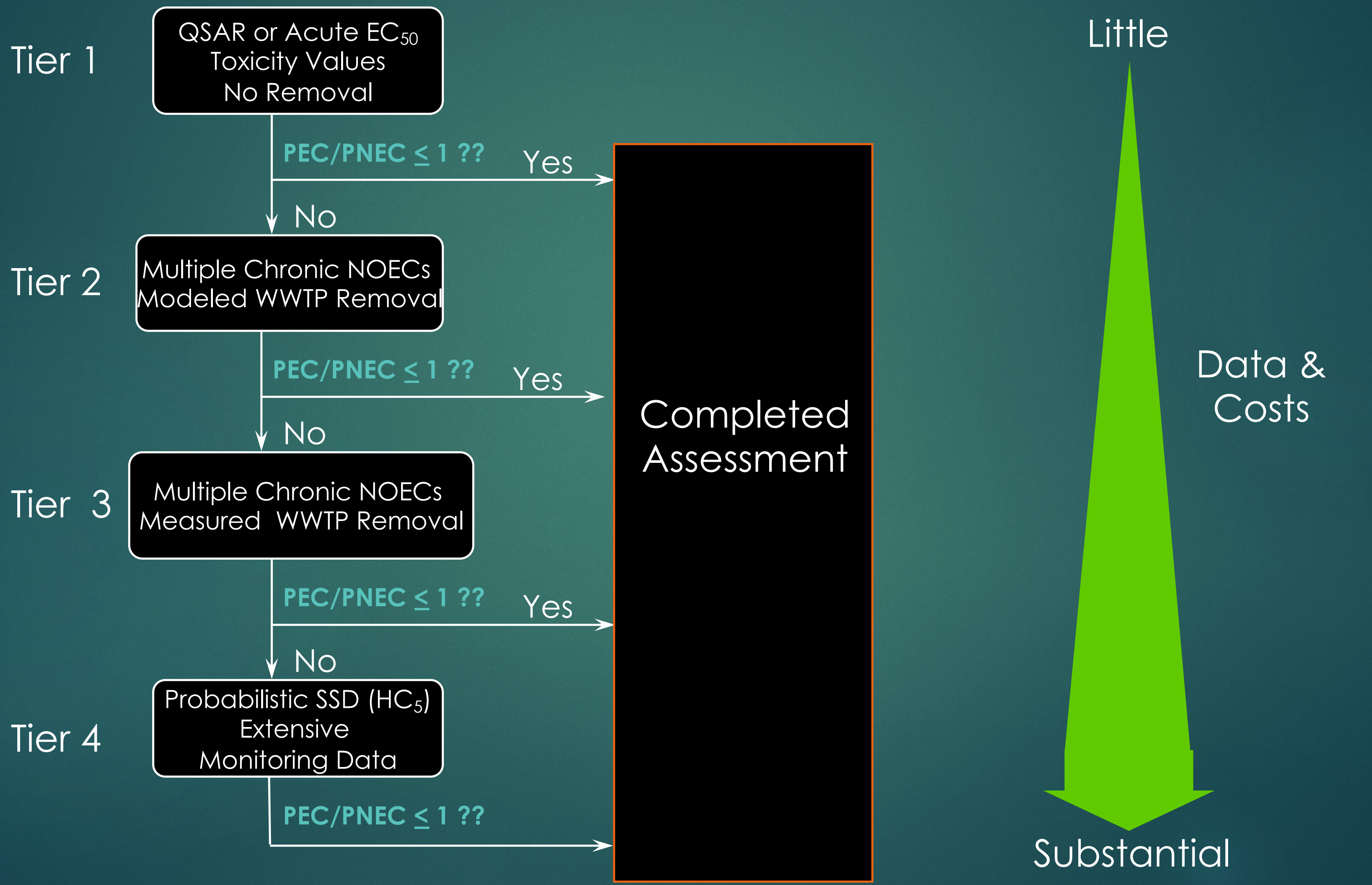
Species Sensitivity Distributions

(Mesocosm)

Iterative Assessment Process

Chemical Released in Wastewater

Assessing the Aquatic Environment in a WWTP Mixing Zone



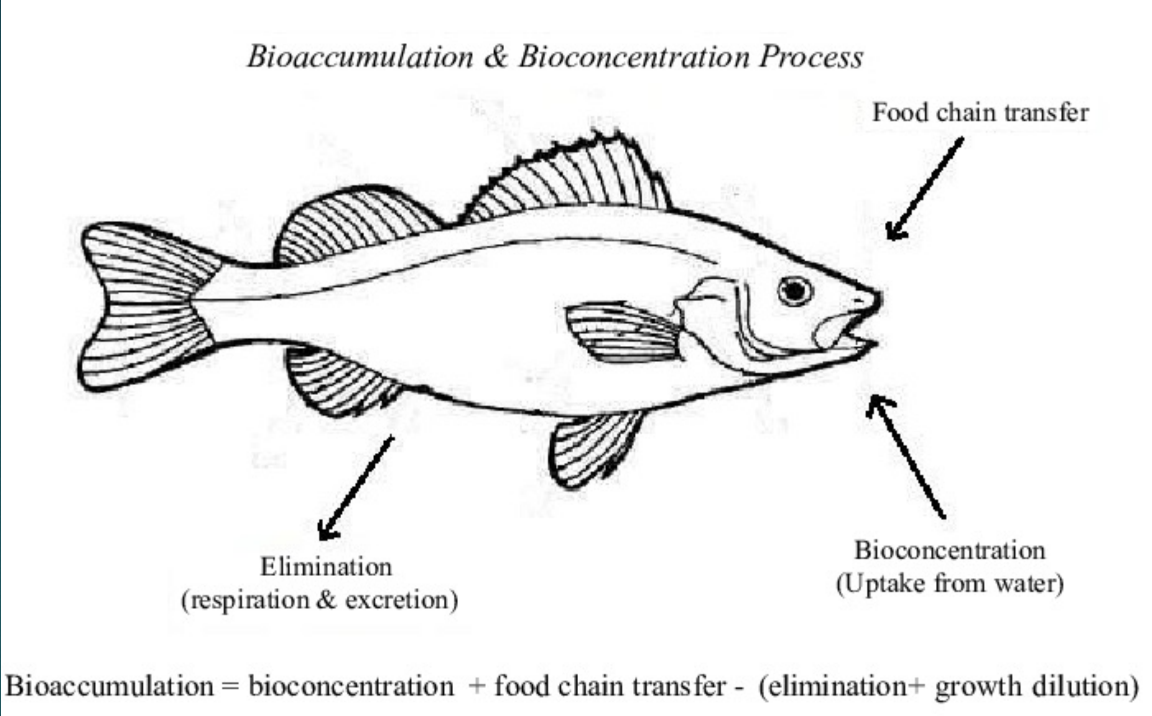
REACH - Beyond Risk Assessment – Classification
Troublesome Combination of Characteristics (PBT)

