Docket ID Number: EPA-HQ-OPPT-2016-0733

Comments to the U.S. Environmental Protection Agency (EPA) on the Scope of its Risk Evaluation for the TSCA Work Plan Chemical:

CARBON TETRACHLORIDE (CTC) CAS Reg. No. 56-23-5

Submitted on March 15, 2017 by

Safer Chemicals, Healthy Families
Environmental Health Strategy Center
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I. INTRODUCTION

The Toxic Substances Control Act (TSCA), as amended in June 2016, requires the U.S. Environmental Protection Agency (EPA) to determine whether existing chemical substances pose an unreasonable risk to human health and the environment, both generally and for vulnerable subpopulations, without consideration of costs or other non-risk factors. When unreasonable risk is found, EPA must enact restrictions on the production (including both domestic manufacture and import), processing, distribution in commerce, use and/or disposal of that chemical, and/or materials and articles that contain that chemical, that are sufficient to extinguish such unreasonable risk.

Congress directed EPA to launch the risk evaluation process expeditiously. Accordingly, in section 6(b)(2)(A) of TSCA, it directed EPA to assure that evaluations are initiated within six months of the law's enactment on 10 substances drawn from the 2014 TSCA Work Plan list. EPA designated these 10 substances on December 19, 2016, and is now developing scoping documents for its evaluations. EPA's initial risk evaluations will provide an early test of the effectiveness of new law. It is therefore critical that they reflect the best information available on hazard and exposure, are based on a comprehensive understanding of the chemicals' conditions of use, and employ sound, precautionary methodologies that fully capture the risks they pose to human health and the environment.

Toward those ultimate environmental public health objectives, these comments provide information and recommendations to EPA on the scope its risk evaluation for one of the first ten Work Plan chemicals subject to the new TSCA requirements. These comments are jointly submitted as a collaborative work product by three not-for-profit organizations:

Safer Chemicals, Healthy Families (SCHF), a coalition of 450 national, state and local organizations committed to ensuring the safety of chemicals used in our homes, workplaces and in the many products to which our families and children are exposed each day.

Environmental Health Strategy Center works at the state and national levels to ensure that all people are healthy and thriving in a healthy economy, through affordable access to safer food, water, and products; and investments that create and retain good, green jobs; and

Healthy Building Network transforms the market for building materials to advance the best environmental, health and social outcomes, including reduced use of hazardous chemicals in building products as a means of improving human health and the environment.

SCHF and its partners took a leadership role during the legislative process that led to the passage into law of the Frank R. Lautenberg Chemical Safety for the 21st Century Act, advocating the most health protective and effective policy on toxic chemicals in use today;

Our comments consists of three parts:

1. **Summary Comment –** This overview provides general comments on the scope of EPA's risk evaluation, summarizes key findings from our attached technical report, and makes recommendations to EPA for related actions needed to meet TSCA requirements;

2. **Technical Appendix –** This technical report provides information on the production, trade, use, recycling, and disposal of this chemical, citing authoritative sources (with web links), emphasizing information not included in EPA's chemical use profile; and

3. **Consumer Appendix** – This document profiles specific consumer product uses of the chemical as reported by retailers, distributors, and/or product manufacturers.

II. GENERAL COMMENTS

As discussed in detail in our separate submission, "General Comments of Safer Chemicals Healthy Families on Risk Evaluation Scoping Efforts for Ten Chemical Substances under the Toxic Substances Control Act," in order to properly scope its risk evaluation to determine whether this chemical poses an unreasonable risk to human health and the environment:

- EPA must evaluate the complete life cycle of the chemical, including production and imports, *all* uses, and its fate at the end of its useful life;

- EPA must evaluate exposure to *all* vulnerable groups, including communities of color and low-income people who may be disproportionately exposed;

- If EPA finds that data on any chemical use, hazard or exposure are insufficient to support risk evaluation, EPA must require industry to produce such data;

- EPA must assess the aggregate exposure to the most vulnerable groups and the general population for this chemical;

- EPA should assess cumulative exposure and risk, whenever practicable, for this chemical in combination with other risk factors;

- EPA should abandon its presumed safety threshold model for non-cancer effects, as recommended in the expert "Science and Decisions" report.

III. METHODS and SOURCES

We accessed and analyzed several sources of information in an effort to identify manufacturers, importers, and uses of HBCD that were not included or not fully characterized in EPA's recent chemical use profile.[1] These sources included:

- Panjiva – the trade data authority. Panjiva offers an extensive database of U.S. imports and exports of goods, including chemicals, and materials or articles containing chemicals. EPA should access these data for a modest subscription fee;
- European, United Nations and other non-domestic agency sources;
- Chemical industry sources – from web sites, trade reports and other documentation;
- U.S. EPA data sources – the Toxics Release Inventory (TRI) database, Chemical Data Reporting (CDR) submissions (including 2016 submissions obtained through a Freedom of Information Act request), and other EPA sources; and
- Pharos Chemical and Material Library – a user-friendly hazard database available free for a 14-day trial.

For carbon tetrachloride, we also examined various reports related to the science and regulation of chemical substances with ozone-depletion and global-warming potential.

IV. SPECIFIC COMMENTS

The findings below, and recommendations that follow, are specific to carbon tetrachloride (CTC). The specific comments below provide an executive summary of our technical

[1] U.S. EPA, Preliminary Information on Manufacturing, Processing, Distribution, Use and Disposal: Carbon Tetrachloride, EPA-HQ-OPPT-2016-0733-0003, February 2017. https://www.regulations.gov/document?D=EPA-HQ-OPPT-2016-0733-0003

analysis. Please refer to the attached technical report for details, methods, additional information, and citations to authoritative sources that factually support all comments.

A. Chemical Production and Trade

FINDING 1: CTC production has sharply declined from its historic peak due to health risks and a global phase-down driven by its ozone depletion potential

FINDING 2: However, a poorly justified, ill-considered loophole in the Montreal Protocol on the ozone layer allows continued use of CTC as a feedstock

FINDING 3: CTC production is poised to significantly increase due to rising feedstock demand for refrigerant replacements with a lower global warming potential, and to an industry wedded to fluorine chemistry that's replacing hydrofluorocarbons (HFCs) – most of which don't require CTC to make – with hydrofluoroolefins (HFOs) that do use carbon tetrachloride

Carbon tetrachloride production and use peaked in the 1970's and was driven further downward after the Montreal Protocol on Substances that Deplete the Ozone Layer was agreed to in 1987. CTC has an ozone depletion potential (ODP) of 0.82, which makes it nearly as potent as several of the CFCs.[2] Carbon tetrachloride also has a significant global warming potential (GWP), which makes it 1,730 times more potent than carbon dioxide.[3]

From a TSCA perspective, exposure to carbon tetrachloride may present a significant cancer risk and the chemical has been identified as a potential endocrine disruptor. However, the market for production and use of CTC continues to be largely driven by ozone-depletion and climate-change considerations, which make those worth examining.

As reported to EPA through chemical data reporting (CDR) submissions from the chemical industry, U.S. production (domestic manufacture and import) of carbon tetrachloride has remained relatively flat from 2010 through 2015, averaging about 136 million pounds per year. Most of that production is for use as a feedstock to manufacture a variety of other chemicals. (See use discussion below).

The Montreal Protocol created a huge loophole for carbon tetrachloride that allows its continued legal use as a chemical intermediate (or feedstock) for chemical production. That feedstock loophole was based on two false assurances: (1) that CTC would be phased out over time as chlorofluorocarbons (CFCs) were also phased out; and (2) that fugitive

[2] U.S. Environmental Protection Agency, Ozone Layer Protection: Ozone-Depleting Substances. https://www.epa.gov/ozone-layer-protection/ozone-depleting-substances
[3] Greenhouse Gas Protocol, Global Warming Potential Values, Adapted from the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report (2014).

emissions of CTC were negligible.

In fact, CTC production has held steady and is projected to significantly increase, and fugitive emissions have been grossly underestimated. In 2009, the European Union closed the feedstock loophole to end all uses of CTC, even while such use continues unrestricted and is projected to grow in the United States and China.

Historically, carbon tetrachloride was used in the manufacture of CFC-11 and CFC-12, two of the most dominant refrigerants and blowing agents. CFCs were phased out under the Montreal Protocol. One of the primary CFC replacements was the HFCs, a class of chemicals that contains no chlorine and therefore has no ODP. Most HFCs, such as HFC-134a used in automobile air conditioners, do *not* require carbon tetrachloride for their manufacture. However, CTC is used as a feedstock to produce HFC-245fa and HFC-365mfc, which reportedly accounted for 71% and 23% of global consumption in 2016.

In a classic case of regrettable substitution, the HFCs are now also targeted for replacement because of their unacceptably high GWP. The fluorine chemical industry is strongly marketing HFOs, which are simply HFCs that have double-carbon bonds, to replace other HFCs. By remaining wedded to fluorine chemistry, industry is repeating the mistakes of the past, and forgoing other alternatives with less health and environmental footprint.[4] Significantly, some of these projected high-volume HFOs will be manufactured using carbon tetrachloride as a feedstock.

CTC is used to manufacture HFO-1234yf for automotive air conditioning to replace HFC-134a, which does not require carbon tetrachloride to produce. This is projected to increase demand for CTC by 50% or more in coming years. Carbon tetrachloride is also used to manufacture HFO-1234ze, which is used as a blowing agent for polyurethane, polystyrene and other polymers used to make thermal insulating foam, and as an aerosol propellant. HFO-1234ze is a replacement for both HFC-134a and HFC-152a.

The impacts of increased undue reliance on carbon tetrachloride are becoming evident.

Chemours, expecting "exponential growth in demand," is building a new HFO-1234yf plant in Corpus Christi, Texas. In an early sign of yet another regrettable substitution, earlier this year a producer in France shipped 2.3 million pounds of CTC to Chemours in Texas, creating a toxic trade route where one had not previously existed. Earlier this year, Occidental's plant in Geismar, LA, obtained an air permit for a new unit to produce refrigerants -- and carbon tetrachloride feedstock. In nearby Baton Rouge, LA, Honeywell's carbon tetrachloride releases soared after the plant began producing HFO-1234ze in 2015.

