Supporting Information

An inventory of fluorspar production, industrial use, and emissions of trifluoroacetic acid (TFA) in the period 1930 to 1999

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The derivation of all the data in paper-Table 1. Inventory: Summary of production and consumption of fluorspar and TFA emissions 1930-1999 is in this supporting information. Further information is provided for fluoride mineral production and consumption, aluminium production, and other uses of HF not resulting in TFA formation.

The information here is the cumulative calcium fluoride consumption and TFA emissions for the applications in paper Table 1. Figures 1, 2 and 3 in the paper show annual TFA emissions and CaF_2 consumption compiled from the referenced data sources for each of the applications included. Also included is Figure S1 showing global fluorspar production by grade.

Contents

1   Production of fluorspar and other fluoride minerals

Currently about 60-65% of the global production is acid grade (> 97% purity) used mainly to make anhydrous HF. There are numerous applications for HF, with fluorochemicals and aluminium production being the main uses. Other significant uses of HF are chemical derivatives, pickling of stainless steel, alkylation catalyst for petroleum and processing of uranium.   Metallurgical grade fluorspar has a calcium fluoride content typically > 80%, but it can be as low as 60%, depending on requirement. Metspar is currently about 35-40% of global production and is used mainly as a flux for manufacture of steel. Ceramics grade may be defined as a separate grade to metspar, although purity requirements are similar. All ceramic grade uses are inorganic (ceramic, glass and enamel) and for this inventory there is no requirement to discuss it in any detail and it is included in metspar production. Data are available for global production of fluorspar prior to 1930 (Hamrick& Voskuil,1949). Overall, by around 2000 in the USA about 60% of the calcium fluoride produced was used by the fluorochemicals industry (Agency for Toxic Substances and Disease Registry, 2003).

The trend for increasing production of acid spar and its percentage of total fluorspar production changed significantly in the period 1930 to 1999, with the development of the fluorochemicals industry based on HF. The reduction in global production of fluorspar from 1990 to 1994 was driven by the phase-out of CFCs. Demand for fluorspar and production then increased as alternatives to CFCs were introduced, and China expanded its fluorochemicals production. Chart S1 shows the production of acidspar and metspar/ceramic grade fluorspar from 1930 to 1999.
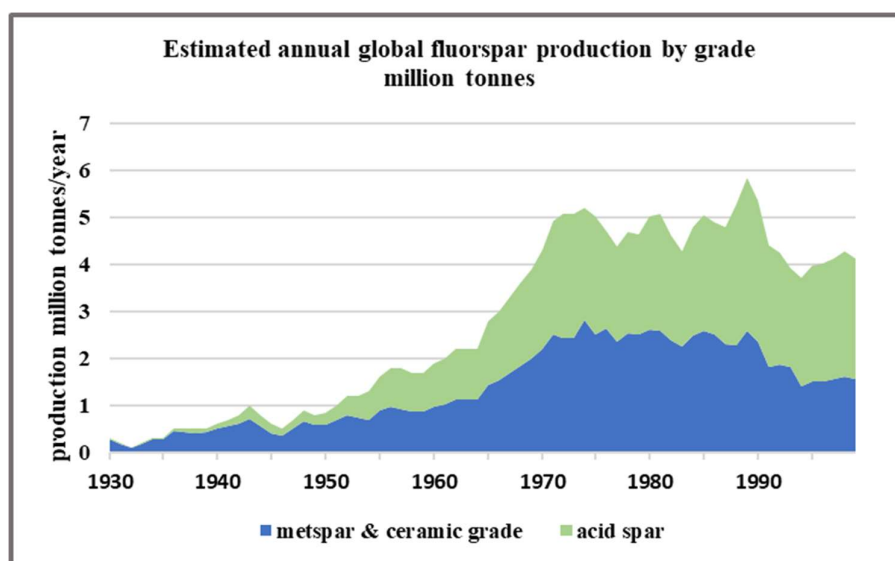
Figure S1. Global production of fluorspar by grade 1930 to 1999

1.1   Cryolite

Cryolite mineral (sodium hexafluoroaluminate Na_3AlF_6) was commercially mined in Greenland from the mid-19th to mid-20th century. The June 1963 issue of World Mining announced that the ore body had been mined out (Berry, 2013), although tailings and spoil heaps continued to be worked. Mining for cryolite from 1854 to 1987 in Greenland resulted in 3.7 million tonnes of ore with an average content of 58% cryolite in the ore (Geological Survey of Denmark and Greenland, 2002), although production of 3.8 million tonnes of cryolite was recorded by the Greenland Geology Survey Department (International Mining, 2021). The consumption of natural cryolite for aluminium production is discussed in the section on aluminium. Synthetic or artificial cryolite is made from fluorspar and is used in the electrolytic production of aluminium and other metallurgical applications. Natural cryolite was also reported to be used as an abrasive and insecticide.

