Unexpected CFC-11 Emissions: the Ramifications for CTC

CTC: An update on its Production

How much is available?

David Sherry

Unexpected CFC-11 Emissions: the Ramifications for CTC

- CFC-11 is made by the reaction of AHF and CTC
- CFC-11 usually co-produces an amount of CFC-12*, maybe 15-30%
- When we can estimate the actual production of CFC-11, we will know how much CTC is required: at best we expect +/- 1.18 units of CTC
- CTC used to make CFC-11/12 is a feedstock use and therefore is non-controlled; there will be fugitive losses
- This presentation is about how CTC is made, and where it is to be found, in and what quantity

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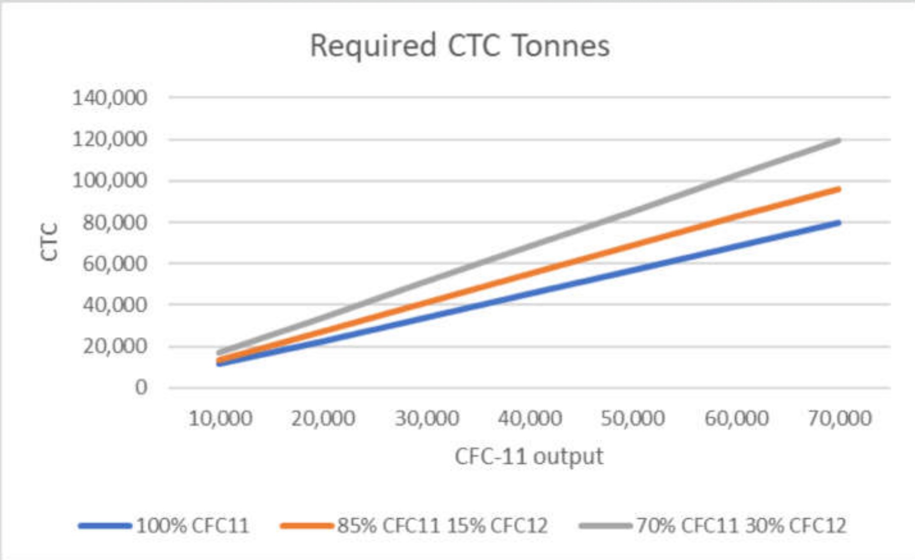
- The annual quantities of CFC-11/-12 being produced are likely to be between 10ktpa (100% CFC emitted) and 60kt (20% emitted, balance retained)
- We do not yet know how much CFC-12* has been co-produced. We assumed 0%, 15%, and 30%. We don't know how it was used, or if it was
- The range of CTC required lies between 12kt to 20kt in the low range, and 70-100,000kt in the worst case

**Important not just as an ODS but has a potent high-GWP, of 10,900*



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How is CTC made?

- CTC is made today by two processes: on chloromethanes (CMs) plants and on Perchloroethylene/CTC plants (PCE/CTC plants)
- On CM plants, CTC is an inevitable part of the chlorination process. Demand decline → minimising CTC production, usually seen as 5% of total CMs, but flexible to make more if required.
- PCE/CTC plants were initially built to feed demand to CFCs at maybe 5:95 ratio of PCE/CTC. Like CM plants, minimisation led to 85:15 PCE:CTC ratios. Investment of $10-20m necessary to upgrade to 100% PCE; many exited. Flexible back to 95% CTC if needed.

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CTC from "Higher" Chloromethanes

- There are 52 chloromethane producers globally, many having two or more locations.
- *Installed CM capacity is 4 million tons. 70% of the capacity is in Art. 5 countries*
- Chloromethanes are made by reacting methyl chloride with chlorine: co-production of methylene chloride, chloroform and CTC is inevitable
- *CTC has been minimised because supply >demand. Excepting China, a good global average is 5% on DCM/CFM. Some Chinese plants maintain that 3% is the norm on new equipment, although it seems low*
- Some producers have higher ratios and some produce CTC deliberately for intermediate. CM producers agree that up to 15% CTC on "highers" is possible without disruption.