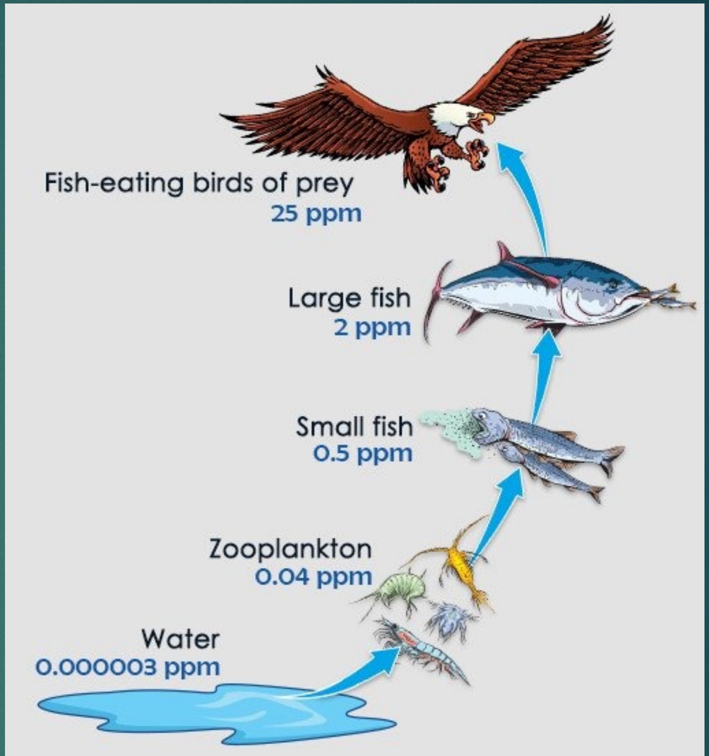
- Persistence (vP)
  - Absence of biodegradation or other degradation processes in water, sediments, soil or air, which results in potential long-range transport
  - Criteria – Greater than a Series of Half lives for water, sediment, soil etc.
- Bioaccumulation (vB)
  - Tendency to bioconcentrate from the water, bioaccumulate within organisms & biomagnify through food chains
    - B Criteria – BCF >2,000 (log P > 3.5) vB Criteria – BCF > 5,000 (log P > 5)
- Toxicity
  - Criteria - Aquatic Toxicity (NOEC <10 µg/L)
- vPvB equivalent to PBT
- If >0.1% of constituents are PBT (vPvB), the entire substance is classified.

MCCP Toxicity

- A substance fulfils the toxicity criterion (T) if the NOEC or EC_{10} < 10 µg/L for marine or freshwater organisms.
- Aquatic toxicity data exist for fish, invertebrates and algae,
- MCCP is a difficult to test substance in water, so most test concentrations were above the solubility limit.
- The most sensitive organism was Daphnia ($C_{14\text{-}17}$ 52% Cl)
  - Acute EC_{50} = 5.9 µg/L (immobilization)
  - Chronic NOEC = 10 µg/L (immobilization, **growth** & reproduction)
  - Disparity is explained by the presence of algae in the chronic test
- UK EA and ECHA concluded MCCPs are **T**

Bioaccumulation





$$BCF = \frac{Concentration\ in\ Organism}{Concentration\ in\ Water}$$

$$BMF = \frac{Concentration\ in\ Organism}{Concentration\ in\ Food}$$

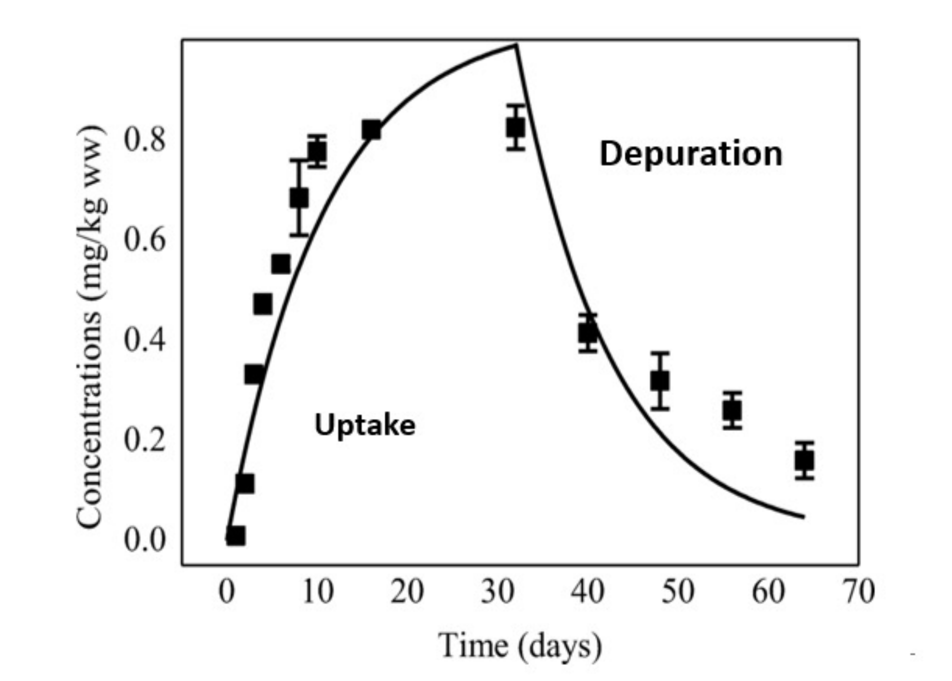
under equilibrium conditions

Biomagnification

TMF = Average BMF in a Food Chain

OECD Test No. 305: Bioaccumulation in Fish: Aqueous and Dietary Exposure

A substance fulfils the bioaccumulation criterion for B when the BCF > 2,000 and vB when BCF > 5,000



$$BCF = \frac{k_{uptake}}{k_{depuration}}$$

- Depuration rate is corrected for dilution related to the growth rate of the fish.
- Concentrations are normalized for fish lipid content.
- Feeding studies are used for insoluble or sparingly soluble substances (MCCP)
- No regulatory criteria exist for measured BMFs from such studies. Consequently, "Tentative BCFs" are calculated using
  - the experimentally determined depuration rate in the feeding study, and
  - up to 15 modelled uptake rates based upon fish weight, log P, and other parameters

OECD 305: Bioaccumulation Results

ECHA considered 2 studies reliable

- **BCF Study ^{14}C- C_{14} 45% Cl at 0.34 ug/L**
  - Rainbow Trout
  - 35-day uptake with 42-day depuration
  - Endpoint was total radioactivity
  - 34% was not extractable
  - Lipid corrected BCF = 3,230
  - Growth corrected BCFs 11,500 -14,600
- **Feeding Study - C_{14} 50% Cl at 15µg/mg food**
  - Rainbow trout
  - 14-day uptake with 56-day depuration
  - Hexachlorobenzene used as a positive control
  - Endpoint was total and individual congeners (ACPI-TOF-HRMS)
  - BMF: 0.47 MCCP vs 1.4 for HCB
  - Tentative BCFs based upon lipid normalized and growth corrected results were all >5,000

Chlorine content,% w/w	Carbon chain length				
	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}
<40			>5 000 L/kg (extrapolated from a dietary test) Fisk *et al.*, 1996		
40 - 45	*>5 000 L/kg (extrapolated from a dietary test) Fisk* et al., *1998b#*				
45 - 50					>5 000 L/kg (extrapolated from a dietary test) Fisk *et al.*, 2000
50 - 55		2 072 L/kg* Thompson *et al.*, 2000			
55 - 65	>5 000 L/kg (extrapolated from a dietary test) Fisk *et al.*, 2000				
>65			>5 000 L/kg (extrapolated from a dietary test) Fisk *et al.*, 1996		

Note: # May be unreliable. * Not lipid corrected.