1.2   Fluorapatite

Fluorapatite ($Ca_5(PO_4)_3F$) is mined along with other apatites for its phosphate content and is used mostly to produce fertilizers. Most of the Earth's fluorine is bound in this mineral, but because the percentage within the mineral is low (3.5%), the fluorine historically was mainly discarded as waste. Only in the United States was

there significant recovery. To supplement fluorspar supplies, fluorosilicic acid is recovered from phosphoric acid plants processing phosphate rock in the United States. In 2001, 65,200 tonnes of fluorosilicic acid (equivalent to 104,000 tonnes of fluorspar) were produced as a by-product. About 41,200, 4,700, and 13,200 tonnes of fluorosilicic acid were sold for water fluoridation, AlF_3 production for the aluminium industry, and for other uses, such as sodium silicofluoride production, respectively. The chemicals most used by American waterworks for water fluoridation are fluorosilicic acid, sodium silicofluoride, and sodium fluoride. Fluorosilicic acid, as a 1–2% solution, is used widely for sterilizing equipment in brewing and bottling. Other concentrations of fluorosilicic acid solutions are used in electrolytic refining of lead, in electroplating, for hardening cement, for crumbling lime or brick work, for removal of lime from hides during the tanning process, for removals of molds, and as a preservative for timber. Sodium fluorosilicate is also used in enamel glazing of china and porcelain, in the manufacturing of opal glass, as an insecticide, as a rodenticide, and for mothproofing of wool (Agency for Toxic Substances and Disease Registry, 2003). The consumption of fluorosilicic acid by the primary aluminium industry is discussed in the section on aluminium.

1.3   HF production yield from acid spar

Anhydrous HF is produced from acid spar by reaction with concentrated sulphuric acid. Acid spar has a minimum purity of 97%. Typical specifications are < 1.5% $CaCO_3$, < 1% SiO_2, < 0.03- 0.1% S, 10-12 ppm As, < 100-550 ppm Pb. Silica (SiO_2) decreases the yield of HF due to the formation of SiF_4. There are stringent limits on the sulphur, arsenic and phosphorus contents (British Geological Survey, 2011). The yield of HF from acid spar has increased since the 1930s as the manufacturing process has improved. Table S1 contains the yield of HF from acid spar by decade based on available information.
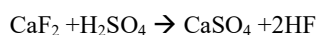
$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

Table S1. Yield of HF from acid spar and accounting for fluoride losses

	Tonnes of acid spar per tonne HF	Yield from acid spar assuming 97.5% spar purity	References
1930s	2.8	71%	Assumed the same as the 1940s
1940s	2.8	71%	Calculated from reported 1944 US fluorspar consumption for HF and production data for HF For 1944, 2.83 tonnes of fluorspar per tonne of HF production is calculated from the reported fluorspar use and HF production (Hamrick & Voskuil, 1949).
1950s	2.4	83%	Assumed to be the same as value reported for 1960s
1960s	2.3	87%	"About 2.4 tons of acid spar is required to produce a ton of HF, according to the U.S. Bureau of Mines; however, it is suspected that some plants may use approximately 2.2 tons, and recent technological advances may lower the figure still further." (Bradbury, Finger, & Major, 1968). Therefore, use rate of 2.3 tonnes is assumed
1970s	2.2	91%	From United States Bureau of Mines (1976).
1980s	2.15	93%	Industry expert estimate
1990s	2.15	93%	Industry expert estimate
Overall acid spar consumption & HF yield 1930-99	95.0 million tonnes	Weighted average yield 1930-99 91%	
Accounting for losses due to HF yield from acid spar purity (97.5%)		8.9 million tonnes	
Overall availability of HF as CaF_2 equivalent		86.1 million tonnes	

Explanatory note: Yield is applied for all HF production within a decade, except that the 1950s yield data are also applied to years 1945 to 1949, in the absence of other data. This has very minimal effect on the overall inventory.

2 Estimated calcium fluoride consumption and TFA emissions for all applications listed in paper-Table 1

2.1 Chlorofluorocarbons (CFCs)

AFEAS compiled annual production data for reporting companies from 1931 for the main CFCs: 11,12, 113, 114 and 115 (AFEAS, 2000; 2003). According to industry experts, the fluoride efficiency for CFC-11 and 12 production is estimated at 97% and for CFC-113,114 and 115 it is 95%. The AFEAS data excludes Chinese CFC production. Therefore, the annual production for CFC-11 and CFC-12 also considers more comprehensive data in the TEAP Report on Unexpected Emissions of CFC-11 (TEAP, 2019). Data on the production of CFC-113,114 and 115 will be an underestimate because of the absence of Chinese production data. The data collected by AFEAS for 2000 are estimated (by comparison with UNEP totals) to represent about 30% of global CFC production. Accounting for fluoride efficiencies, the CaF_2 required to produce the CFCs in the period 1930 to 1999 are shown in the table. TFA is not a breakdown product of CFCs. Table S2 has cumulative production of CFCs and required calcium fluoride consumption.