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Why is CTC made?

Parties to the MP may only produce or consume CTC if it is for feedstock/process agent use, and small amounts of essential uses (lab and analytical)

- Fluorocarbons: new generation fluoro-propanes and butanes such as HFC236fa, HFC245fa and HFC365mfc require the reaction of CTC with an olefin (ethylene, perchloroethylene..). Some HFOs use a similar reaction, but there are (more expensive) alternatives based on HCFC-22 (India, China, Japan)
- DV Acid Chloride uses CTC as feedstock in its early stages of manufacture (India, China)
- "Crude" CTC from CM plants can be fed to PCE/CTC plants to make either PCE or feedstock-grade CTC (US, EU)
- Some CTC is dehydochlorinated back to CFM, DCM or methyl chloride, which can produce more chloromethanes or be diverted to silicone production, where it is vital to the production chain (China, Japan)
- In China, fluorocarbon-grade PCE is made by the reaction of CTC with methane and chlorine. Six such plants have been notified, two more coming

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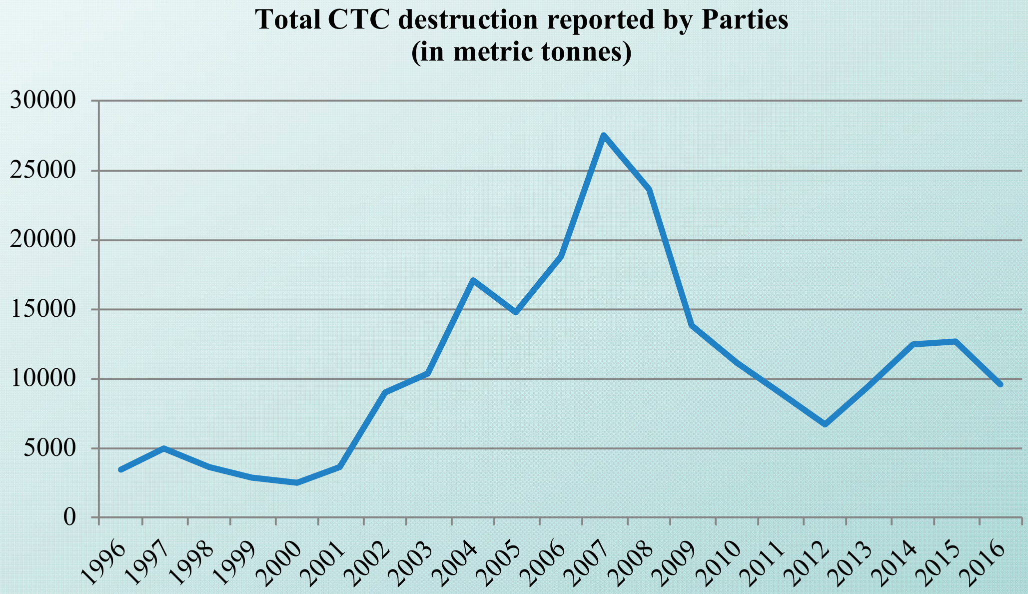
…..or failing this, must be destroyed, which is a cost



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CTC from Higher Chloromethanes

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One way to look at CTC from CMs is by capacity utilisation (2018 figures)

Global CTC Potential, ktpa minimum and maximum		
Capacity	At 5% CTC	At 15% CTC
4000	200	600
Actual	At 5% CTC	At 15% CTC
2700-2900	135-145	415-425

Global Capacity, CMs, 2018 (ktpa)		
Region	Capacity	Available CTC from CMs
Europe	<500	5-10
Russia	<100	?5
USA	<500	10
China	>2500	125-250
Japan	<250	5-10
India	<250	0
Other Asia	<100	(-10
TOTAL	4000	
Utilisation	70-75%	

These tables demonstrate that by today's look, some regions would have capacity to supply 10-20ktpa but few have enough capacity to cover the amount of CTC at the higher end of estimated CTC feedstock for the unaccounted CFC-11

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CTC from Higher Chloromethanes