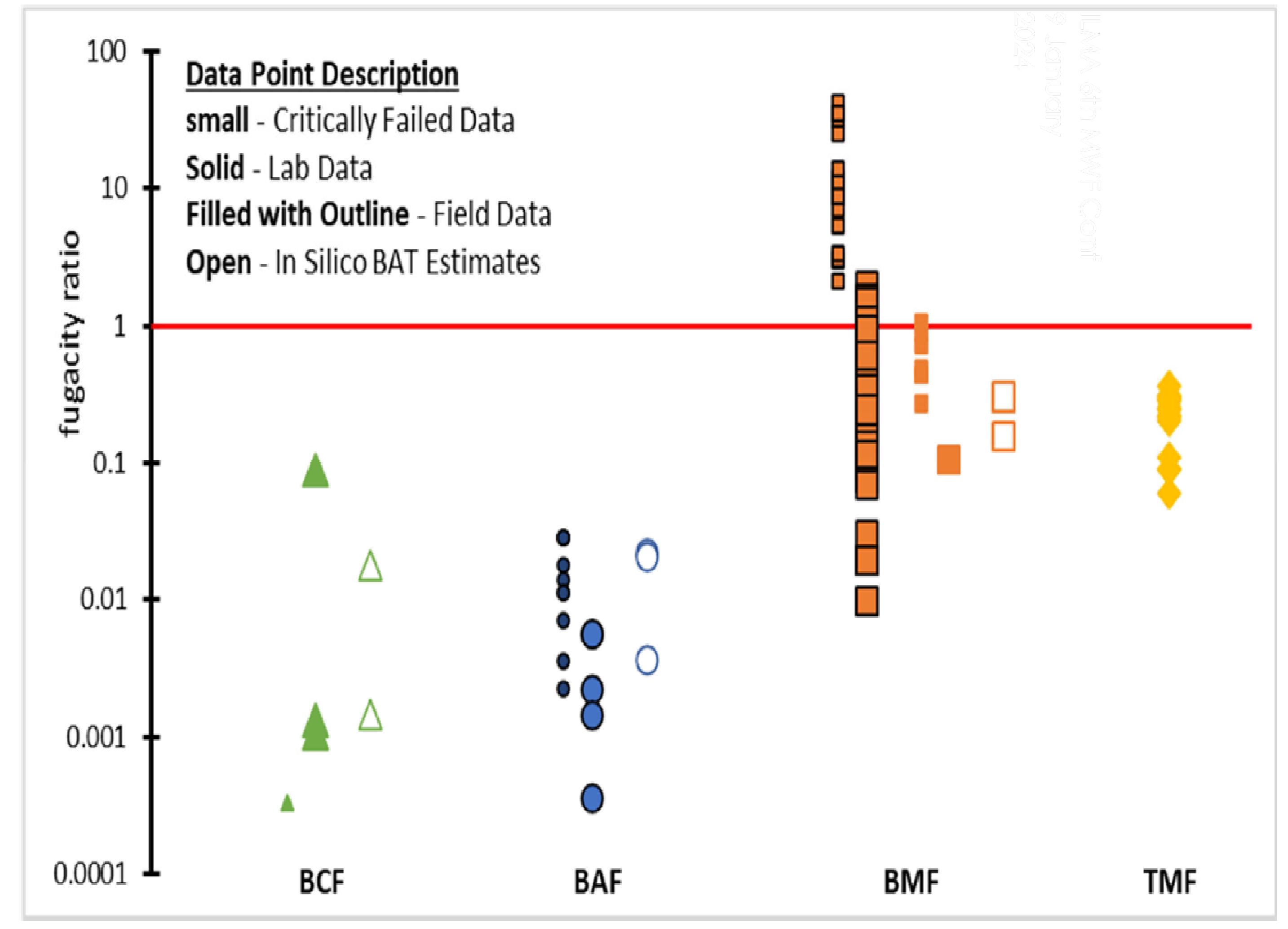
Bioaccumulation Assessment Tool (BAT)

- Weight of evidence (WoE) tool (v.2.0)
  - Lead developer John Arnot with support from CEFIC and ACC
  - Its approach is consistent with OECD and SETAC weight of evidence principles.
- Incorporates multiple lines of evidence (LOEs)
  - Phys-chem properties, biotransformation rates, lab BCFs and BMFs, BCFs, BAFs, BMFs and TMFs from the field along with QSAR estimates of these factors.
- Evaluates the reliability of each LOE
- A total of 113 measured LOEs were identified of which 77 were deemed reliable for B assessment.
- BAT's food web bioaccumulation models calculated an additional 7 LOEs for comparison to the measured data..
- With regard to measured LOEs considered reliable:
  - 82% indicated MCCPs are not bioaccumulative
  - 18% indicated MCCPs are very bioaccumulative (vB)

Bioaccumulation Assessment Tool (BAT)

- An additional WOE involves fugacity ratios, which address whether a chemical biomagnifies in the environment or not.

- Of the 77 reliable quality LOEs converted to fugacity ratios, 92% of these data were below the biomagnification threshold of 1 indicating it is unlikely that MCCPs biomagnify in fish and the aquatic environment.



Assimilation Efficiency (α) for MCCP

- In multiple feeding studies a values were unusually low (7 – 11%) suggesting that assimilation of MCCB is different from that of most unequivocally B substances.

- For example, in the C14 50% Cl study, its a was 6.8% compared to 82.5% for HCB.

Persistence - Biodegradation

A substance fulfils the persistence criterion (**P** or **vP**) in any of the following situations: T½ > **60** days in marine water; T½ > **40** (**60**)days in fresh- or estuarine water; T½ > **180** days in marine sediment; T½ > **120** (**180**) days in fresh- or estuarine sediment; T½ > **120** (**180**)days in soil

Factors that Limit the Biodegradation of Substances

- Inherent to the Molecular Structure
  - The needed biochemical reactions (enzymes) and pathways are not available in nature
    - Pathways can be postulated leading to extensive biodegradation of most homologues based on known enzymatic reactions assuming there are not multiple Cl substitution on the same carbons or on multiple adjacent carbons
- Inherent to the Molecule but Exacerbated by the Environment (Situational)
  - A molecule's low solubility and high sorptivity can render a chemical poorly bioavailable
- Other Situational Factors
  - Competent degraders are absent, occur at a low levels.
  - Environmental factors affect microbial activity (temperature, oxygen, nutrient limitation, etc.)