Table S2. Cumulative CFC production 1930 to 1999 and required calcium fluoride use

	Cumulative production (kilotonnes)	Calcium fluoride equivalent (million tonnes)	CFC Production comments
CFC-11	9700	2.8	1935-99 estimate
CFC-12	13,100	8.7	1931-99 estimate
CFC-113,114,115	3780	3.1	AFEAS data excludes Chinese production CFC-113: 1944-99 CFC-114: 1934-99 CFC-115: 1964-99
Total CaF₂		**14.6**	

2.2 Hydrofluorochlorocarbons (HCFCs) - non-feedstock uses

AFEAS production data are available for most of the major commercial HCFCs, except HCFC-123. For HCFC-123 the available emissions data are assumed to equal production however this will be an underestimate. In 2000, the AFEAS data accounts for more than 93% of all non-feedstock HCFC production.

Table S3. Cumulative HCFC (non-feedstock) production to 1999, required calcium fluoride use and TFA emissions.

	Cumulative production (kilotonnes)	Calcium fluoride equivalent (million tonnes)	HCFC Production comments
HCFC-22 non-feedstock	5200	5.0	1943-99 (AFEAS,2003)
HCFC-123, 124, 141b, 142b	1200	0.6	HCFC-123: estimate for emissions (McCulloch,2006) not production. HCFC-124: 1991-99 AFEAS HCFC-141b: 1990-99 AFEAS HCFC-142b: 1981-99 AFEAS
Total CaF₂		**5.6**	
TFA emissions	(tonnes)	**TFA emissions comments**	
HCFC-123	7400	From reported emissions, 60% TFA yield (EEAP, 2022), 1.3 yrs atmospheric lifetime (IPCC, 2021) AR6 values.	
HCFC-124	8700	From reported emissions, (Simmonds et al., 2017) 100% TFA yield (EEAP, 2022), 5.9 yrs atmospheric lifetime (AR6)	
Total TFA tonnes	**16,100**		

According to industry experts, the fluoride efficiency for HCFC-22 is estimated at 94%, in part due to formation of HFC-23 as a by-product. For the other HCFCs it is 97%. Accounting for fluoride efficiencies, the CaF_2 required to produce the HCFCs in the period 1943 to 1999 are shown in Table S3. TFA is a breakdown product of HCFC-123 and HCFC-124. The quantity of TFA formed from each substance in the period up to 1999 depends on the substance emissions, its atmospheric lifetime and TFA yield. Emissions of the major HCFCs and HFCs are well characterised either by atmospheric measurements (top-down) or from production, use and emission factors (bottom-up, e.g. AFEAS data). Table S3 has cumulative production of HCFCs (non-feedstock), required calcium fluoride consumption and estimated TFA emissions.

2.3 Hydrofluorocarbons (HFCs)

AFEAS production data are available and in 2000 is thought to represent about 98% of global HFC-134a production. For HFC-125 and HFC-143a, production has been estimated from reported emissions.

Table S4. Cumulative HFC production to 1999, required calcium fluoride use and TFA emissions

	Cumulative production (kilotonnes)	Calcium fluoride equivalent (million tonnes)	HFC production comments
HFC-134a	585	0.9	1990-99 (AFEAS, 2003)
HFC-125,143a	123	0.2	Only emissions data available production assumed to be 2.5 times emissions for HFC-125 (Simmonds et al., 2017) and 2 times emissions for HFC-143a (O'Doherty et al.,2014)
Total CaF₂		**1.1**	
TFA emissions	**(tonnes)**	**TFA emissions comments**	
HFC-134a	**6400**	From reported emissions (Fortems-Cheiney, 2015), 14% TFA yield (Luecken et al., 2010; Wallington et al., 1996), 14 yrs atmospheric lifetime (AR6)	
HFC-227ea	**200**	From reported emissions, (Vollmer et al., 2011) 100% TFA yield (World Meteorological Organization, 2010) 36 yrs atmospheric lifetime (AR6)	
HFC-143a	**80**	From reported emissions, 2% TFA yield (EEAP, 2022), 51 yrs atmospheric lifetime (AR6)	
HFC-125	**20**	From reported emissions, 1% TFA yield (EEAP, 2022), 30 yrs atmospheric lifetime (AR6)	
Total TFA tonnes	**6700**		

According to industry experts, the fluoride efficiency for these HFCs is estimated at 97%, Accounting for fluoride efficiencies, the CaF_2 required to produce the HFCs in the period up to 1999 are shown in the table. According to the TEAP HFC PFC (1999) task force report (page 94) commercial introduction was not expected before 2002 for HFC-365mfc and HFC-245fa so these are not relevant in the period up to 1999. TFA is a breakdown product of HFC-134a, HFC-227ea, HFC-143a and HFC-125. Table S4 has cumulative HFC production, required calcium fluoride and TFA emissions.