Lets step back to 2013……

Global CTC Potential, ktpa minimum and maximum		
Capacity	At 5% CTC	At 15% CTC
3650	180	550
Actual	At 5% CTC	At 15% CTC
2700-2900	140	420

Global Capacity, CMs, 2013 (ktpa)		
Region	Capacity	Capacity to supply CTC from CMs
Europe	<800	30-705
Russia	<100	5
USA	<500	10-20
China	<1800	150-300
Japan	<250	5-10
India	<210	0
Other Asia	<100	5-10
TOTAL	3365060-370	

It is not clear from the total that CFM declined (phase-down emissive HCFC-22) whilst DCM increased (HFC-32). Some areas could have capacity for the low-end (10kt) of our CTC range, but few would have more than 20ktpa available

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CTC from PCE/CTC plants

- **High temperature reaction of C_1-C_3 chlorinated waste streams (from VCM/EDC plants, from CH-PO plants, and incl "crude" CTC from CMs) with chlorine to make pure PCE and CTC streams.**
- ***Mainly made for CFC boom: bias to CTC, some PCE to CFC113, some to solvent. CTC was once >1 million tpa. First plants could work 10:90 PCE/CTC to 80:20 PCE/CTC***
- **Investment to 100% PCE cycle about $10m-$20m. Many Plants closed.**
- ***Global capacity for PCE/CTC is <360 ktpa (5 plants, USA/EU only). Deliberate production CTC ≥80kt and increasing. Spare capacity in Europe, none in USA. This is "made on Demand CTC". But is it likely……?***

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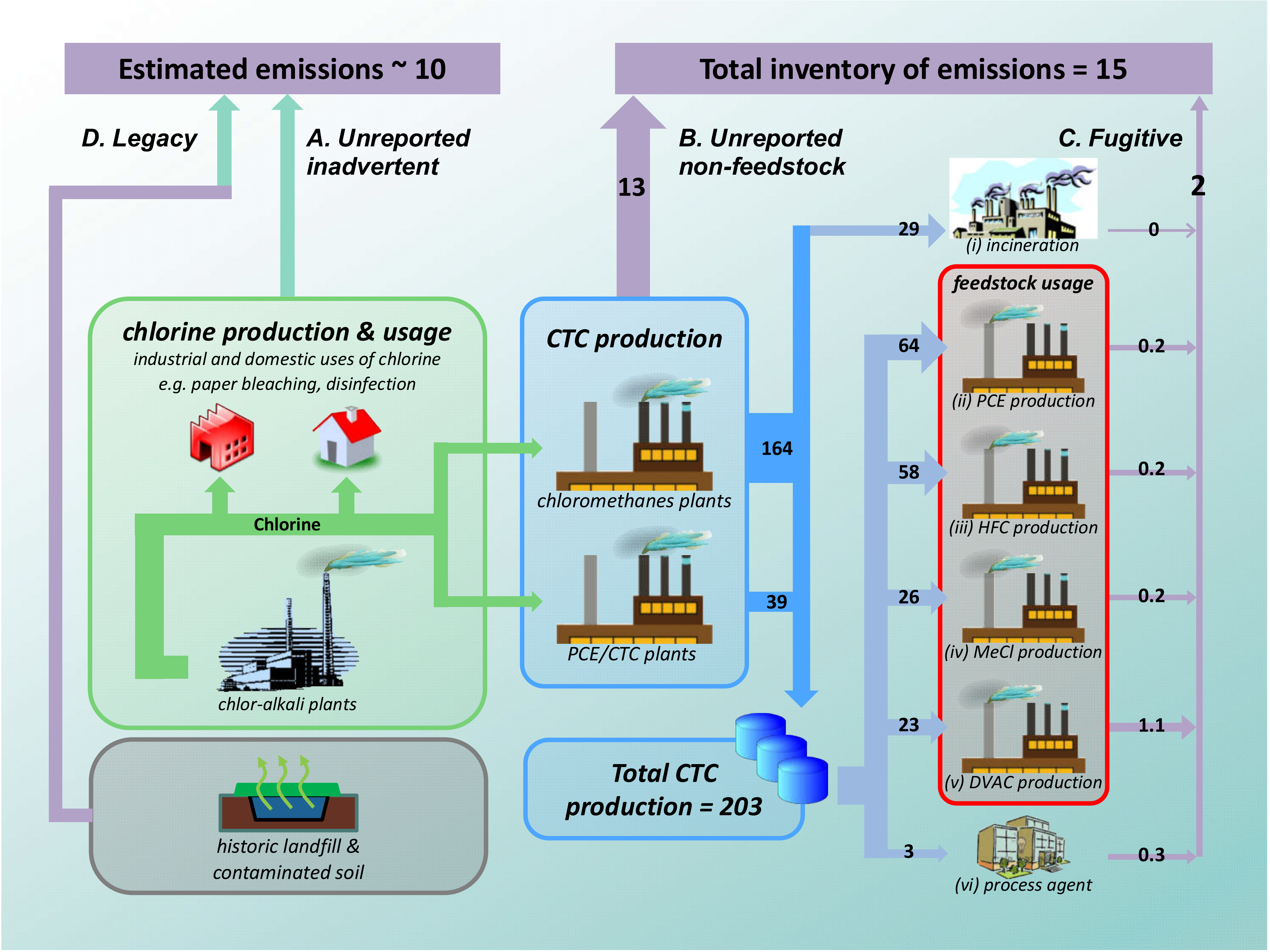
Summing it all up…