[4] Greenpeace, HFOs: the new generation of F-gases, Greenpeace Position Paper, July 2016. http://www.greenpeace.org/international/Global/international/documents/climate/HFOs-the-new-generation-of-f-gases.pdf

B. Chemical Use

FINDING 4: Fugitive emissions of CTC from its production and its use as a feedstock in chemical manufacturing have been grossly under-reported

FINDING 5: The production and use of chlorinated paraffins is another source of CTC feedstock use, fugitive emissions, and contamination of products

FINDING 6: CTC is reportedly used as a feedstock for a wide variety of chemical manufacturing processes and products, each with fugitive emissions

FINDING 7: There are some remaining CTC uses in commercial & consumer products

Carbon tetrachloride is a co-product of manufacturing chloromethanes (CMs) and perchloroethylene (PCE). It's primary use now is as a feedstock to make other chemicals.

An expert international climate science panel has been working to resolve the discrepancy between the persistence of ozone-depleting and global-warming carbon tetrachloride in the atmosphere, which cannot be explained by air emissions reported on the ground. By atmospheric measurements, the experts estimate that 25 to 40 Gg/year of CTC are emitted. Yet air emission inventories only report releases of about 2 Gg/year of CTC. (For equivalent units, a Gigagram (Gg) equals 1 million kilograms or 2.2 million pounds).

This July 2016 expert report, SPARC Report on the Mystery of Carbon Tetrachloride, concluded that unreported emissions of carbon tetrachloride during its production and fugitive emissions from its use as a chemical feedstock have been seriously unreported and underestimated. They conservatively accounted for carbon tetrachloride air emissions as:

13 Gg/yr (52%)	Unreported non-feedstock emissions from production of CMs and PCE
10 Gg/yr (40%)	Unreported inadvertent emissions from chlor-alkali production and the use of chlorine gas (amount also includes legacy emissions below)
[Included above]	Legacy emissions from contaminated industrial sites and landfills
2 Gg/yr (8%)	Fugitive emissions from feedstock use, process agents, incineration

This under-reporting of carbon tetrachloride air emissions, along with projected increases in its production and use, presents serious implications for TSCA implementation. Cancer risks and other health risks may be much higher than previously believed for workers, occupational bystanders, and fenceline community residents who work and live around major sources. NIOSH estimated that more than 58,000 workers are potentially exposed to carbon tetrachloride in the United States. Major CTC sources may likely include:

- Chemical manufacturing plants that produce:
    - Chlor-alkali (chlorine)
    - Vinyl chloride monomer
    - Chloromethanes (from co-production as well as feedstock use)
    - Perchloroethylene (from co-production as well as feedstock use)
    - Hydrochloric acid
    - Hydrofluorocarbons (e.g. HFC-227ea, HFC-245fa, and HFC-365mfc)
    - Hydrofluoroolefins (e.g. HFO-1234yf and HFO-1234ze)
    - Chlorinated paraffins
    - Chlorinated pyridine
    - Hydrochloric acid
    - Processing aids for agricultural chemicals
    - Polyfunctional aziridines
    - Polyols
    - 1,1,1,3,3-Pentachlorobutane
    - Aluminum trichloride
    - Methyldichlorophosphane
    - Synthetic pyrethroids
    - Triamcinolone benetonide
    - Divinyl acid chloride (feedstock for synthetic pyrethroids, especially cypermethrin)
- Chlorine gas users, such as treatment plants for disinfection of water or wastewater
- Industrial sites where the above manufacturing activities ever took place
- Landfills and uncontrolled sites of historic disposal of carbon tetrachloride waste
- Cement kilns and incinerators

Carbon tetrachloride is still used in some commercial and consumer products, as documented in the attached Technical Report and Consumer Profile of products advertised for sale. Among others, these reported product uses include:

- Adhesives
- Plastic bonders
- Specialty paints and coatings

C. Chemical Recycling and Disposal

FINDING 8: Recycling and disposal of CTC is another source of fugitive emissions

Nearly 6 million pounds of carbon tetrachloride were reportedly recycled on-site in 2015, according to the Toxic Release Inventory. In the same year, nearly 3,000 pounds were shipped offsite for recycling and more than 12,000 pounds were sent to off-site disposal facilities. These activities represent another potential source of fugitive emissions.

V. RECOMMENDATIONS

Based on our research and findings above, we urge EPA to take the following actions in parallel during the scoping and conduct of the risk evaluation for carbon tetrachloride.

A. EPA should include *all* uses and exposures within the scope of risk evaluation

The scope of the risk evaluation for CTC should include, but not necessarily be limited to:

1. A characterization of all unreported and fugitive emissions of carbon tetrachloride, as informed by the SPARC report (July 2016) and other authoritative sources;

2. An aggregate assessment of all exposures to carbon tetrachloride, including general population exposure to the chemical in the ambient air as "background";

B. EPA should assess *all* potentially exposed or susceptible subpopulations

1. An assessment of specific exposures and risks to all workers, occupational bystanders, and fenceline community residents from direct and fugitive emissions from facilities that manufacture carbon tetrachloride or other chemicals that use carbon tetrachloride as a feedstock, now and projected into the future; from chlor-alkali production and all uses of chlorine gas; and from industrial sites, other uncontrolled sites, and landfills that contain CTC wastes or contaminants;

2. A determination as to whether any of the CTC production, use or disposal activities above result in disproportionate exposure to women of reproductive age, pregnant women and their fetuses, infants, children, and the elderly;

3. A determination as to whether any communities of color, or people of lower socioeconomic status, and their local community environments, are disproportionately exposed to CTC and thus constitute a "potentially exposed or susceptible subpopulation", based on Census Bureau data, geocoded locations of industrial facilities and disposal sites, and modeled or measured exposures; and

4. In addition to its direct risk of cancer and other hazards, EPA should consider CTC's ozone-depletion potential and global-warming potential in determining whether the chemical poses an unreasonable risk to human health and the environment.

C. EPA should require industry to develop new information to close data gaps

Whenever information is insufficient to support a determination of unreasonable risk, EPA should require, in parallel to the scoping and conduct of the risk evaluation, that chemical manufacturers and processors fill the data gaps. If so determined by EPA, candidates for additional data gathering under TSCA include but are not limited to the following:

1. Exposure and modeling data as necessary to inform the above exposure assessments; and

2. New hazard data on the endocrine activity, and the developmental and reproductive toxicity of carbon tetrachloride.

D. EPA should require notification of *all* new uses, including in imported articles

In order to ensure the completeness of the risk evaluation to support an unreasonable risk determination, EPA needs to establish with some certainty which uses in the United States are truly historic or never took place in this country, and also ensure that such uses are not encouraged or take place again in the future without EPA's knowledge. Therefore:

1. EPA should propose a Significant New Use Rule (SNUR) for carbon tetrachloride, and for imported articles that contain carbon tetrachloride, including its use as a feedstock to produce new HFOs and other chemicals, and other now historic uses;

By proposing a SNUR soon, i.e. during the risk evaluation of CTC, EPA would enable industry to step forward and assert with clear evidence whether any such uses are in fact *existing* uses that continue rather than historic uses that would trigger notification if later reintroduced as new uses. This mechanism would provide EPA with more complete information on which to base its risk evaluation and unreasonable risk determination.

VI. CONCLUSION

We urge EPA to use its full authority under TSCA to support an expansive scope for the risk evaluation of carbon tetrachloride, as recommend above. CTC emissions have been seriously under-reported and are projected to significantly increase. All sources of carbon tetrachloride releases associated with chemical manufacturing and use require evaluation. We believe that the marketplace and international community have already determined that carbon tetrachloride poses an unreasonable risk to human health and the environment because of its ozone-depletion potential and global-warming potential, along with its risk of cancer. So should the U.S. Environmental Protection Agency under TSCA.

Technical Appendix

Carbon Tetrachloride

Technical Report on production, imports, use, recycling, disposal, exposure scenarios, and associated environmental and human health hazards.

Healthy Building Network

in collaboration with Safer Chemicals Healthy Families

and Environmental Health Strategy Center

March 15, 2017

Contents

Carbon Tetrachloride

1. Identifying Information

CAS No.: 56-23-5

UN Shipping Code: UN1846

Harmonized Tariff Schedule Number:
HTS No.: 2903.14.0000 Carbon tetrachloride

Synonyms: Carbona, carbon chloride, tetrachloromethane, carbon tet, methane tetrachloride, perchloromethane, tetrachlorocarbon, CCl_4

Trade names: Benzinoform, Fasciolin, Flukoids, Freon 10, Halon 104, Necatorina, Necatorine, Tetrafinol, Tetraform, Tetrasol, Univerm, Vermoestricid

TSCA Docket No.: EPA-HQ-OPPT-2016-0733

2. Research Methods

In collaboration with Safer Chemicals Healthy Families and the Environmental Health Strategy Center, the Healthy Building Network research team reviewed the Chemical Data Reporting forms submitted for carbon tetrachloride and the EPA Preliminary Information on Manufacturing, Processing, Distribution, Use, and Disposal (released in February 2017). It cross-referenced this data with the EPA Toxics Release Inventory and a variety of national, European and United Nations reports, chemical industry literature, and a shipping database (Panjiva) with the goal of identifying potentially missing producers, importers, and uses of carbon tetrachloride. Chemical hazard information is drawn from the Pharos Chemical and Material Library, available to any user for 14 days, after which a subscription is required.

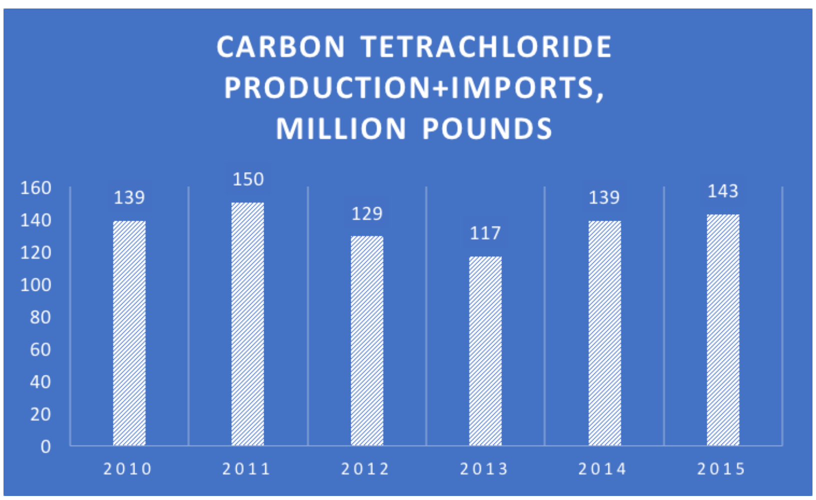
Findings that are not included in the EPA Preliminary Information document, or were not publicly reported in CDRs, are highlighted in yellow.