2.4 Anaesthetics

Halothane was first used clinically in 1956 and isoflurane was introduced into clinical use in 1981 (Crystal, 2017), with estimated annual global emissions of 750 tonnes in 2002 (Wallington et al., 2002). Desflurane was introduced in 1987 and sevoflurane in 1995. By 1995 the annual production of halothane was estimated as a maximum of 1500 tonnes globally (Boutonnet et al., 1999). In 2008, annual production of volatile anaesthetics was estimated to be well over 2,000 tonnes (Terrell & Warner, 2008). Use of halothane declined, as it was replaced by newer anaesthetics and 2014 global emissions of these four anaesthetics was about 3300 tonnes (Vollmer et al., 2015), with desflurane accounting for 960 tonnes. From these reports, anaesthetic production, calcium fluoride consumption and TFA emissions can be estimated and are shown in Table S5.

Table S5. Cumulative anaesthetic production, required calcium fluoride use and TFA emissions until 1999

	Cumulative production (tonnes)	Calcium fluoride equivalent (tonnes)	Anaesthetic production comments
Halothane	52,000	34,000	Fluoride efficiency 90% based on side reactions
Isoflurane, Sevoflurane, Desflurane	19,500	26,000	Fluoride efficiency of 90% is assumed
Total CaF$_2$		**60,000**	
TFA emissions	(tonnes)		**TFA emissions comments**
Halothane	18,000		Emissions equal production, 60% TFA yield (Boutonnet et al., 1999) atmospheric lifetime 1 year (AR6)
Isoflurane	5500		Emissions equal production, 95% TFA yield (EEAP,2022), atmospheric lifetime 3.5 years (AR6)
Sevoflurane	30		Emissions equal production, 2% TFA yield (EEAP, 2022), atmospheric lifetime 1.9 years (AR6)
Desflurane	30		Emissions equal production, 3% TFA yield (Sulbaek Andersen et al., 2012), atmospheric lifetime 14.1 years (World Meteorological Organization, 2018).
Total TFA tonnes	**23,600**		

2.5 Trifluoroacetic acid manufacture

Trifluoroacetic acid became available in commercial quantities in 1962 in the USA, supplied in 80 pounds carboys (about 36.3 kg). The acid was claimed to be useful in a wide range of applications from an acid catalyst to a zein (protein) solvent (United States Bureau of Mines, 1962). The reported USA productions ranges for the years from 1986 are in Table S6. Data is not publicly available for the USA for production quantities before 1986 (PubChem, 2023).

Table S6. Reported US production ranges for trifluoroacetic acid (TFA)

Year	pounds	tonnes
1986	10 thousand - 500 thousand	4.5 to 227 tonnes
1990	10 thousand - 500 thousand	4.5 to 227 tonnes
1994	10 thousand - 500 thousand	4.5 to 227 tonnes
1998	> 1 million - 10 million	453 to 4536 tonnes
2002	> 1 million - 10 million	453 to 4536 tonnes

The production ranges reported for the USA in the 1990s are consistent with the total quantity manufactured in the 1990s according to the estimate in Boutonnet et al, 1999. *"According to (Elliott, 1994) trifluoroacetic acid is manufactured by only three companies: Halocarbon Products Corporation in the United States, and Rhône-Poulenc and Solvay in Europe. The quantities involved are relatively small — of the order of 1000 metric tons per year (J. Franklin, personal communication), an estimate that is consistent with the quoted revenue of the major U.S. producer."* According to Boutonnet et al, in the 1990s, TFA was widely used in the fine chemicals industry and as a laboratory reagent: for derivatizing carbohydrates, amino acids and peptides; as a catalyst in esterification reactions and the Beckmann rearrangement of oximes to amides, and for protein synthesis.

According to a market research report (publicly available summary), production of TFA has increased and is now produced in China, North America, Europe and India, with global production about 21,000 tonnes in 2012, estimated as 26,000 tonnes in 2017 and 34,000 tonnes in 2023. China's output is reported as about 8,000 tonnes in 2012 and about 12,000 tonnes in 2017 (Pmarketresearch, 2021). The timing of the start of TFA manufacture in China is not available, but it is known that large scale PFOA and PFAS production commenced in 2003 (Li et al., 2021), and that China gradually moved downstream from fluorspar to HF to fluorochemicals from the 1990s. Therefore, an estimate of trifluoroacetic acid production in the period until 1999 is highly uncertain.

For both production and use of TFA, Boutonnet et al. comment that any persistent loss is likely to be in the form of solution in chemical waste streams, the disposal and treatment of which will be subject to local controls. More recently, discharges of TFA have been identified from a production site that produces inorganic and organic fluorinated chemicals, including TFA and a TFA derivative. Significant concentrations of TFA were measured in a river downstream of the production site (Scheurer et al., 2017).

TFA is used in a wide range of chemicals applications, potentially at large numbers of locations, which means that it is not possible to estimate emissions from use in the period until 1999. Furthermore, some derivatives prepared from trifluoroacetic acid may degrade in the environment to regenerate TFA, but TFA or trifluoroacetic anhydride were not widely used to introduce CF_3 groups for pesticides. The production routes for pesticides used traditional multistep procedures for CF_3 arene production, most notably the radical chlorination of aryl methyl groups followed by high-pressure treatment in hydrofluoric acid. This current industrial standard has been demonstrated to be highly effective (Beatty et al., 2015). However, it is reported that in China, TFA is manufactured from CFC-113a by hydrolysis (TEAP, 2021), and it is used to manufacture the insecticide chlorfenapyr (AgNews, 2022), which was first registered in Japan in 1996 and the USA in 2001 (Pesticide Properties DataBase (2022).