Ready Biodegradation Tests

Methods

- The OECD closed bottle test (301D) is considered the most stringent of all the ready tests due to the small size of its inoculum.
- Between 2009 & 2018, 25 OECD 301D closed bottle tests were conducted on 11 distinct MCCP substances (Kees vanGinkel at Akzo Nobel)
- Eight test were inoculated with river water and the rest with activated sludge.
- In all cases, the substance (2mg/L) was emulsified with a nonbiodegradable surfactant to enhance its bioavailability.
- Endpoint – Oxygen Uptake

Results

- There was a clear, inverse, relationship between chlorination level and the ability of the test substances to meet the criteria for ready biodegradability (28 days) and for providing proof for non-persistence when studies were prolonged into enhanced ready tests (60 days).
- In the case of tests with substances with chlorine content equal to or less than 45.6%, 6 of 8 tests met the criteria for ready biodegradability, and the substances that did not meet the criteria in one experiment did so in another.
- All experiments with substances with chlorine content equal to or less than 50% met the criteria needed to provide evidence that the substances were not persistent (>60% in 60 days)

SUMMARY OF 301D TEST RESULTS

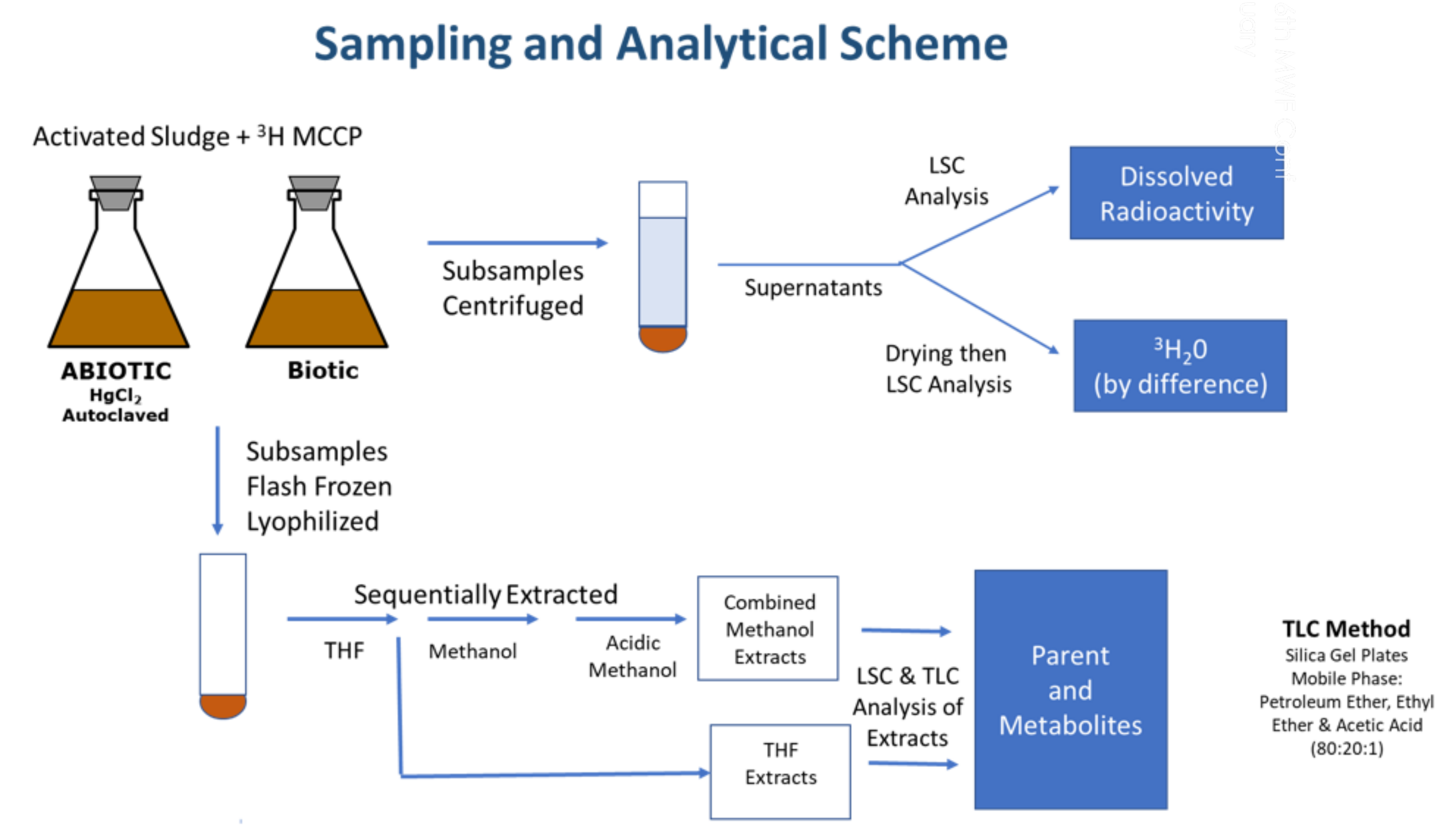
% Chlorine by wt	Chain Length	Inoculum	Biodegradation ≥ 60% in ≤ 28 days	Biodegradation ≥ 60% in ≤ 60 days	Max Observed % Biodegradation in ≤ 60 days
41.3	C14	Act. Sludge	Yes	Yes	74% (Day 56)
41.3	C14	Act. Sludge	Yes	Yes	83% (Day 56)
41.3	C14	River Water	Yes	Yes	65% (Day 56)
45.0	C14	Act. Sludge	Yes	Yes	67% (Day 42)
45.5	C14	Act. Sludge	No	Yes	74% (Day 56)
45.5	C14	Act. Sludge	Yes	Yes	73% (Day 56)
45.5	C14	River Water	No	Yes	70% (Day 56)
45.6	C14-17	Act. Sludge	Yes	Yes	63% (Day 42)
50.0	C14	Act. Sludge	No	Yes	63% (Day 56)
50.0	C14	Act. Sludge	No	Yes	78% (Day 56)
50.0	C14	Act. Sludge	No	Yes	61% (Day 60)
50.0	C14	River Water	No	Yes	63% (Day 56)
51.0	C15	Act. Sludge	No	Yes	63% (Day 60)
51.0	C15	Act. Sludge	No	No	40% (Day 60)
51.0	C15	River Water	No	No	57% (Day 60)
51.7	C14-17	Act. Sludge	No	No	57% (Day 60)
55.0	C14	Act. Sludge	No	No	58% (Day 84)
55.0	C14	Act. Sludge	No	No	57% (Day 56)
55.0	C14	Act. Sludge	No	No	15% (Day 60)
55.0	C14	River Water	No	No	39% (Day 56)
60.0	C14	Act. Sludge	No	No	13% (Day 42)
60.2	C14	Act. Sludge	No	No	40% (Day 56)
60.2	C14	Act. Sludge	No	No	49% (Day 56)
60.2	C14	River Water	No	No	4% (Day 56)
63.2	C14-17	Act. Sludge	No	No	10% (Day 60)