3. Production/Trade

Under the terms of the Montreal Protocol to protect the ozone layer, in 1995, developed countries eliminated many uses for carbon tetrachloride (such as its use as a solvent in cleaning fluids, lacquers, as a dry cleaning agent, and as a grain fumigant). Developing countries, according to the United Nations Environment Programme, achieved a total phase-out of carbon tetrachloride products (if not production) in 2010.

However, the Montreal Protocol phase-outs exempted the use of carbon tetrachloride (CCl_4) as a chemical feedstock. In 2009, a European Commission regulation closed the feedstock loophole for that region for most end uses, including, it seems, chlorinated paraffin production.[1] Others countries – including the United States and China – have not followed suit. Production levels, in the US alone, are more than 15 times higher than chemical companies promised before the feedstock loophole was enacted. (See Ozone Depletion section later in this report.)

CCl_4 is a co-product of chloromethanes, and is consumed primarily in the production of some, but not most, hydrofluorocarbon (HFC) blowing agents. CCl_4 is also a key feedstock for some chlorinated paraffins and vinyl chloride monomers produced in the US and Asia. Demand for CCl_4 is poised to increase due to its role in making the next generation of blowing agents and refrigerants: hydrofluoroolefins (HFOs).



HBN graph based on EPA CDR Information for the US.

[1] See: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:286:0001:0030:EN:PDF

- **Trade and Production Chronology**

1907: Large-scale production of CCl_4 begins in the US.[2]

1970 to 1974: Driven by use as propellant, production of CCl_4 is "at its peak" before "other forms of propellants became commercially available."[3]

1974 to 1994: Production declines by about 8 percent per year as FDA bans sale in any home product and EPA regulates chlorofluorocarbons under the Montreal Protocol.[4]

1989: Worldwide, countries report producing 144,000 tons (over 316 million pounds) of CCl_4 feedstock.[5]

1989: US establishes baseline production allowance of 63,000 tons (~138 million pounds).

1993: Industry-dominated committee assures parties to the Montreal Protocol that worldwide usage of CCl_4 as a chemical feedstock will not exceed 5,000 tons per year. The panel said "this should be substantially reduced over the next 5 years" and "can be completely destroyed."[6]

1995: Montreal Protocol exempts CCl_4's use as a chemical feedstock.

2000: Production of CCl_4 for non-feedstock uses is prohibited in the US.[7]

2004 : Vulcan Materials (later Occidental) has a combined capacity of 130 million pounds (about 60,000 tons) to produce chlorinated solvents (including CCl_4) in Wichita, KS and Geismar, LA.[8]

2009: Twenty-six manufacturers worldwide, including three in the US, produce CCl_4.[9]

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[2] http://web.archive.org/web/20110708135105/http://ntp.niehs.nih.gov/ntp/roc/twelfth/profiles/CarbonTetrachloride.pdf
[3] https://www.atsdr.cdc.gov/toxprofiles/tp30-c5.pdf
[4] https://www.atsdr.cdc.gov/toxprofiles/tp30-c5.pdf
[5] Miller, Melanie, and Tom Batchelor. "Feedstock Uses of ODS: Information Paper on Feedstock Uses of Ozone-Depleting Substances." Touchdown Consulting, December 2012. https://ec.europa.eu/clima/sites/clima/files/ozone/docs/feedstock_en.pdf.
[6] UNEP Solvents, Coatings and Adhesives Technical Options Report of 1991
[7] https://www.atsdr.cdc.gov/toxprofiles/tp30-c5.pdf
[8] https://www.atsdr.cdc.gov/toxprofiles/tp30-c5.pdf
[9] http://web.archive.org/web/20110708135105/http://ntp.niehs.nih.gov/ntp/roc/twelfth/profiles/CarbonTetrachloride.pdf

2011: Countries report the production of over 194,000 tons (over 425 million pounds) of carbon tetrachloride worldwide, which is 50,000 tons more than were produced in 1989.[10]

2012: Trade and CDR data for 2012 and subsequent years show that very little carbon tetrachloride is imported into the US. In 2012, the International Trade Commission reported 5.1 million pounds of imports, compared to the CDR-reported total (production and imports) of 129.1 million pounds.

2013: CDR forms show a total of 116.7 million pounds of production and imports in the US. ITC reports just 222,940 pounds of imports.

2014: CDR forms show a total of 139 million pounds of production. ITC reports no imports. The Stratosphere-Troposphere Processes And their Role in Climate (SPARC) research team estimates that over 447 million pounds of CCl_4 were produced worldwide in 2014. Most of that was consumed as feedstock for perchloroethylene (PCE) or for hydrofluorocarbon (HFC) blowing agents.[11]

2015: According to CDR forms, US companies produced 143 million pounds of carbon tetrachloride (63,000 tons). ITC reports no imports.

2016: ITC reports 41,536 pounds of imports from Spain, which corresponds with Panjiva records.

2016: Industry analysts state: "Four regions account for the vast majority of consumption: the United States, Western Europe, the Indian Subcontinent, and Northeast Asia. The production of hydrofluorocarbons HFC-245fa and HFC-365mfc accounted for 71% and 23%, respectively, of total carbon tetrachloride consumption in 2016."[12]

2017: A large CCl_4 shipment (2.3 million pounds) arrives on January 18 from France for delivery to the Chemours Co. in Wilmington, Delaware, according to Panjiva.

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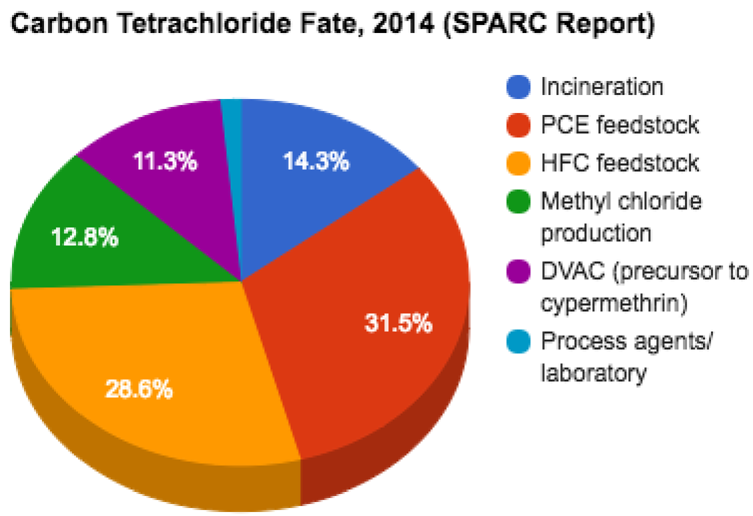
[10] Miller, Melanie, and Tom Batchelor. "Feedstock Uses of ODS: Information Paper on Feedstock Uses of Ozone-Depleting Substances." Touchdown Consulting, December 2012. https://ec.europa.eu/clima/sites/clima/files/ozone/docs/feedstock_en.pdf.

[11] SPARC (2016), SPARC Report on the Mystery of Carbon Tetrachloride. Q. Liang, P.A. Newman, S. Reimann (Eds.), SPARC Report No. 7, WCRP-13/2016 https://www.wcrp-climate.org/WCRP-publications/2016/SPARC_Report7_2016.pdf

[12] https://www.ihs.com/products/chlorinatedmethanes-chemical-economics-handbook.html



- **About Carbon Tetrachloride**

In 2016, a global scientific team endeavored to account for all the possible sources, and fates, of carbon tetrachloride. "CCl_4 is not decreasing in the atmosphere as rapidly as expected, given what we know about its total lifetime (based on loss processes), and the small remaining emissions that are known," wrote the authors of the SPARC project paper. They found that industrial processes are releasing and consuming more carbon tetrachloride than previously understood.

Carbon tetrachloride forms during the production of perchloroethylene (PCE) and chlorinated methanes such as chloroform and methyl chloride.[13] The SPARC team found that older, unmodified chemical equipment yields higher percentages (6-8%) of CCl_4 than newer plants (~4%), although older PCE plants "can be modified to produce zero CCl_4."[14]

They estimated that over 447 million pounds of CCl_4 were produced in 2014, intentionally or otherwise. Most of that was consumed as feedstock for PCE or for hydrofluorocarbon (HFC) refrigerants and blowing agents[15] (see above graphic).

[13] https://www.atsdr.cdc.gov/toxprofiles/tp106-c4.pdf
[14] https://www.wcrp-climate.org/WCRP-publications/2016/SPARC_Report7_2016.pdf
[15] https://www.wcrp-climate.org/WCRP-publications/2016/SPARC_Report7_2016.pdf

Companies will likely produce more carbon tetrachloride as industry replaces HFCs (most of which aren't produced with carbon tetrachloride) with hydrofluoroolefins (HFOs), such as HFO-1234yf and -1234ze, that consume CCl_4 as a feedstock.[16]

- **Domestic Producers and Consumers (Summary)**

In 1992, the US International Trade Commission Synthetic Organic Chemicals directory listed three US producers of carbon tetrachloride. The producers withheld individual and cumulative production data, which is an enduring feature of the chemical industry's opacity. The three companies listed were Occidental Chemical, Vulcan Materials, and Dow.[17]

Today, Occidental may be the only company intentionally manufacturing carbon tetrachloride, the others producing it as byproducts of other processes.

In the latest CDR reporting period (2012 to 2015), at least seven sites reported producing, and one reported importing, carbon tetrachloride. Another company redacted information about whether its reportable quantities were produced domestically or imported.

While all individual volumes of CDR production were redacted, Toxics Release Inventory data can provide a glimpse into the relative scale, and industrial relationship, of these companies' releases of CCl_4. Cross-referencing TRI data with plant production information also identifies several carbon tetrachloride uses not identified in EPA's February 2017 data summary, highlighted in yellow. (Table 1)

One caveat: The use of CCl_4 as an intermediary generates fugitive emissions that are likely underreported in TRI data (see Exposure Scenarios discussion below).