According to Boutonnet et al, the reported total production in the 1990s is *"of the order of 1000 metric tons per year"*, i.e. only an approximation. It is assumed that trifluoroacetic acid production reached 1000 tonnes/year by 1977 (15 years after commercial introduction) and remained at this level until end 1999. The estimated production is about 30,000 tonnes in the period from 1962 until end 1999, but this excludes any TFA production in China that may have occurred in the 1990s. The highly uncertain production estimate is used as a proxy for the potential TFA burden that could have been released to the environment.

There may be an additional burden due to any discharges to the aqueous environment during production, but any discharges during use are accounted for as part of the estimated production. More recently, concentrations of TFA in waste streams from fluorochemical sites in China are relatively large (Xie et al., 2020).

2.6   Trifluoromethyl aromatics

One group of fluorochemicals, which may, for some substances, form TFA, are trifluoromethyl aromatics, including trifluoromethylbenzene, chlorotrifluoromethylbenzene and substituted derivatives. These have uses as vulcanizing agents and intermediates in the production of dyestuffs, insulating fluids, herbicides, pharmaceuticals, antimicrobial agents, and the lampricide, 4-nitro-2-(trifluoromethyl) phenol (Technical Resources International, 2013). The environmental degradation of trifluoromethyl aromatics and the potential generation and yield of TFA depends on the structure and the degradation pathways (atmospheric oxidation, aqueous photolysis, biodegradation).

2.6.1   Trifluoromethylbenzene

Trifluoromethylbenzene is a high production volume chemical used as a solvent in large scale industrial applications or as a feedstock for the preparation of substituted derivatives which have uses as vulcanizing agents and intermediates in the production of dyestuffs, insulating fluids, herbicides, pharmaceuticals, antimicrobial agents, and the lampricide, 4-nitro-2-(trifluoromethyl)phenol. According to industry figures, 10,000 - 50,000 tonnes of trifluoromethylbenzene was used in the European Union around year 2000 (Technical Resources International, 2013). It degrades in the atmosphere by reaction with hydroxyl radical (the half-life for this reaction in air is estimated to be about 35 days) with a trifluoromethylphenol suggested as an initial reaction product (Atkinson et al., 1985). The aqueous photolysis of trifluoromethylphenols has been investigated but TFA was not generated in one study, and found at a maximum of 5% yield for 4-(trifluoromethyl)phenol (see below).

2.6.2   1-Chloro-4-(trifluoromethyl)benzene

1-chloro-4-(trifluoromethyl)benzene does not degrade to TFA. According to a 2009 summary (National Toxicology Program, 2009), it is used as an intermediate in the synthesis of dyes, pharmaceuticals, pesticides, insecticides, and herbicides, and as a solvent, mainly in paint and coating formulations. When used as a solvent, studies have shown that emissions result in atmospheric oxidation followed by aqueous photolysis of an intermediate and leads to complete dehalogenation with 3,4-dihydroxybenzoic acid (an approved food additive considered to be nontoxic) as the final product (Young et al., 2009).

2.6.3   Trifluoromethyl phenols

The lampricide, 4-nitro-2-(trifluoromethyl) phenol (TFM) and related phenols and quinones degradation pathways have been investigated to determine the effect of structure and other environmental factors on the generation of TFA (Ellis & Mabury, 2000). According to this paper about 1600 tonnes of TFM have been added to the Great Lakes between 1958 and 1999. The yield of TFA by aqueous photolysis at 365 nm depends on the pH and is influenced by the initial reduction of the nitro group to an amine. Assuming the maximum reported yield of TFA (17.8%) results in the formation of 156 tonnes of TFA over the period. Other degradation pathways produce fluoride with the trifluoromethyl group being converted to an acid group (benzoic acid grouping). The aqueous photolysis of 2-, 3-, and 4-(trifluoromethyl)phenols was also investigated, with no generation of TFA. The photolysis of 4-Amino-3-trifluoromethylphenol resulted in approximately 11% yield of TFA through a complex mechanism after 100% conversion of the parent compound with fluoride also being formed.

A recent paper has also studied the aqueous photolysis of 2-, 3-, and 4-(trifluoromethyl)phenols. TFA was only observed when $-CF_3$ was in the para-position 4-(trifluoromethyl)phenol. The percentage of total initial fluorine that was converted to TFA was a maximum of 5%, with the yield dependant on pH and oxidising conditions. Results also indicate that TFA may not be formed from the deprotonated phenolic species, which is consistent with past results (Bhat et al. 2022).