OECD 308 Aerobic Transformation in Aquatic Sediment Systems Test "The Persistence Maker"

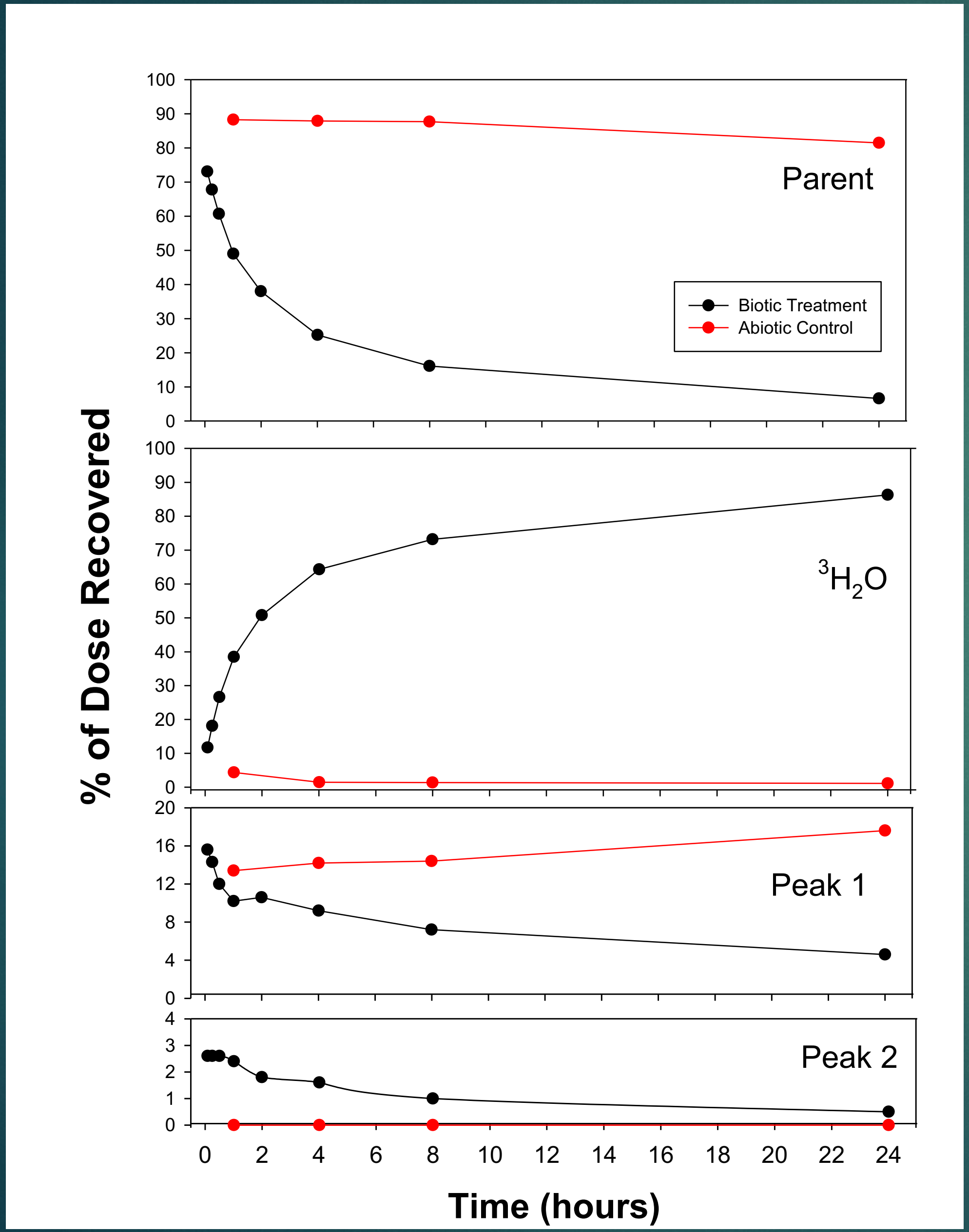
- C_{14} 50% Cl CP was tested at 5 µg/g sediment
- Test System : 3:1 ratio of sediment to water from two relatively "pristine" locations incubated at 12°C for up to 120 days.
- CP was loaded onto sand in THF (evaporated), and the dosed sand mixed into the sediment.
- Inactive samples (frozen) served as controls for analytical recovery.
- Periodically test systems were sacrificed and congeners analyzed using APCI-TOF-HRMS.
- Measured concentrations were highly variable at each time point and within each treatment.
- There was no systematic pattern of loss with time or significant differences between the active and inactive samples to indicate any evidence of biodegradation.

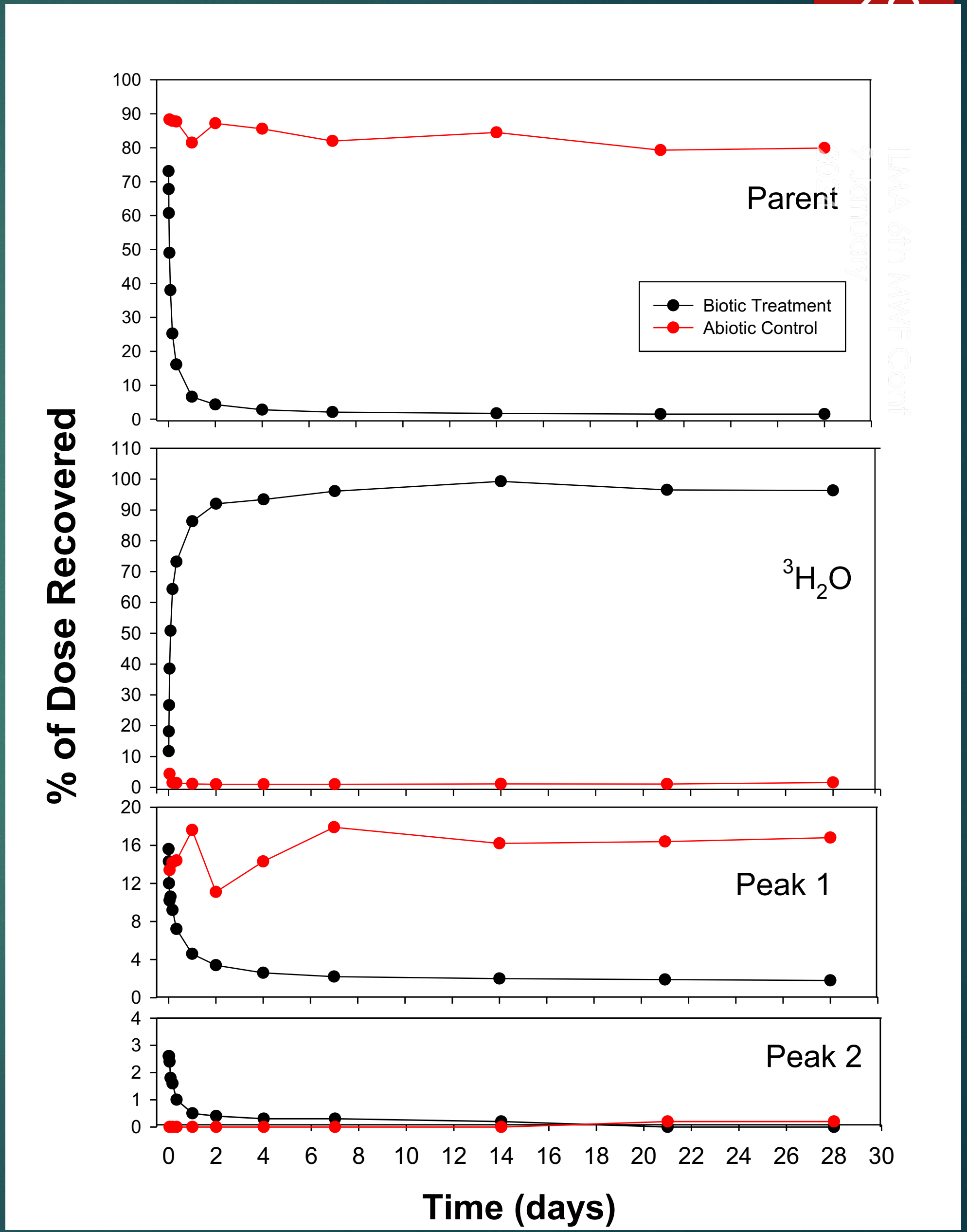
OECD 314B: Simulation Tests to Assess the Biodegradability of Chemicals Discharged in Wastewater - Activated Sludge