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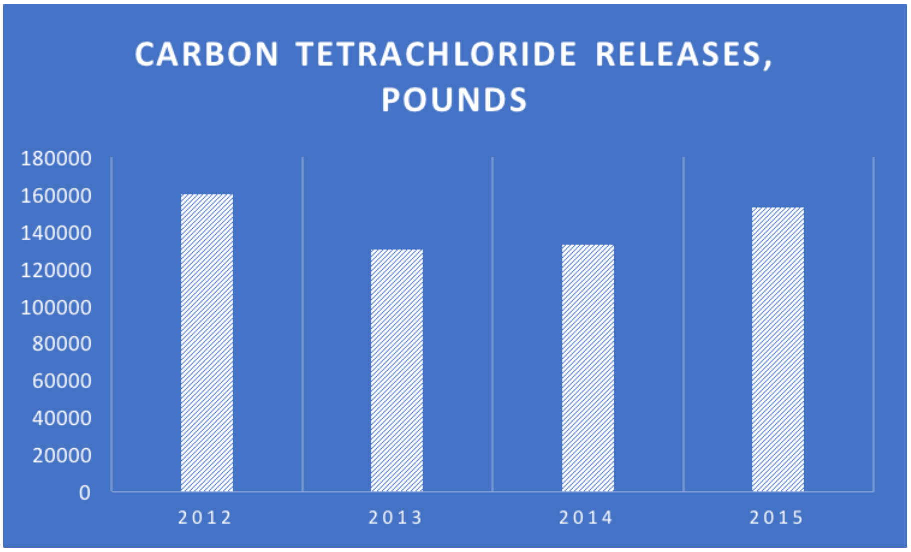
16 https://www.wcrp-climate.org/WCRP-publications/2016/SPARC_Report7_2016.pdf
17 https://www.usitc.gov/publications/332/pub2720.pdf

Table 1. Carbon Tetrachloride Releases from the US Chemical Industry, 2012 to 2015				
Rank	Chemical Producer/ Location	Type of Plant (Relevant Chemicals)	CDR Report Filed?	Ave. CCl_4 Releases lbs./yr. (TRI)
1	Rubicon (Huntsman/Chemtura JV); Geismar, LA	Polyurethane (Hydrochloric Acid, Polyols)	?	28,950
2	Occidental; Wichita, KS	Chlor-Alkali (CCl_4,, Chloroform, Methylene Chloride)	likely	28,426
3	Occidental; Geismar, LA	Chlor-Alkali (CCl_4, Chloroform) *coming soon: HFOs*	yes	23,994
4	GB Biosciences Corp. (Syngenta); Houston, TX	Pesticides (esp., cypermethrin)	?	10,450
5	Westlake Vinyls; Calvert City, KY	Chlor-Alkali	?	6,774
6	Dover Chemical; Dover, OH	Chlorinated Paraffins	?	5,363
7	Olin (formerly Dow); Plaquemine, LA	Chlor-Alkali, chloromethanes	yes	5,159
8	Chemours; El Dorado, AL	HFC-227ea	?	4,170
9	Dow Chemical; Pittsburg, CA	Byproduct of chlorinated pyridine production	Yes	3,778
10	Olin (formerly Dow); Freeport, TX	Chlor-alkali, chloromethanes	Yes	3,633
15	Syngenta Crop Protection; St. Gabriel, LA	Pesticides (esp., cypermethrin)	yes	1,612
16	Honeywell; Baton Rouge, LA	HFO-1234ze	?	1,256
18	Geon Oxy Vinyl; Laporte, TX	Chlor-alkali	yes	517
-	Ineos Chlor America; Wilmington, DE	Chlorinated Paraffins	yes	No TRI data found

Source: 2012 to 2015 Toxics Release Inventory Data, 2012-2015. Ten highest releasing, and all CDR reporting, locations

(?) - One producing company's name was redacted in CDR data, so it is not possible to state whether any of the plants listed here with a question market were represented in that redacted CDR.



Healthy Building Network Graphic based on Toxics Release Inventory

- **CDR-Reporting Domestic Producers**

CDR-reporting companies are listed in order of average TRI releases over the reporting period.

- <u>Occidental (Wichita, KS and Geismar, LA; formerly Vulcan Materials)</u>

Although one of Occidental's CDR forms redacts the location of one site where it produces carbon tetrachloride, its own website discloses the information: "OxyChem [Occidental and affiliates] produces one grade of carbon tetrachloride as Technical Grade manufactured at both Wichita, KS and Geismar, LA facilities."[18]

The second Occidental CDR, for Geismar, LA, lists Intermediates as the use, with the sector of use redacted. The CDR of the other location (that is, Wichita) lists uses as Intermediates, Process regulators, and Laboratory chemicals, but redacts the sectors.

OxyChem's Wichita and Geismar plants rank second and third, respectively, for annual TRI releases. (See Table 1 above). The Geismar and Wichita facilities are chlor-alkali plants that use a combination of membrane and diaphragm technology. Occidental purchased the facilities

18 http://www.oxy.com/OurBusinesses/Chemicals/Products/Documents/ChlorinatedOrgancis/ChlorinatedOrganicsHandbook.pdf

from Vulcan Materials in 2005.[19] In 2005, an Agency for Toxic Substances and Disease Registry (ATSDR) toxicological profile for carbon tetrachloride described these two plants as the country's only producers of carbon tetrachloride.[20] Both plants also produce chloroform, and the Wichita plant also produces methylene chloride.[21]

According to a company guide: "The OxyChem chlorinated organics technology uses a versatile process to produce perchloroethylene (perc) and carbon tetrachloride (carbon tet), with anhydrous hydrogen chloride (HCl) and crude 1,2-dichloroethane (EDC) by-products. A wide variety of feedstocks including C_1 to C_3 hydrocarbons and partially chlorinated hydrocarbons are utilized in this process. Chlorine (Cl_2), in excess of stoichiometric requirements, is reacted at high temperature with the organic feed to produce perc and carbon tet."[22]

The Geismar plant's emissions of carbon tetrachloride are poised to increase. A $145 million expansion is underway to produce refrigerants.[23] A 2017 air permit for this facility cited an increase in estimated VOC emissions of 7.44 tons per year from the "Utilities Process Unit," which "includes an increase in carbon tetrachloride."[24] This may be related to a joint venture with Dow Chemical to produce "the new chlorocarbon, known as HCC-1230xa," used in the production of HFO-1234yf.[25]

- Olin (Plaquemine, LA and Freeport, TX)

In 2015, Olin took ownership of Dow Chemical's chlor-alkali facilities in Plaquemine, LA and Freeport, TX. The Freeport plant is the largest chlorine factory in the country, and Plaquemine is among the top five.

The Plaquemine and Freeport plants reported the country's seventh and tenth highest CCl_4 releases between 2012 and 2015. Olin and Dow's CDRs state that carbon tetrachloride is used as an intermediate, with little other specificity.

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[19] http://www.businesswire.com/news/home/20050607005977/en/Vulcan-Materials-Company-Closes-Sale-Chemicals-Business
[20] https://www.atsdr.cdc.gov/toxprofiles/tp30.pdf
[21] http://www.oxy.com/OurBusinesses/Chemicals/Products/Documents/ChlorinatedOrgancis/ChlorinatedOrganicsHandbook.pdf
[22] http://www.oxy.com/OurBusinesses/Chemicals/Products/Documents/ChlorinatedOrgancis/ChlorinatedOrganicsHandbook.pdf
[23] http://neworleanscitybusiness.com/blog/2016/04/18/145m-expansion-planned-for-geismar-manufacturing-facility/
[24] http://www.deq.louisiana.gov/apps/pubNotice/show.asp?qPostID=9118&SearchText=&startDate=1/1/2017&endDate=2/22/2017&category=
[25] http://newsroom.dow.com/press-release/company-news/dow-and-oxychem-form-joint-venture-produce-new-chlorocarbon-next-generati

On its website, Olin lists technical grade carbon tetrachloride for chemical processing and fluorocarbon feedstock.[26] The corporation's 2015 annual report explains, "The Chlor Alkali Products and Vinyls segment manufactures and sells chlorine and caustic soda, ethylene dichloride and vinyl chloride monomer, methyl chloride, methylene chloride, chloroform, carbon tetrachloride, perchloroethylene, trichloroethylene and vinylidene chloride, hydrochloric acid, hydrogen, bleach products and potassium hydroxide… [This] segment also includes the acquired chlorinated organics business which is the largest global producer of chlorinated organic products that include chloromethanes (methyl chloride, methylene chloride, chloroform and carbon tetrachloride) and chloroethenes (perchloroethylene, trichloroethylene, and vinylidene chloride)...Intermediate products are used as feedstocks in the production of fluoropolymers, fluorocarbon refrigerants and blowing agents, silicones, cellulosics and agricultural chemicals."[27]

- Dow Chemical (Pittsburg, CA)

Dow filed a CDR form that lists its Pittsburg, CA facility as a manufacturer of CCl_4, and reports that it is used as an intermediate for "all other basic organic chemical manufacturing." This plant had the ninth highest releases of CCl_4 among chemical companies over the 2012-2015 period.

A Bay Area Air Quality Management District permit describes the Pittsburg plant's relevant technology. A production unit for chlorinated pyridine products generates hydrogen chlorine gas and carbon tetrachloride as byproducts.[28] Dow recycles the CCl_4 or stores it in case it is "needed for use in the [plant's] utility system."[29]

Dow's 2010 sustainability report states that it also brings in carbon tetrachloride from other manufacturers who want to be rid of this process chemistry byproduct. "One example of the use of recycled material coming from external companies is in the production of perchloroethylene by Dow Chlorinated Organics," it reads. "Carbon tetrachloride by-product streams are used to harvest the chlorine molecules needed to make our product. The

[26] https://olinchlorinatedorganics.com/products/carbon-tetrachloride/
[27] https://www.sec.gov/Archives/edgar/data/74303/000007430316000090/oln-2015x1231x10xk.htm
[28] http://www.baaqmd.gov/~/media/files/engineering/title-v-permits/a0031/a0031_2015_11_renewal_proposed_sob_app-18262_04.pdf
[29] https://yosemite.epa.gov/r9/air/epss.nsf/735056a63c1390e08825657e0075d180/4b67c2e9f656e0c488256dbb0081a6a8/$FILE/A0031SOB_CBI.pdf

relationship benefits both parties – the generators of carbon tetrachloride avoid high disposal costs and Dow captures chlorine molecules as a useful raw material."[30]

- Geon Oxy Vinyl - Laporte, TX

Production quantities on the CDR are redacted. Use is listed as intermediates for "all other basic organic chemical manufacturing."

This plant produces vinyl chloride monomer (VCM). This was part of a joint venture between the Geon Company and OxyChem.[31] Geon later merged with the M.A. Hanna Co. to form Polyone Corporation.[32] Polyone does not list manufacturing in LaPorte on their website (only a warehouse).[33] TRI releases in the above table are reported for Oxy Vinyls in Laporte, TX.

- Syngenta Crop Protection (Saint Gabriel, LA and Houston, TX)

Syngenta reported production of CCl_4 in its CDR submission for its Saint Gabriel, LA plant. The use was listed as "processing aids, not otherwise listed" for the "pesticide, fertilizer, and other agricultural chemical manufacturing" sector.