2.7   Agrochemicals

A potential significant source of TFA are agrochemicals that contain a trifluoromethyl aromatic group. Some contain a trifluoromethyl aliphatic group. Typically, these are complex molecules, that may have unknown or uncertain degradation pathways. Fluorine substitution is used as a means of improving biocidal performances. A recent publication stated that there are currently, in 2021, 45 active substances containing a $C-CF_3$ group approved for use as plant protection products within the EU. Degradation studies indicating the formation of TFA were submitted as part of the approval procedure for the plant protection products flurtamone and flufenacet. Various field studies have also identified TFA for other active substances, although the exact degradation pathway is not known. During ozonation, a process applied in wastewater and drinking water treatment, TFA was observed to form from the active substances tembotrione, flufenacet, flurtamone and fluopyram. However, it was not possible to quantify the rate at which it forms. Flufenacet is one of the few substances for which TFA formation is not just a theoretical assumption but has been proven in laboratory studies (German Environment Agency, 2021).

2.7.1   Trifluralin and other dinitroanilines

The dinitroaniline herbicides (trifluralin, benfluralin and ethalfluralin) and a dinitroaniline fungicide (fluazinam) were in use in the period before 1999, see Figure S2. Trifluralin was the first fluoro-herbicide introduced in 1963 and is also one of the most globally used herbicides (Ogawa et al., 2020). According to Jordan & Frank, 1999, several pesticides at that time had a trifluoromethyl-substituted aromatic ring system, "*with trifluralin being the compound with greatest production volume, about 50,000 tonnes in 1986. A fraction of the applied pesticide may volatilize, undergo photooxidation, and will be wet deposited. Ring-cleavage has not been observed to date and is not to be expected as the electronegative CF₃-group decreases the OH-reactivity of the aromatic ring. Although metabolism of trifluoromethylated aromatics in soils has been suggested to produce TFA, studies with [¹⁴C-]trifluralin showed slow degradation.*"

According to a trifluralin review, trifluralin with a $^{14}CF_3$ label was used in one early study to show that after an 83-day incubation, 8−10% of trifluralin was lost to volatilisation, 1.4−3.1% was mineralized to $^{14}CO_2$, 10−70% was immobilized as bound residues, and the remainder was converted to dealkylated and cyclized derivatives. It is clear from many studies that biodegradation is a major mechanism of trifluralin degradation in soil (Coleman et al., 2020). In a separate study, no TFA was detected during a biodegradation study after 32 days in a landfill soil microbial culture system (Sun et al., 2020). According to a soil photolysis study, photolysis is not expected to be a significant degradation route of trifluralin in the environment and no major photolysis products were identified (European Food Safety Authority, 2005). However, photodegradation of benfluralin (Dow, 2010) and ethalfluralin (U.S. EPA, 1995) occurs in sunlight.
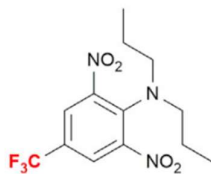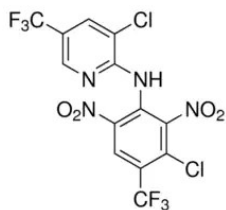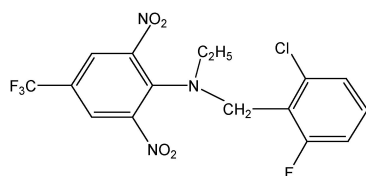
trifluralin
1963
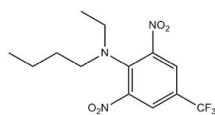
benfluralin **1963**
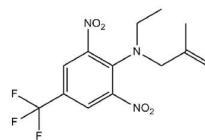
ethalfluralin **1975**

fluazinam **1990**

flumetralin **1983**

Figure S2. Relevant dinitroaniline herbicides and year of first commercial use

Crop rotation studies for benfluralin, which has a very similar structure to trifluralin found that TFA was the major metabolite in rotational crop studies in all tested commodities (European Food Safety Authority, 2014). This report also concluded that fluazinam would form TFA on degradation. Although the study did not comment on ethalfluralin, based on its similar structure to benfluralin, TFA formation might be expected. Therefore, it can be assumed that these five agrochemicals in use before 1999 all breakdown to give TFA, but in unknown yields. The formation and detection of TFA in the crop rotation studies is consistent with soil-based degradation and not atmospheric degradation to TFA. Flumetralin is a dinitroaniline plant growth regulator used for tobacco and was introduced in 1983.

It is estimated that approximately 7000 tonnes of dinitroanilines are applied globally per year in 2020, which represents around 1% of global herbicide use, and within this, about 4400 tonnes is trifluralin. It has been banned in the European Union (EU) since 2008 due to concerns over its toxicity. The use of trifluralin has decreased since the 1980s, with the US reporting approximate use in 1987: 12,500 tonnes; 1997: 10,500 tonnes; 1999: 9300 tonnes; and 2001: 6400 tonnes, the average quantities of the range quoted (U.S. EPA, 2004). None of the other three pesticide dinitroanilines are included in the top 25 active pesticide ingredients in the USA in 2001, which means their individual use was less than about 1500 to 3000 tonnes.