- Radiolabeled a commercial MCCP mixture ($C_{14\text{-}15}$ 52%Cl) with tritium
- Dosed at 50 µg/L in surfactant (325 µg/L) to activated sludge
- Pulse-Chase Experiment



Biodegradation Curves





Disposition of Radioactivity (% of Initial) at Key Time Points

Disposition of Radioactivity (% of Initial)	Abiotic Control			Biotic		
	1 hr	24 hrs	28 days	1 hr	24 hrs	28 days
Parent	88.3	81.5	79.0	49.0	6.6	1.5
Peak 1	13.4	10.2	17.6	10.2	4.6	1.8
Peak 2	0	0	0.2	2.4	0.5	0
Mineralized to ^3H_2O[a]	4.4	1.1	1.6	38.5	86.3	96.3
Extracted Residue	0.9	1.3	1.6	1.8	1.5	1.6
Total	107.0	101.9	101.5	101.9	99.5	100.4

Kinetic Parameters

$k_1 = 39.8\ day^{-1}$

$k_2 = 2.89\ day^{-1}$

g = 0.47

DT50 = 1.4 hrs

DT90 = 13.8 hrs

Conducted a follow-up experiment dosing the same level of ^{3}H-MCCP with unlabeled MCCP (10 mg/L) in activated sludge to demonstrate that the decline of parent MCCB based on tritium corresponded with a decrease in total MCCP determined by GC-ECD analysis.

Summary

- Evaluation of MCCP's environmental safety was superseded by a focus on determining its classification as a PBT.
- Due to its complexity as a UVCB and its hydrophobicity and low water solubility, making it a difficult to test substance, its performance in standard environmental tests is compromised and further complicated by analytical challenges.
- MCCP has been classified as T based on its adverse effects on Daphnia, even though these effects occurred above the solubility limit and likely were physical versus toxicological in nature.
- MCCP has been classified as vB based on BCF studies even though there is strong lines of evidence indicating it does not biomagnify and differs in behavior from truly vB substances such as hexachlorobenzene.
- MCCP has been classified as vP based upon a sediment test in which it was likely not bio-available, despite a series of ready tests and activated sludge simulation test showing evidence of its biodegradability at the molecular level, when bioavailable and not overly chlorinated.

What's New in the Field?

- A Google Scholar Search (12/11/2023) turned up 56 scientific publications related to MCCP related to the environment in 2023 alone.
- Source of Publications: 27 China, 21 EU, 4 Japan, 3 Canada, 1 Argentina, 0 USA
- Some good news
  - Removal efficiency of MCCP in Municipal WWTP - 97% (27% attributed to biodegradation)
  - Concentrations of CPs in endangered St. Lawrence Estuary belugas have declined
- Human exposure & risk, Emission patterns, Sampling and analytical techniques, Metabolism, Mechanism of toxicity & species sensitivity
- Matrices containing MCCPs

Dust - indoor & road (4)	Human Breast Milk (3)	Human serum or blood (5)
Soil (3)	Sediment (3)	Atmospheric particulates
Sewage & sludge	Air (2)	Estuary & marine systems(3)
Whales	Fish	Honeybee Products
T shirts and Socks	Recycled pulp	Consumer Products (2)
Food Packaging	Food contact Rubber	Tibetan Butter
Chicken Eggs	Nut-Nougat	Chocolate Spreads
Vegetable Oils	Baby Food	Toys

Regulatory Landscape – Overview of Recent Changes in U.S, EU, Canada, and Globally

ANDREW JAQUES, CPIA EXECUTIVE DIRECTOR

Regulatory Landscape

- North America
  - U.S. TSCA
  - Canadian Environmental Protection Act
- Europe
  - European Union REACH
  - U.K. REACH
- Global
  - Stockholm Convention
  - REACH-like regulations

U.S. Situation

- CPIA members are using new CAS numbers that have been added to the U.S. Chemical Inventory (aka TSCA Inventory)
  - See table on next slide
- These substances are considered "new chemicals" because they were added to the Inventory via the Pre-manufacture Notice (PMN) procedure for new chemicals
- Several legacy ("existing") CP substances are still on the Inventory and are occasionally used by importers. EPA had previously called these substances "illegal" (in a presentation by Maria Doa at the 5th MWF conference) but has not taken any new enforcement actions.
- All of the "new" chemicals are regulated either via consent orders (direct agreements between the manufacturer/importer and EPA) or via Significant New Use Rules (SNURs)
  - The CO/SNUR requirements vary by substance but all require recordkeeping and new testing.