Syngenta sells four varieties of pesticides that contain cypermethrin as an active ingredient.[34] The process of manufacturing cypermethrin, according to the SPARC research team, is a significant consumer of carbon tetrachloride. See pie chart above.

There is no apparent CDR submission for Syngenta's Houston plant location, which ranked as fourth for CCl_4 releases from 2012-2015. The St. Gabriel plant ranked 15th.

- **Importers (and related foreign producers)**

Ineos Chlor America is the only identifiable company that submitted a CDR for carbon tetrachloride imports.

[30] http://www.dow.com/en-us/science-and-sustainability/highlights-and-reporting
[31] http://www.prnewswire.com/news-releases/geon-and-bayer-announce-alliance-and-plans-for-pipeline-to-transport-hydrogen-chloride-77011067.html; https://www.icis.com/resources/news/1998/06/25/61201/us-geon-oxy-form-two-300m-pvc-jvs/
[32] http://ech.case.edu/ech-cgi/article.pl?id=PC3
[33] http://www.polyone.com/center-of-excellence/polyone-north-america
[34] http://ppis.ceris.purdue.edu/ and http://www.syngentaprofessionalproducts.com/pdf/msds/03_474504202009.pdf

- Unknown supplier → Ineos Chlor America, Inc - (Wilmington, DE)

Ineos' CDR form reported that it imported CCl_4 for use as intermediates for "all other basic organic chemical manufacturing." No corresponding records on Panjiva could be found.

Ineos Chlor America reached a settlement with the EPA in 2012 for importing chlorinated paraffins without providing the required notice. As part of the settlement, the company stopped importing short-chained chlorinated paraffins and agreed to "provide proper premanufacture notices to the EPA for any other chlorinated paraffin it wishes to manufacture."[35]
CCl_4 is used as a solvent in the production of chlorinated paraffins[36] and is a common residual in the final product.

- Kem One (Lavera, France) → The Chemours Co (Corpus Christi, Texas)

Chemours recently imported significant amounts of CCl_4 from Kem One of France. There was one small shipment in 2016. Then on January 17, 2017, a very large bulk shipment, weighing 1,042,000 kilograms (2.3 million pounds), arrived in Houston.

Chemours is a chemical company that spun off from DuPont in 2015.

The French supplier, Kem One, says its carbon tetrachloride "is mainly used as a solvent and a cleaning agent. It is also used in the production of coolants, propellants and other fluorinated hydrocarbons."[37] Kem One produces 130,000 tons of chloromethane each year (which includes four types of chloromethane: methyl chloride, methylene chloride, chloroform, and carbon tetrachloride).[38] It says its "chloromethane plant at Lavéra is the biggest production plant in continental Europe (20% of production)."[39]

An ongoing phaseout of ozone-depleting HFC and HCFC refrigerants[40] is driving the rapid expansion of capacity to produce a new generation of coolants called hydrofluoroolefins (HFOs).

Chemours is capitalizing upon this technology shift. The company expects "exponential growth in demand" for HFO refrigerants. It is investing $230 million in a new HFO-1234yf refrigerant

[35] https://www.epa.gov/enforcement/ineos-chlor-americas-settlement
[36] http://www.google.ch/patents/CN1210133A?cl=en
[37] http://www.kemone.com/en/Products-and-markets/Products/Chlorochemicals-products/Chloromethane
[38] http://www.kemone.com/en/Products-and-markets/Products/Chlorochemicals-products/Chloromethane
[39] http://www.kemone.com/en/The-company/Sites/Lavera
[40] https://www.epa.gov/ods-phaseout/phaseout-class-ii-ozone-depleting-substances

factory in Corpus Christi, Texas, which it markets under the trade name, Opteon™ YF. The chemical is a replacement for HFC-134a in automobile air conditioners.[41] Chemours expects "that 40 million cars using HFO-1234yf will be on the road by end of 2017, growing to 140 million by end of 2020."[42]

Carbon tetrachloride is a feedstock for HFO-1234yf,[43] which would explain the 2.3 million pound shipment from France to Houston in January 2017.

Chemours has developed additional HFO products for "coolers in supermarkets and stores, refrigerated trucks, air conditioning systems, heat pumps, chillers, and industrial applications."[44] It is not clear if these use CCl_4 as a feedstock.

- Menadiona (Spain) → Polyaziridine LLC

Polyaziridine received a shipment (19 metric tons) of carbon tetrachloride from Spain in 2016 (after the CDR reporting period). This company produces polyfunctional aziridines for cross-linking of acrylic emulsions and polyurethane dispersions in coatings, inks, and adhesives. Listed applications include pressure sensitive adhesives, wood coatings, protective films, printing inks, leather coatings, adhesives, textile coatings, over-print varnishes, and plastic films.[45] How Polyaziridine specifically uses CCl_4 in its formulations could not be determined.

- Tramaco (Germany) → P.A.T. Products

In 2015, P.A.T. Products imported 581 pounds of a product called Trapylen 777 from Tramco in Germany. Shipping records indicate that this epoxy resin contains carbon tetrachloride. Tramaco's website lists Trapylen as a coating for plastic parts - as a primer or pigmented primer.[46]

- **Companies Reporting Large Releases** (not otherwise discussed above)

- Rubicon (Geismar, LA)

Rubicon is a large polyurethane plant in Geismar, Louisiana. It is a joint venture between the Huntsman and Chemtura chemical companies. Products include methylene diphenyl

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41 https://www.chemours.com/businesses-and-products/fluoroproducts/opteon-yf/
42 https://www.chemours.com/Refrigerants/en_US/assets/downloads/20160502-HFO-1234yf-plant-triple-opteon-product-supply.pdf
43 https://www.wcrp-climate.org/WCRP-publications/2016/SPARC_Report7_2016.pdf
44 https://www.chemours.com/businesses-and-products/fluoroproducts/opteon-refrigerant/
45 http://polyaziridine.com/applications/
46 http://www.tramaco.de/en/products/primer-and-adhesion-promoter/trapylenr-for-coating-of-plastic-parts.html

isocyanates, maleic anhydride, hydrochloric acid, polyols, nitrobenzene, aniline, and diphenylamine.[47]

According to TRI data, the Rubicon facility in Geismar, LA, released more CCl_4, around 27,000 pounds or more per year, than any other company in the 2012-2015 period. The specific process causing these releases is unclear.

CCl_4 may be used to produce hydrochloric acid[48] and in polyol synthesis. The Rubicon venture has the capacity to produce 160 million pounds of polyols each year[49] and 99 million pounds of methylene diisocyanate.

- Westlake Vinyls (Calvert City, KY)

Westlake Vinyls operates a membrane technology chlor-alkali plant in Calvert City, Kentucky. It reported the fifth highest amount of carbon tetrachloride releases in the 2012-2015 period. It's production is standard fare for chlor-alkali plants (chlorine, caustic soda, vinyl chloride monomer, polyvinyl chloride), and it is not a particularly large operation.
The rate of CCl_4 releases recently tripled as the plant expanded its PVC[50] and ethylene[51] production capacities. Releases were around 2,700 pounds in 2012 and 2013, and increased to over 10,000 pounds in 2014 and 2015. This follows a $300 million expansion in 2014 related to switching ethylene production from propane to natural gas and increasing PVC production.

It is unclear precisely why the Calvert City plant releases more carbon tetrachloride than other chlor-alkali plants, or which part of the operation it comes from. At least two processes can introduce carbon tetrachloride into (and release it from) chlor-alkali production.

47 http://www.huntsman.com/polyurethanes/Media%20Library/a_MC1CD1F5AB7BB1738E040EBCD2B6B01F1/Locations_MC1CD1F5B3BCA1738E040EBCD2B6B01F1/Americas_MC1CD1F5B3C171738E040EBCD2B6B01F1/USA_MC1CD1F5B3D5F1738E040EBCD2B6B01F1/files/Geismar%20Fact%20Sheet%20v2.pdf

48 Touchstone.
https://ec.europa.eu/clima/sites/clima/files/ozone/docs/feedstock_en.pdf.

49 https://www.sec.gov/Archives/edgar/data/1089748/000104746915000900/a2222928z10-k.htm

50 http://www.prnewswire.com/news-releases/westlake-chemical-celebrates-expansion-of-its-calvert-city-facility-855500500.html

51 http://www.westkentuckystar.com/News/Local-Regional/Western-Kentucky/Westlake-Chemical-in-Calvert-Expanding-Capacity.aspx and http://www.plasticsnews.com/article/20160719/NEWS/160719822/westlake-restarts-kentucky-complex

1. Carbon tetrachloride solutions have been used to recover and purify[52] waste chlorine emissions from chlor-alkali plants.[53] In an old EPA survey, four out of 24 plants surveyed used absorptive scrubbing equipment that could use CCl_4 to recover waste chlorine gas.
2. Carbon tetrachloride has been used to eliminate nitrogen trichloride (NCl_3).[54] "The presence of some nitrogen compounds in the brine gives rise to the formation of nitrogen trichloride (NCl_3), which is an explosive substance," explains a European chlor-alkli best practices guide.[55]

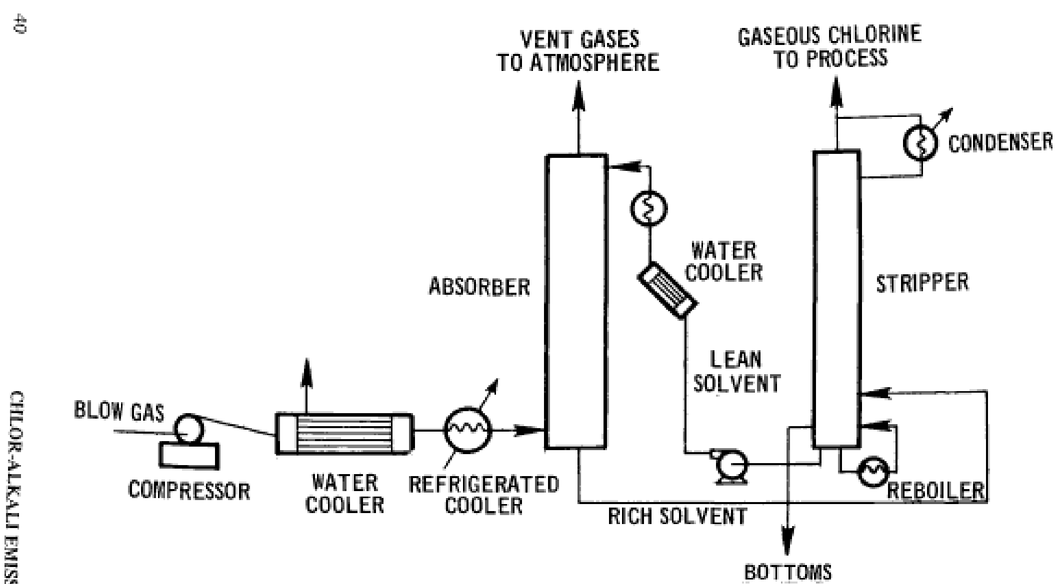

Figure 11. Recovery of blow-gas chlorine by carbon tetrachloride absorption (Source: U.S. Patent 2,765,873).