2.7.2   Diphenyl ether herbicides

Four diphenyl ether herbicides that were approved for use before 1999 (Figure S3) are oxyfluorfen (1976), fluorodifen (1968, now obsolete), acifluorfen (1980, current but expired in EU), fluoroglycofen (1987, EU expired), data from Pesticide Properties DataBase, 2022. The European Food Safety Authority concluded oxyfluorfen can degrade to TFA and it can therefore be assumed that these four agrochemicals in use before 1999 all breakdown to give TFA, but in unknown yields.
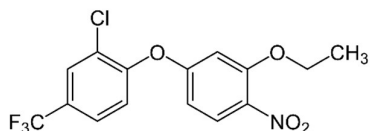
oxyfluorfen **1976**
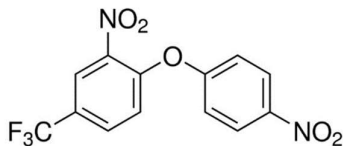
fluorodifen **1968**
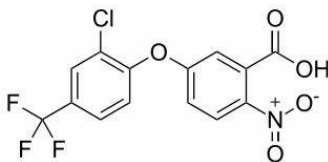
acifluorfen **1980**
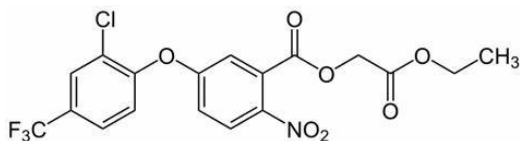
fluoroglycofen **1987**

Figure S3. Relevant diphenyl ether herbicides and year of first commercial use

2.7.3 Potential emissions of TFA from pesticide use until 1999

TFA generated from pesticides, by decomposition in soil, will enter surface and ground waters. Trifluralin had the greatest production volume in 1987 (about 50,000 tonnes according to Jordan & Frank, 1999) for these relevant pesticides, with the USA accounting for about 25% of its global use in that year. Available data for the reported use in the USA for other relevant pesticides was much lower in this period: Oxyfluorfen:1992, 208 tonnes; 1997,320 tonnes. Ethalfluralin: 1990, about 1500 tonnes; Benfluralin: 2006, 450 tonnes. Flumetralin use according to a USA GAO report gave usage at about 40 tonnes annually in the period 1994-1998.

For the EU, to account for the potential TFA contribution from agricultural pesticide use prior to 1999, a review of EU pesticide usage was performed based on Eurostat data. The EU pesticide usage report for 2000-2003 covers pesticide usage from 1992-2003. The diphenyl ether herbicide class contains 4 substances with a CF_3 group in a category of 6 substances. The dinitroaniline herbicide class had 3 out of 8 substances containing a CF_3 group. The dinitroaniline fungicide class had 1 out of 2 substances containing a CF_3 group. Table S7 is a summary of the CF_3 containing pesticides in the report.

Table S7. Pesticides with CF_3 group in use prior to 1999

Pesticide	Type of Pesticide	Year Approved in EU *(note)*	Listed in the 1992-2003 Eurostat report
Oxyfluorfen	Diphenyl ether herbicides	1976	yes (one of 6 compounds in this category)
Fluorodifen	Diphenyl ether herbicides	1968	yes (one of 6 compounds in this category)
Acifluorfen	Diphenyl ether herbicides	1980	yes (one of 6 compounds in this category)
Fluoroglycofen	Diphenyl ether herbicides	1987	yes (one of 6 compounds in this category)
Fluazinam	Dinitroaniline fungicide	1990	yes (one of 2 compounds in this category)
Benfluralin	dinitroaniline herbicides	1963 (USA)	yes (one of 8 compounds in this category)
Ethalfluralin	dinitroaniline herbicides	~1975 (Turkey)	yes (one of 8 compounds in this category)
Trifluralin	dinitroaniline herbicides	1961 (USA)	yes (one of 8 compounds in this category)
Flumetralin -for tobacco only	2,6-dinitroaniline plant growth regulator	1983	No (not required to report tobacco use), have US GAO report for 1994-1998 pesticide usage for tobacco

Table note: Year Approved in EU from Pesticide Properties DataBase, 2022.

An indication of the potential TFA generation can be estimated from the tonnage use for these groups of pesticides, which do not all contain the CF_3 group. In Table S8, the usage is based on the reports for specific crop use and with the same annual use over a period of 20 years. No data was found for flumetralin in EU, so the USA use data was assumed to provide an indicative quantity. Potential TFA generation is in the range 25 to 35% by weight of pesticide use, apart from fluazinam, which has two CF_3C groups and could potentially result in 50% TFA by weight of pesticide use, assuming a 100% yield (200% for fluazinam). Assuming the theoretical yield of 34% by weight of TFA (the yield from trifluralin) for all these substances would result in potential TFA generation of about 30,000 tonnes based on the data in Table S8.

Assuming that EU consumption these substances is 15% to 20% of the global consumption, results in potential estimated TFA generation of 140,000 to 200,000 tonnes (Our World in Data, 2022). Another approach is to estimate potential TFA from the available trifluralin use data. Assuming increasing use from 1963 until the mid-1980s and then 50,000 tonnes annually until 1999, results in about 1.1 million tonnes of global trifluralin use,

equivalent to about 380,000 tonnes of TFA generation assuming 100% molar yield. The decreasing use of trifluralin in the USA after 1987, and the relatively smaller quantities of other relevant pesticides, and their later introduction, suggests that this quantity of TFA is a possible indicative maximum estimate.