New CP Substances on TSCA

CAS Number	Substance Name	PMN	SNUR (40 CFR) (Year)
Medium-Chain (MCCP) (C14-17)			
198840-65-2	Tetradecane, chloro derivs.	P–12– 283 P–14–683	721.11073 (2019)
1372804-76-6	Alkanes, C14-16, chloro	P–12–282 P–14–684	721.11072 (2019)
85535-85-9	Alkanes, C14-17, chloro	P–12–453	721.11076 (2019)
Long-Chain (LCCP) (C18+)			
2097144-48-2	Octadecane, chloro derivs.	P–12–284	721.11074 (2019)
106232-85-3	Alkanes, C18-20, chloro	P–12–433	721.11075 (2019)
2097144-45-9	Alkanes, C20-24, Chloro	P–12–281	721.11071 (2019)
2097144-43-7	Alkanes, C20-28, chloro	P–12–277	721.11068 (2019)
2097144-44-8	Slackwax (petroleum), Chloro	P–12–278	721.11069 (2019)
Very Long-Chain (vLCCP) (C21+)			
1417900-96-9	Alkanes, C21-34-branched and linear, chloro.	P–12–539	721.10673 (2016)
1401974-24-0	Alkanes, C22-30-branched and linear, chloro.	P–13–107	721.10674 (2016)
288260-42-4	Alkanes, C22-30, chloro	P–12–505	721.11077 (2019)
1402738-52-6	Alkanes, C24-28, chloro	P–13–109	721.10675 (2016)
2097144-46-0	Hexacosane, chloro derivs.	P–12–280	721.11070 (2019)
2097144-47-1	Octacosane, chloro derivs.	P–12–280	721.11070 (2019)

EPA MCCP Evaluation

- CPIA has concluded testing program on MCCP (per the CO/SNURs) and submitted all reports/data to EPA
  - No additional MCCP testing is planned at this time
- EPA (New Chemicals Office) has given no timeline for completing its review of MCCP
- EPA (International) is active on the Stockholm Convention evaluation of MCCP
  - Discussed at POPRC-19 meeting (October 9-13, 2023)
  - CPIA worked with EPA to propose exemptions for MCCP uses in MWFs for a range of applications including aerospace, automotive and defense;
- POPs outcome may impact EPA decision, though U.S. is not an official member of the Stockholm Convention

LCCP or vLCCP?

- During the PMN review period (2012-2017) EPA began using “LCCP” to refer to just C18-20 chloroalkanes and vLCCP to review to C21+ chloroalkanes.
  - There is no natural/obvious reasons for a brightline at C20/C21
  - In the U.S. C18-20 is not a common product, though several products (C20-24, C20-28) include C20
- vLCCP PMNs were approved at a time (2013) when EPA was still evaluating the MCCP and LCCP PMNs (products contain C18-20 constituents)
  - vLCCP PMNs contained a tiered testing program focused on chemical analysis and soil and sediment biodegradation and bioaccumulation
  - Requirements under the CO were suspended in 2017 pending the testing and evaluation of MCCP
- EU and UK have requested more testing on the LCCP/vLCCP range but U.S. is still awaiting MCCP decision before it takes further action

CEPA Reauthorisation

- Bill S-5 passed this summer in the Canadian Parliament
- Major features include:
  - Dividing CEPA Schedule 1 (CEPA toxic substances) into two parts with Part 1 slated for prohibition; C10-C20 chloroalkanes are listed in Part 1 of Schedule 1
  - Includes consideration of cumulative effects of chemicals
  - Create a new 'watch list' of substances deemed capable of becoming toxic
  - New confidential business information (CBI) provisions.
- Environment and Climate Change Canada (ECCC) ECCC indicates that it is still working through the CEPA changes and it will likely be a year or more until any new proposals come out
- C10-13 chloroalkanes have been prohibited since 2012, so no futher action is required on them
- ECCC indicates that it is open to considering exemptions in any future prohibition regulation of C14-20 chloroalkanes.
- ECCC has requested information on key use of C14-20 chloroalkanes; CPIA is interested in working with any impacted users/industries in Canada to seek exemptions/extensions.
- ECCC is conducting a CEPA Section 71 survey on all imports/uses of C14-20 chloroalkanes.

European Situation

EU Chemicals Strategy for Sustainability

- European Commission adopted Chemicals Strategy for Sustainability (CSS) in October 2020.
- Part of the European Green Deal
  - Zero pollution ambition
  - Protect citizens and the environment from harmful chemicals, and boost innovation by promoting the use of safer and more sustainable chemicals
  - Transform Europe into a sustainable and carbon neutral economy
  - Shifting towards chemicals and production technologies that require less energy
  - Green Deal needs the "right" chemistry.
- ECHA's own European Green Deal pledge, as an EU organisation and employer, includes its environment certification with the EU Eco-Management and Audit Scheme (EMAS) and to become climate neutral by 2030.

Commission's CSS Strategy

- Ban the most harmful chemicals in consumer products – allowing those chemicals only where their use is essential.
- Pay attention to the cocktail effect of chemicals when assessing chemical risks.
- Phase out per- and polyfluoroalkyl substances (PFAS) in the EU, unless their use is essential.
- Boost investment and innovative capacity for the production and use of chemicals that are safe and sustainable by design throughout their lifecycle.
- Promote the EU's supply and sustainability of critical chemicals.
- Establish a simpler "one substance, one assessment" process for assessing the risks and hazards of chemicals.
- Play a leading role globally by championing and promoting high chemical safety standards and not exporting chemicals banned in the EU.

ECHA's Roles for CSS

- Developing criteria for chemicals that are safe and sustainable by design.
- Assessing how to introduce mixture assessment factors in REACH.
- Establishing a "one substance, one assessment" process to coordinate hazard and risk assessment across chemicals legislation.
- Developing an indicator framework on chemicals as part of the Zero Pollution and 8th Environment Action Programme monitoring framework.
- Improving enforcement of chemicals legislation.
- Developing a strategic research and innovation agenda for chemicals.
- Developing EU-wide human and environmental biomonitoring in the context of the Partnership for the Assessment of Risk from Chemicals (PARC).
- Establishing an EU chemical early warning and action system.

CLP Revisions

CLP is “hazard” only

New classifications for:

- persistent, mobile and toxic (PMT) and very persistent and very mobile substances (vPvM)
- terrestrial organisms;
- immunotoxicity and developmental neurotoxicity;
- endocrine disrupters
- persistent, bioaccumulative and toxic (PBT) and very persistent, very bioaccumulative substances (vPvB).

REACH Updates

- ECHA under tremendous pressure from NGOs, Commission, some member states to add more substances to the candidate (SVHC) list and to implement more restrictions, authorizations, classifications, etc.
- Increased focus on certain hazards/endpoints
  - PBT/vPvB (and now PMT); focus is making biodegradation testing a critical endpoint (just being P/vP seems to be enough to raise concerns within some circles)
  - Endocrine disruption (ED)
- Evaluation of traditional endpoints (CMR, STOT) is still very much alive
- ED will be a particular challenge as there remains little understanding on how to properly evaluate/test for ED properties; focusing exclusively on thyroid/thyroid hormone disruption gives a very incomplete picture

MCCP and REACH

- On July 8, 2021, "MCCP" added to the REACH Candidate list for substances of very high concern (SVHC)
  - Listing is unique; based on congener groups within the $C_{14\text{-}17}$ range
  - Industry did not agree on the basis for the listing given the total biodegradation and bioaccumulation database
- The SVHC listing was followed by a restriction proposal in July 2022
  - After a ~15 month review period the ECHA committees forwarded the final recommendation to the Commission in October 2023
  - Recommended text includes a 10 year phase-out period for use in MWFs
  - Commission expected to issue the regulations in 2024