Recovery of blow-gas chlorine by carbon tetrachloride absorption. Reproduced from Cooperative Study Project, Manufacturing Chemists' Association, Inc. and Public Health Service, *Atmospheric Emissions From Chlor-Alkali Manufacture,* Environmental Protection Agency, January 1971.

Another possibility is that Westlake is accounting for what the SPARC report identifies as unreported emissions from chlor-alkali plants. See Exposure Scenarios discussion below.

52 https://www.google.com/patents/US2765873
53 https://acd-ext.gsfc.nasa.gov/Documents/O3_Assessments/Docs/WMO_2010/2010assessment/CTOC_2010_Assessment_Report.pdf
54 https://acd-ext.gsfc.nasa.gov/Documents/O3_Assessments/Docs/WMO_2010/2010assessment/CTOC_2010_Assessment_Report.pdf
55 http://eippcb.jrc.ec.europa.eu/reference/BREF/CAK_Adopted_072014.pdf

- Dover Chemical Company - Dover, OH

TRI releases of CCl_4 for 2012-2015 ranged from 3,788 to 7,856 pounds annually. Dover Chemical produces chlorinated paraffins with chlorine content greater than 70%.[56] Highly chlorinated paraffins such as these are commonly produced using CCl_4 solvent.[57] Products containing such paraffins often also contain CCl_4 residual. For example, a product that primes concrete for fluid applied flooring contains chlorinated paraffins and residual carbon tetrachloride.[58]

In 2012, Dover Chemical reached a settlement with the EPA over unauthorized manufacture of various chlorinated paraffins. The resulting agreement was to cease manufacture of short-chained chlorinated paraffins and "provide proper pre-manufacture notices to the EPA for any other chlorinated paraffin."[59]

Chlorinated paraffins are used in solvent-based intumescent coatings.[60] They are common in wet-applied HVAC duct sealant[61] and in fireblock single component spray polyurethane foam.[62] They can also be used in adhesives, for example in a gypsum ceiling product.[63] Other uses of chlorinated paraffins in building and construction reported in the EU are: road marking paints, anti-corrosive coatings for metal surfaces, swimming pool coatings, decorative paints for internal and external surfaces, masonry paints, primer for polysulphide expansion joint sealants, intumescent coatings, and textile printing inks.[64]

- Chemours (El Dorado, Arkansas)

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56 http://www.doverchem.com/Products/Chlorez%c2%aeResinousChlorinatedAlkanes.aspx
57 http://www.regnet.com/cpia/status_report.html
58 http://www.tremcosealants.com/fileshare/msds/252164_164_C.PDF
59 https://www.epa.gov/enforcement/dover-chemical-company-settlement
60 http://www.doverchem.com/Portals/0/Fire%20Retardant%20Coatings%20-%20Chlorinated%20Paraffins%20in%20Intumescent%20Coatings.pdf
61 https://pharosproject.net/uploads/files/sources/1828/e17c2ce0e82c62d1cb2d3395c19ce9807bdeab0b.pdf; https://pharosproject.net/uploads/files/sources/1828/6422a9b88631da67251c0f14a4dfa3ab6103ec57.pdf
62 https://pharosproject.net/uploads/files/sources/1828/33aa4e49fcfb98f5b5bd5b8b99aa1e40d1bb8207.pdf; https://pharosproject.net/uploads/files/sources/1828/a3e36fe9a70a3f62c62edb67cc2f161f4b9e400d.pdf; https://pharosproject.net/uploads/files/sources/1828/27bc9c94ef157c3f9f073f1711d62cd59ce3b0de.pdf; https://pharosproject.net/uploads/files/sources/1828/a36c84a629523de07b13af88a1fb9db24935c945.pdf; https://pharosproject.net/uploads/files/sources/1828/06fbddb37f5af1a645ced6eea809ec7742760c2b.pdf; https://pharosproject.net/uploads/files/sources/1828/f8d3e9894811abc1242ba313e7af5bd88e89a47c.pdf
63 https://pharosproject.net/uploads/files/sources/37/Envirogard_MSDS_2009.pdf
64 https://dibk.no/globalassets/avfall-og-miljosanering/publikasjoner/master-thesis-fixed---karoline-petersen.pdf

In El Dorado, Arkansas, Chemours produces fluorochemicals at a unit that DuPont purchased from Chemtura in 2008.[65] This plant was the eighth largest industry source of CCl_4 releases between 2012 and 2015.

Chemours produces two chemicals in El Dorado: HFC-227ea (CAS no. 431-89-0, sold under the brand name FM-200), and 2-bromo-1,1-difluoroethane (BDFE, or HBFC-142B1, CAS no. 359-07-9).[66]

EPA's February 2017 Information Document for carbon tetrachloride lists three HFCs (HFC-245fa, HFC-365mfc, and HFC-236fa) that use carbon tetrachloride feedstock, but not HFC-227ea.

HBFC-142B1 (a/k/a BDFE) is a fluorinated intermediate used in the synthesis of pharmaceuticals.[67] Hydrobromofluorocarbons (HBFCs), or bromoethanes, are low production volume ozone-depleting substances.[68] No literature could be found connecting carbon tetrachloride emissions to HBFC production.

- Honeywell (Baton Rouge LA)

For the CDR reporting period (2012-2015), Honeywell's chemical plant in Baton Rouge ranked sixteenth for carbon tetrachloride releases, but moved into the top ten of CCl_4 releases in 2015 as it ramped up production of the hydrofluoroolefin blowing agent, HFO-1234ze. Honeywell owns the patent for the chemical, published in 2013.[69]

HFO-1234ze is a "blowing agent for polyurethanes, polystyrene and other polymers; as well as an aerosol propellant,"[70] says Honeywell. "HFO-1234ze is considered a preferred replacement for both HFC-134a (which has GWP of 1,300) and HFC-152a (which is flammable and has a GWP

65 http://investor.chemtura.com/releasedetail.cfm?releaseid=825937

66 https://www.chemours.com/Titanium_Technologies/en_US/sales_support/about_us/manufacturing_sites/iso_certs/iso-14001-2004-ems-oversight-certificate.pdf

67 https://www.scottecatalog.com/PDFFiles.nsf/f4ee1b98bd36b61485256f3900678fc7/7df2256ebb830b0285257339004d307b/$FILE/BDFE%20CHEM-001.pdf

68 https://ec.europa.eu/clima/sites/clima/files/ozone/docs/feedstock_en.pdf

69 https://www.google.com/patents/US20130211156

70 https://www51.honeywell.com/sm/lgwp-fr/common/documents/FP_LGWP_FR_Honeywell-HFO-1234ze_Literature_document.pdf

of 138) in aerosol applications and thermal insulating foams, including extruded polystyrene board and polyurethane foams."[71]

4. Use

Our review of the trade, production, and releases of carbon tetrachloride identified many uses of carbon tetrachloride that are not included in the February 2017 EPA information document. An internet search for product safety data sheets and other literature listing carbon tetrachloride identified additional uses in products and chemical manufacturing processes (Table 2).

The most significant new use of carbon tetrachloride is in HFO refrigerants and blowing agents. CCl_4 is used in production of the leading commercialized HFOs, HFO-1234yf and HFO-1234ze. Exponential growth is underway, and we are already seeing increases in carbon tetrachloride imports (Chemours) and toxic releases (Honeywell).

Table 2. Carbon tetrachloride historical uses or uses not listed in EPA Preliminary Information (highlighted fields are new or more specific information)

Uses	CDR reports (2012 - 2015)	Listed in EPA Use Profile (2017)	Historic (sources)	Current (sources)
Products				
Lava lamps	no	no	Doherty	
Trapylen 777 (Tramco, Germany) plastic parts primer	no	no		P.A.T. products (above)
Residual in medicine	no	no	FDA; USPC	
Chemical Processes				
Intermediate in chlorinated paraffin manufacture	no	no		See Dover Chemical and Ineos

[71] https://www.honeywell.com/newsroom/pressreleases/2015/01/honeywell-starts-full-scale-production-of-low-global-warming-propellant-insulating-agent-and-refrigerant

Reactant in HFC-227ea production	no	no		See Chemours
Reactant in HFO-1234yf and HFO-1234ze production	no	no		See Chemours and Honeywell
Feedstock for production of hydrochloric acid	no	no		Touchdown. See also Dow - Pittsburg CA.
Chlorinated pyridine byproduct	no	no		See Dow - Pittsburg CA
Feedstock for 1,1,1,3,3-pentachlorobutane	no	no		Touchdown
Aluminum trichloride production	no	no		Touchdown
Polyfunctional aziridine production	no	no		Polyaziridine LLC
Methyldichlorophosphane production	no	no		Touchdown
Synthetic pyrethroids production, including the pesticide, cypermethrin	no	no		Touchdown. See also Syngenta.
Triamcinolone benetonide production	no	no		Touchdown
Polyol production	no	no	PU	
Chlorine waste gas recovery inchlor-alkali production	no	no	See Westlake	
Nitrogen trichloride elimination in chlor-alkali production	no	no	See Westlake	

Sources:

Doherty. Doherty RE. A History of the Production and Use of Carbon Tetrachloride, Tetrachloroethylene, Trichloroethylene and 1,1,1-Trichloroethane in the United States: Part 1-Historical Background; Carbon Tetrachloride and Tetrachloroethylene. Environ Forensics. 2000;1:69–81.

FDA. FDA lists carbon tetrachloride as a solvent that may occur in some medications. Federal Register Vol. 57, No.178 / Monday, September 14, 1992 , p. 42404.

Honeywell. https://www.google.com/patents/US20130211156

PU. Ionescu, Mihail, Chemistry and Technology of Polyols for Polyurethanes, iSmithers Rapra Publishing, 2005.