CTC from Chloromethanes

- **Inevitable, but can be minimised to 5%. Ground zero is 140kt**
- **More can be made by ratio management**
- **Some areas could produce enough for low-end need 12-20kt, few could deliver 40-100kt**

CTC from PCE/CTC plants

- **Can produce 0-100% CTC, CTC is made to demand**
- **Spare capacity to produce, after existing PCE and CTC commitments are met**



Estimated emissions ~ 10
Total inventory of emissions = 15
D. Legacy
A. Unreported inadvertent
13
B. Unreported non-feedstock
C. Fugitive
2
29
(i) incineration
0
feedstock usage
64
(ii) PCE production
0.2
58
(iii) HFC production
0.2
26
(iv) MeCl production
0.2
23
(v) DVAC production
1.1
3
(vi) process agent
0.3
chlorine production & usage
industrial and domestic uses of chlorine
e.g. paper bleaching, disinfection
Chlorine
chlor-alkali plants
CTC production
chloromethanes plants
164
PCE/CTC plants
39
Total CTC production = 203
historic landfill & contaminated soil

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Estimated CTC Consumption by application 2018

Region	Use in HFC/HFO	Use in PCE/CTC	CTC→PCE	Use in DVAC	Dechlorination to CFM,DCM and MeCl	Destruction or not-known	TOTAL
Europe	16.0	20.0	0	0	0	8.0	44.0
Russia	0	0	0	0	0	2.0	2.0
NAFTA	69.0	21.0	0	0	0	0	90.0
China	24.0	0	60.0	4.0	30.0	5.0	123.0
India	0	0	0	20.0	0	0	20.0
Japan	14.0	0	0	0	0	0	14.0
S Korea	0	0	0	0	0	3.0	3.0
TOTAL	**123**	**41**	**60**	**24**	**26**	**18.0**	**296**

Approx. 33% PCE/CTC, 67% CMs)

Thank you for your kind attention

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Kharasch reactions are vital to CTC intermediate use

- $CH_2=CH_2$ + CTC = $CH_2Cl-CH_2-CCl_3$ (HCC250fb: starter to HFO1234yf)
- $CH_2=CHCl$ + CTC = $CHCl_2-CH_2-CCl_3$ (HCC240fa: starter for HFC245fa, HFCO1233xd, HFO1234ze)
- $CH_2=CH-CN_3$ +CTC = tetrachlorobutyronitrile (starter to DVAC synthetic pyrethroid)
- And… CTC + $2Cl_2$ + CH_4 = $CCl_2=CCl_2$ (PCE + 4HCl)