LCCP Evaluation in EU and UK

- Both EU and UK have requested more testing on LCCP
- Focus of testing is on bioaccumulation as the MCCP persistence in sediment conclusion is expected to be carried over to LCCP
  - LCCP has lower water solubility and less bioavailability than MCCP so the bioaccumulation potential is expected to be lower
- Testing and evaluation is expected to take 4-5 years

Stockholm Convention (POPs)

- UK proposed to list C14-17 chlorinated paraffins (≥45% Cl wt.) on the POPs list in 2021
- Very controversial listing as some members (EU/CH) want a listing based on congener groups, which effectively just eliminates the chlorination level cut-off, and some members (China) don't support the listing.
- Proposal has been discussed now at 3 POPs Review Committee meeting (POPRC-17, -18, and -19). At POPRC-19 the session became so contentious that they had a members only session to completed the draft decision
  - Draft decision is to list MCCP, though with a large list of exemptions
- Select data/interpretations are driving the basis for the listing (similar to the REACH SVHC decision)

POPs Action with North American Agencies

- Given the changes to CEPA, Canada is likely to accept the nomination and adopt restrictions once it is finalized
  - ECCC is nonetheless still very interest in any information about MCCP use in Canada and what challenges might exist for substitution.
- U.S. never ratified the Stockholm Convention but does actively participate in the Convention as an observer
  - EPA will generally implement POPs decisions
- Canada (ECCC) and U.S. (EPA) are open to the idea of requesting exemptions for critical uses
  - Metalworking applications have come up the most by U.S. and Canadian downstream users.
  - Continue to press downstream users for data on uses that cannot be replaced.

Independent Lubricant Manufacturers Association

6TH INTERNATIONAL METALWORKING FLUIDS CONFERENCE

CHLORINATED PARAFFINS IN METALWORKING FLUIDS

AN INDUSTRY PERSPECTIVE

MIKE PEARCE

W.S. DODGE OIL CO.

JANUARY 9, 2024

AGENDA

- WHY USE THEM?
- WHAT ARE CRITICAL USES?
- CASE FOR USING CHLORINATED PARAFFIN
- CASE AGAINST USING CHLORINATED PARAFFIN
- BRIEF CASE STUDIES
- CONCLUSION

DODGE

CRITICAL USES

- Centerless grinding of aerospace bolts, especially titanium
- Wire drawing (mostly stainless steel)
- Deep drawing stainless steel
- Machining high-nickel alloys (Inconel, Waspalloy, numerous others) in a variety of applications
- Tapping high-nickel and titanium nuts
- Certain drilling and tapping applications in aluminum parts
- Numerous Others

WHY USE CHLORINATED PARAFFIN?

- Excellent EP (“Extreme Pressure”) additive for metalworking fluids (“MWF”)
- Often used in conjunction with sulfurized, phosphorus, and polar additives
- Cost effective, safe on most metals
- Clear, pleasant smelling
- Known performance, benefits, and handling characteristics
- For critical applications, <u>no practical substitute</u>

DODGE

THE CASE AGAINST CP

- Disposal
- Potential for Staining
- Weldability
- Cleanability
- Must be removed prior to heat treating
- "Alpha case" issue with titanium (sort of)
- Parts issues
  - Example: medical parts often require fluids to have zero sulfur and chlorine
- Regulatory challenges?
- Site-specific issues

GENERAL OVERALL INDUSTRY REACTION?

- Give me something that works!
- Don't give me anything that will cost significantly more!
- Don't disrupt my operations!
  - Hidden cost of testing and qualifying is enormous
- I will obey any regulations that apply to me, but you just said that for the moment we are OK, with no clear guidance on when CPs will really be a problem.

CASE STUDY-AEROSPACE FASTENER MANUFACTURER #1

- Located in So. California
- Makes both bolts and nuts
- 95% High-nickel alloys and titanium, 5% other
- Primary operations
  - Heading
  - Machining (automatic screw machines)
  - Deep Drawing
  - Centerless Grinding
  - Numerous "2nd Operations" (tapping, thread rolling, many others)
  - CNC Machining

DODGE

CASE STUDY-AEROSPACE FASTENER MANUFACTURER #1

- They had a major push to eliminate CP
  - Problem was their new parts washer, not regulations
- Successful:
  - Screw Machines (cost went up 15%)
  - Most tapping (cost up 40%)
  - Heading (cost up 100%, but better performance compared to CP)
  - CNC (no net cost difference)
- Unsuccessful:
  - Deep drawing stainless steel
  - Centerless grinding titanium, Inconel, A286
  - Waspalloy and some difficult Inconel tapping

CASE STUDY-AEROSPACE FASTENER MANUFACTURER #1

- ISSUES WITH CP REPLACEMENT IN CENTERLESS GRINDING OIL
  - Cost: 5,000 gallons in use to be replaced by fluid 80 to 100% more expensive (estimated $100 to $150K)
  - Replacement will likely need routine disposal and cleanout
  - Replacement may not be compatible with filtration
  - Current replacement technology is not operator friendly

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CASE STUDY-AEROSPACE FASTENER MANUFACTURER #1

- <u>DISPOSAL OF CP NOT A THREAT TO THE ENVIRONMENT</u>
- About 1,200 gal./month waste oil generated
  - Hauled as "hazardous" waste (you have to love California!)
  - Converted to marine diesel fuel
- About 5,000 gal. water per month to sewer
  - Average daily CP component estimated to be 4 to 8 OUNCES
- Stormwater testing confirms no significant ground oil discharge of any kind.
  - The parking lot is far worse than the plant

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CASE STUDY-AEROSPACE FASTENER MANUFACTURER #2

- Division of Fortune 50 company
- Company declared an initiative to eliminate all CP worldwide
- Platarg press
  - Transfer press (also called an "Eyelet" press
    - Classic part-Liptstick Tubes
  - Each station has independent stroke length
  - Uses the principle of "reverse draw"

CASE STUDY-AEROSPACE FASTENER MANUFACTURER #2

- Part was a severe deep draw
- A286 Stainless Steel
- Original oil contained 40% CP plus sulfur and fats
- New design, with a longer draw, had very short die life-200 pieces per sharpening
- Tried 5 different chlorine-free formulations
  - Best die life was 7 parts per sharpening
- Tested an oil with 70% CP plus sulfur and fats
- 7,000 parts per sharpening
- **Still using after 15 years**

DODGE

CONCLUSIONS

- Industry wants better performance, for less money
- Not terribly concerned with regulations off in the future
- No universal regulations at present against using CP
- Site-specific issues largely determine whether to use CP or not
- CP is not getting into the environment from modern manufacturers
- For the most part, they do not see CP as a problem

Questions?

DODGE

Concluding Thoughts/Next Steps

- ILMA/MWF industry has made very real positive impacts on the CP regulatory process
  - Regulators often focus on the theoretical hazards and not the benefits/societal impacts.
- Regulatory push from Europe is already threatening/impacting MCCP globally
  - EU overall assessment on MCCP not well balanced, though consideration for MWF use was a highlight
- More to come on LCCP/vLCCP as new test results are expected in the coming years
- Next steps for MWF industry?