Touchdown. Miller, Melanie, and Tom Batchelor. “Feedstock Uses of ODS: Information Paper on Feedstock Uses of Ozone-Depleting Substances.” Touchdown Consulting, December 2012. https://ec.europa.eu/clima/sites/clima/files/ozone/docs/feedstock_en.pdf.

USPC. The U.S. Pharmacopeial Convention limits CCl4 residual to 4 ppm. https://www.usp.org/sites/default/files/usp_pdf/EN/USPNF/generalChapter467Current.pdf

5. End of Life

Outside the chemical industry, waste disposal companies account for the balance of carbon tetrachloride releases reported in the Toxics Release Inventory.

Table 3. Carbon Tetrachloride Releases from Disposal, 2012-2015 (top five)

Company	Location	Type	CCl_4 Releases (lbs./year)
Chemical Waste Management	Arlington, OR	Landfill[72]	6,508
Chemtron Corp.	Avon, OH	Recycling and Disposal[73]	589
Clean Harbors	Kimball, NE	Incinerator[74]	505
Giant Cement Co.	Harleyville, SC	Cement kiln[75]	373
Clean Harbors	Grantsville, UT	Incinerator[76]	103

Source: Toxics Release Inventory

6. Potentially Vulnerable Populations / Exposure Scenarios

A. Production Emissions

Workplace releases are a primary pathway for human health impacts. The ATSDR warns:

> "People who work with carbon tetrachloride are likely to receive the greatest exposure to the compound. The National Institute for Occupational Safety and Health (NIOSH) estimates that 58,208 workers are potentially exposed to carbon tetrachloride in the United States."[77]

Accidental releases can also harm workers.[78]

The potential scale of this exposure is poorly understood. A July 2016 report from SPARC, identified many processes that can generate emissions, such as incineration, feedstock usage, the production of chlorine and chloromethanes production, and even the domestic use of

[72] https://www.wmsolutions.com/pdf/factsheet/CWM_Arlington.pdf
[73] http://www.chemtron-corp.com/index_files/ServicesVideo.html
[74] http://www.cleanharbors.com/location/kimball-incineration-facility
[75] http://www.giantcement.com/History.html
[76] http://www.cleanharbors.com/location/aragonite-incineration-facility
[77] https://www.atsdr.cdc.gov/toxprofiles/tp30-c1-b.pdf
[78] https://www.osha.gov/pls/imis/accidentsearch.accident_detail?id=14409049

chlorine bleach. They found: "This is due to the relative ease with which hydrocarbons are chlorinated; thus, CCl_4 may be formed in many chlorination procedures and released into the environment, atmosphere, or surface water."[79]

B. Wastewater Releases / Soil

Wastewater from carbon tetrachloride production can contain chloromethanes and chlorinated solvents like TCE and PCE.[80]

ATSDR (2005) notes exposure to contaminated soils and water sources as a pathway for exposure, particularly around industrial sites.

> "Exposure to levels of carbon tetrachloride higher than these typical 'background' levels is likely to occur only at specific industrial locations where carbon tetrachloride is still used or near chemical waste sites where emissions into air, water, or soil are not properly controlled. Exposure at such sites could occur by breathing carbon tetrachloride present in the air, by drinking water contaminated with carbon tetrachloride, or by getting soil contaminated with carbon tetrachloride on the skin. Young children may also be exposed if they eat soil that contains carbon tetrachloride. Carbon tetrachloride has been found in water or soil at about 26% of the waste sites investigated under Superfund, at concentrations ranging from less than 50 to over 1,000 ppb."

C. Residuals in Products

Carbon tetrachloride can be transferred through the chlorine production chain into chemicals, resins and, ultimately products. In test data supplied to EPA by the Vinyl Institute in 2010, resin manufactured by PolyOne Corporation in Henry, Illinois was found to contain CCl_4 at up to 0.3 parts per million in the PVC resin.[81] A material safety data sheet for chloroparaffin supplied by Santa Cruz Biotechnology states that it may contain a residual proportion of carbon tetrachloride as high as one percent.[82]

D. Ozone Depletion

In 2002, UNEP observed that rates of change in the amount of ozone-depleting gases in the atmosphere were fairly constant at about -1%/year since 1993. Despite phaseouts of most

[79] https://www.wcrp-climate.org/WCRP-publications/2016/SPARC_Report7_2016.pdf
[80] https://www.epa.gov/sites/production/files/2015-11/documents/2004_effluent-guidelines-plan_tsd.pdf
[81] PVC Industry Resin Concentration Data Aggregation for EPA, Vinyl Institute, Sept. 28, 2010 (spreadsheet)
[82] Chloroparaffin sc-234341 Material Safety Data Sheet, Santa Cruz Biotechnology, Nov. 9, 2011

chemicals with high ozone depletion potential, observations taken from 2002 to 2011 showed a similar rate of decline (-1.1%/year). CCl_4 has an atmospheric life of 50 years.

A recent study concludes that these trend lines are "not consistent with the phase-out schedule of 1996… (and) is likely to be due to fugitive emissions of CCl_4."[83]

Production figures are no more promising than the trend lines: a 2012 study commissioned by the European Union found that the total production of CCl4, 1,1,1-trichloroethane, CFCs and HCFCs for feedstock "more than tripled since 1991." In the year 2010, over one million tons of ozone depleting substances were reportedly produced for feedstock, up from 312,000 in 1991.

The famous phase-out of ODS's like carbon tetrachloride, CFCs, and HCFCs codified in the Montreal Protocol exempted their use as chemical feedstocks. The 1995 phase-out codified this exemption with an assumption (that turned out to be a fiction) that "emission to the atmosphere does not occur" when ozone-depleting substances are used as chemical feedstocks.

A report prepared for the European Community, dated October 1984, long before parties to the Montreal Protocol created this loophole, details the airborne release of carbon tetrachloride from chemical production facilities. Most of the CCl_4 at the time fed the production of CFC-11 and CFC-12 chlorofluorocarbons. These processes routinely discharged CCl_4 to the aquatic environment from which CCl_4 is "readily lost in the atmosphere." This report identified levels of carbon tetrachloride as high as 86 micrograms per cubic meter in the air near areas of manufacture.[84]

The misinformation about carbon tetrachloride feedstock emissions can be traced to a document published seven years after that European Commission study: the UNEP Solvents, Coatings and Adhesives Technical Options Report of 1991. The authors of this report were committee members affiliated with a cross-section of private corporations, non-profit organizations, and governmental agencies. But at least two-thirds represented private industry, including the leading ozone-depleting chemical manufacturers of the time. One of the representatives was from Vulcan Chemicals, the only company that intentionally produced

[83] M. Maione et al., "Ten years of continuous observations of stratospheric ozone depleting gases at Monte Cimone (Italy) – Comments on the effectiveness of the Montreal Protocol from a regional perspective," Science of the Total Environment 445-446 (2013) 155-164.

[84] J. Dequinze, C. Scimar, F. Edeline, "Identification of the substances and their derived products, on the list of 129 substances (list 1 of the directive 76/464/EEC). Present in the refuse of chlorine derived organic chemistry industry," Prepared for the Commission of the European Communities Environment and Consumer Protection Service," Contract No. U/83/205, October 1984.

carbon tetrachloride in the US, as well as Allied-Signal (now part of Honeywell, which releases CCl_4 from its HFC and HFO plant). Dow and DuPont also sat on this influential committee.

The origins of the feedstock loophole are found on page 454, in an annex on the production of carbon tetrachloride. It is written, without citation:

> *World CCl_4 production in 1989 was estimated to be 750,000 tonnes from voluntary manufacture. This production of CCl_4 will cease as CFC production is phased out. Involuntary CCl_4 production where CCl_4 arises as a byproduct will continue. In these cases, CCl_4* ***can be completely destroyed*** *or recycled. Current estimated involuntary production worldwide is about 140,000 tonnes per annum, although the majority of this is isolated from the production process. A small quantity of CCl4 diverted from the involuntary production will continue to be used in applications where it* ***can be completely destroyed****. These include:*
>
> - *As a chemical feedstock*
> - *As a catalyst*
> - *For the stabilisation of sulfur trioxide*
>
> *Total usage in these areas will be about 5,000 tonnes per annum but this should be substantially reduced over the next 5 years.*[85] *(emphasis added)*

In 2015, as noted earlier, the total production of carbon tetrachloride in the United States alone was 63,000 tons. Far from “completely destroyed,” that’s more than ten times higher than what the committee predicted for the entire planet. The same companies that promised carbon tetrachloride’s demise are capitalizing on the revival of this zombie chemical.

[85] UNEP Solvents, Coatings and Adhesives Technical Options Report of 1991

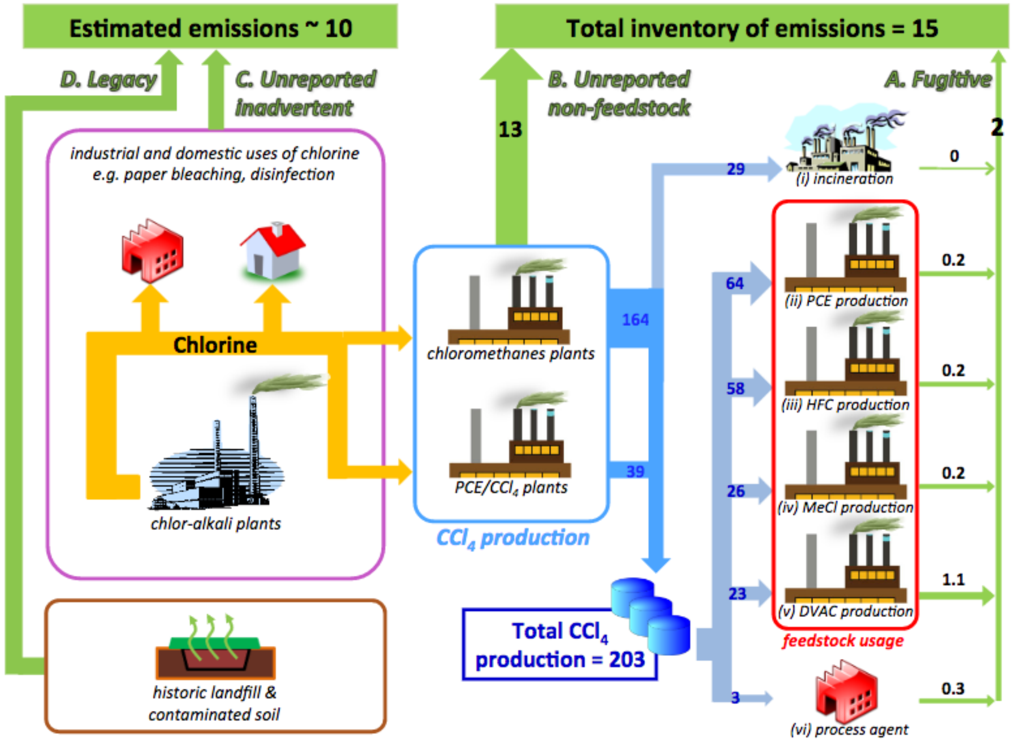

***Figure 12:** Schematic of CCl_4 routes from pre-CCl_4 production of chlorine gas in chlor-alkali plants (left), and production (middle), usage (right), and emissions of CCl_4 (top) (in Gg). Production and use of chlorine gas are shown in yellow arrows. The numbers are 2014 estimates for industry production (blue box and arrows) and use (greyish blue arrows), and emissions of CCl_4 (green boxes and arrows, see **Table 2**). All numbers currently included in UNEP reports are shown in blue, and the ones that are not reported to UNEP are given in black. This 2014 estimate of 203 Gg is in close agreement with reports to UNEP from the Parties to the MP of 200 Gg in 2013. Feedstock uses are outlined in red: ii. PCE is perchloroethylene, iii. HFC is hydrofluorocarbon, iv. MeCl is methyl chloride, and v. DVAC is divinyl acid chloride. Estimates are courtesy of Dr. David Sherry (Nolan Sherry & Associates). More information is available in **Appendix A**. The global legacy emissions from decommissioned industrial sites and landfills as well as unreported inadvertent emissions from the production and use of chlorine gas are estimated based on results from Fraser et al. [2014].*

GRAPHIC REPRODUCED FROM **SPARC REPORT**

Appendix.
Health and Environmental Hazards Associated with Carbon Tetrachloride

Hazards taken from Pharos CML, February 24, 2017
Hazards associated with CAS: 56-23-5
Purple hazards are of urgent concern to avoid; Red are very high concern to avoid; Orange are high concern to avoid. More details on hazards and hazard levels here.

Hazard and Level	Sources
Human Health Hazards	
Cancer	➢ US EPA - IRIS Carcinogens - (2005) Likely to be Carcinogenic to humans ➢ US NIH - Report on Carcinogens - Reasonably Anticipated to be Human Carcinogen ➢ CA EPA - Prop 65 - Carcinogen ➢ US CDC - Occupational Carcinogens - Occupational Carcinogen ➢ US EPA - PPT Chemical Action Plans - Probable human carcinogen - TSCA Criteria met
Cancer	➢ IARC - Group 2B - Possibly carcinogenic to humans ➢ EU - GHS (H-Statements) - H351 - Suspected of causing cancer ➢ MAK - Carcinogen Group 4 - Non-genotoxic carcinogen with low risk under MAK/BAT levels ➢ EU - Annex VI CMRs - Carcinogen Category 2 - Suspected human Carcinogen ➢ New Zealand - GHS - 6.7B - Suspected human carcinogens ➢ Japan - GHS - Carcinogenicity - Category 2 ➢ EU - R-phrases - R40 - Limited Evidence of Carcinogenic Effects ➢ Korea - GHS - Carcinogenicity - Category 2 [H351 - Suspected of causing cancer] ➢ Australia - GHS - H351 - Suspected of causing cancer
Developmental	➢ MAK - Pregnancy Risk Group C
Reproductive	➢ Japan - GHS - Toxic to reproduction - Category 2
Endocrine	➢ TEDX - Potential Endocrine Disruptors - Potential Endocrine Disruptor
Mammalian	➢ EU - GHS (H-Statements) - H311 - Toxic in contact with skin ➢ Québec CSST - WHMIS 1988 - Class D1A - Very toxic material causing immediate and serious toxic effects ➢ New Zealand - GHS - 6.1B (inhalation) - Acutely toxic ➢ Korea - GHS - Acute toxicity (oral) - Category 3 [H301 - Toxic if swallowed] ➢ Korea - GHS - Acute toxicity (dermal) - Category 3 [H311 - Toxic in contact with skin] ➢ Korea - GHS - Acute toxicity (inhalation) - Category 3 [H331 - Toxic if inhaled] ➢ Australia - GHS - H311 - Toxic in contact with skin
Eye Irritation	➢ Japan - GHS - Serious eye damage / eye irritation - Category 2A
Skin Irritation	➢ Japan - GHS - Skin corrosion / irritation - Category 2
Organ Toxicant	➢ EU - GHS (H-Statements) - H372 - Causes damage to organs through prolonged or repeated exposure ➢ New Zealand - GHS - 6.9A (inhalation) - Toxic to human target organs or systems (Cat. 1) ➢ New Zealand - GHS - 6.9A (oral) - Toxic to human target organs or systems (Cat. 1)

	➢ EU - R-phrases - R48: Danger of serious damage to health by prolonged exposure. ➢ Japan - GHS - Specific target organs/systemic toxicity following repeated exposure - Category 1 ➢ Korea - GHS - Specific target organ toxicity - Repeated exposure - Category 1 [H372 - Causes damage to organs through prolonged or repeated exposure] ➢ Japan - GHS - Specific target organs/systemic toxicity following single exposure - Category 1 ➢ Australia - GHS - H372 - Causes damage to organs through prolonged or repeated exposure ➢ Japan - GHS - Specific target organs/systemic toxicity following single exposure - Category 1-2
Environmental Hazards	
Ozone Depletion	➢ US EPA - Ozone Depleting Substances - Ozone-depleting substances - Class I ODP greater than 0.2 ➢ EU - Ozone depletion substances - Annex I Group IV & VI: Carbon tetrachloride& Methyl Bromide - ODP 0.6 and above
Ozone Depletion	➢ EU - GHS (H-Statements) - H420 - Hazardous to the Ozone Layer (formerly EUH059) ➢ EU - R-phrases - R59: Dangerous for the ozone layer. ➢ Australia - GHS - H420 - Hazardous to the Ozone Layer (formerly EUH059) ➢ Japan - GHS - Hazardous to the ozone layer - Category 1
Global Warming	➢ US EPA - Global Warming Potentials - Global Warming Potential greater than 1,000
Acute Aquatic	➢ Japan - GHS - Hazardous to the aquatic environment (acute) - Category 1 ➢ Korea - GHS - Hazardous to the aquatic environment (acute) - Category 1 [H400 - Very toxic to aquatic life]
Chronic Aquatic	➢ Japan - GHS - Hazardous to the aquatic environment (chronic) - Category 1

Docket ID Number: EPA-HQ-OPPT-2016-0733

Consumer Appendix

Consumer Products Containing Carbon Tetrachloride

Introduction. Below is a list of products sold on retail websites, and thus available for purchase by consumers, that have been verified to contain carbon tetrachloride (CTC) (CASRN 56-23-5) from Material Safety Data Sheets (MSDSs) or Safety Data Sheets (SDSs).

Methodology. Safer Chemicals, Healthy Families staff searched via Google for MSDSs and SDSs referring to "56-23-5," including key words for relevant product types, and then confirmed the products are sold on websites such as www.amazon.com or www.walmart.com. Additionally, we reviewed the lists of products in EPA's February 2017 "Preliminary Information on Manufacturing, Processing, Distribution, Use, and Disposal" for CTC to determine which products are sold on retail websites. An asterisk means the product is on EPA's February 2017 list.

Notes. The product descriptions quoted below are from the seller's website, unless otherwise noted. Safer Chemicals, Healthy Families has not verified the accuracy of the product descriptions.

ADHESIVES

➢ ***Devcon Zip Patch****

Product Description:
". . . cures at room temperature and makes permanent, waterproof field repairs to pipes, tanks and containers. High technology, adhesive-impregnated patching system is easy-to-use . . ."

Sold At: https://www.amazon.com/Devcon-11500-Brown-Adhesive-Coverage/dp/B001RSTPYQ & https://www.walmart.com/ip/Devcon-Zip-Patch-zip-patch-kit-old-72250must-ship-m/19296470

Contains 0.1-1% CTC by weight, according to the 2015 SDS: http://www.devcon.com/prodfiles/pdfs/sku_msds_66.pdf

➢ ***Loctite Epoxy Plastic Bonder****

Product Description:
". . . is an acrylic formula that is specially formulated to bond and repair plastic surfaces."

Sold At: https://www.amazon.com/Loctite-Plastic-0-85-Fluid-Syringe-1363118/dp/B0044FBB8C/

Contains 0.1-1% CTC, according to the SDS for Part A available here: http://www.loctiteproducts.com/techdata-msds.shtml#

- ***Permatex MotoSeal Ultimate Gasket Maker Grey****

Product Description:
"... forms a tough flexible bond that is highly effective on irregular and uneven joint surfaces. Ideal for use on frequently disassembled engines and two and four cycle engines."

Sold At: https://www.amazon.com/Permatex-29132-MotoSeal-Ultimate-Gasket/dp/B000HBGHKE

Contains 0.1-1% CTC by weight, according to the SDS: https://www.permatex.com/wp-content/uploads/tech_docs/sds/01_USA-English/29132.pdf

- ***SEM Patch Panel Adhesive***

Product Description from SEM:
" . . a two-component adhesive for quickly bonding metal panels without the use of an external primer."

Sold At: https://www.walmart.com/ip/SEM-PRODUCTS-39897-PATCH-PANEL-ADHESIVE/108856532

Contains ≤1% CTC by weight, according to the SDS available here: https://www.semproducts.com/oem-recommended-panel-bonding-adhesives/dual-mixtm-patch-panel-adhesive

- ***SEM Weld Bond Adhesive****

About This Item:
"a non-sag, two-component methacrylate adhesive system formulated to bond metal surfaces without the use of an external primer"

Sold At: https://www.walmart.com/ip/SEM-PRODUCTS-39537-WELD-BOND-ADHAESIVE/112064302

Contains ≤1% CTC by weight, according to the SDS:

https://www.semproducts.com/manage/html/public/conte nt/msds/39537%20Weld%20Bond%20AdhesiveUSA.pdf

MISCELLANEOUS

- **Dollhouse Miniature Glass Bottle of "Vintage Carbon Tetrachloride Poison"**

Product Description:
"Glass Bottle of 'Vintage Carbon Tetrachloride Poison' made of real glass with a faux vintage label."

Sold At: https://www.amazon.com/Dollhouse-Miniature-Bottle-Vintage-Tetrachloride/dp/B00TIS61K8

No MSDS available. EPA should verify whether this product contains any real carbon tetrachloride poison.