Flurtamone, a herbicide, was introduced in about 1990, and degrades to give TFA (minor molar fraction, 0.055) and trifluoromethylbenzoic acid (major molar fraction, 0.247) as metabolites (Pesticide Properties DataBase, 2022). TFA residues are also discussed in an EFSA peer review (European Food Safety Authority, 2014).

Pesticide use could account for 160,000 to 430,000 tonnes of CaF_2 consumption (as anhydrous HF) assuming a 90% efficiency of anhydrous HF utilisation (optimistic).

Table S8. Worst case estimate of potential TFA from pesticide usage in EU

Approx Ave tonnes/yr for Crop	Diphenyl ether herbicides	Dinitroaniline herbicides	Dinitroaniline fungicide	Flumetralin (approved 1983)	Total usage (tonnes)	Assumed years of use	Total use in EU (tonnes)
Cereal	200	1500			1700	20	34,000
Maize	150	500			650	20	13,000
Oilseed	450*	1000			1450	20	29,000
Potatoes	75*	19	20		114	20	2280
Fruit trees		30	10		40	20	800
Vegetables	50*	300			350	20	7000
Grape		100	15		115	20	2300
Other	20*				20	20	400
Tobacco	0			40	40	16	640
TOTAL (1999)	**945**	**3449**	**45**	**40**	**4479**		**89,420**

*Pesticide not used on crop until 1997

2.7.4 Biocides and Insecticides
Overall, there are currently six active substances containing the C-CF$_3$ group that are approved at an EU level: chlorfenapyr, tralopyril, bifenthrin, lambda-cyhalothrin, flocoumafen and fipronil (German Environment Agency, 2021). The European Food Safety Authority concluded that, bifenthrin, flocoumafen and fipronil would not result in formation of TFA (European Food Safety Authority, 2014). Chlorfenapyr was not registered until 1996, tralopyril is used as an anti-fouling treatment post-2000, and lambda-cyhalothrin, an insecticide, was introduced in 1985 (Pesticide Properties DataBase, 2022). Annual agricultural use of lambda-cyhalothrin in California was consistent at approximately 14 tonnes active ingredient per annum from 2000 to 2003 (He et al., 2008), equivalent to about 3.5 tonnes of TFA if it degraded to give 100% molar yield of TFA.

2.8 Pharmaceuticals

Pharmaceuticals are a much smaller potential source of TFA compared to pesticides. As an example, fluoxetine (Prozac) introduced in 1987 might have been used by about 40 million people globally around year 2000 (Bloomberg, 2001), with a reported maximum dose of 80 mg daily (RxList, 2022; European Agency for the Evaluation of Medicinal Products, 2001). If it is assumed that it breaks down to give 100% yield of TFA then the annual TFA generation might be about 430 tonnes at this maximum dose rate. Over a 12-year period, this is equivalent to about 5000 tonnes of TFA, see Table S9. Fluoxetine has been shown to break down to TFA in waste- water treatment with ozone with a yield of 40% (Scheurer et al., 2017).
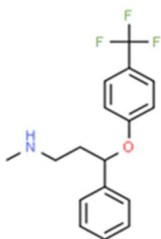
Table S9. An estimate of potential TFA emissions from Fluoxetine (Prozac) until end 1999

Fluoxetine (Prozac) introduced 1987

Fluoxetine mol wt	309.33	
CF_3COOH mol wt	114	
TFA 100% yield by wt	37	%
Reported people using prozac in 2000s	40	million
Maximum dose daily	80	mg
Annual use/per person	29.2	g
Annual use globally	1168	tonnes
Annual TFA at 100% yield	430	tonnes
Maximum 12 years of use 1987-1999 as it assumes 40 million people globally from 1987, at maximum dose. TFA emissions	5165	tonnes

2.9   Halon 1211

World production data for Halon 1211 (CF_2ClBr) and Halon 1301 (CF_3Br) is available in the TEAP HTOC 1993 report (HTOC, 1993). Halon 1211 production stopped in 1993. Fluoride efficiency of 90% is assumed.

Table S10. Cumulative Halon 1211 production until 1993 and required calcium fluoride use

	Cumulative production kilotonnes	Calcium fluoride equivalent million tonnes	Production comments
Halon 1211	197	0.1	1963-1993

Halon 1301, production data are also available, but it is produced from HFC-23, a by-product of HCFC-22. The HCFC-22 fluoride efficiency considers HFC-23. Both these substances are C_1 and do not form TFA. Table S10 has cumulative production and calcium fluoride equivalent.

2.10   Fluoropolymers, HCFC feedstock uses and fluoropolymer degradation

Three subjects are considered for fluoropolymers:

- Calcium fluoride required for fluoropolymers and other feedstock uses.
- TFA emissions resulting from the production or use of feedstocks.
- Fluoropolymer degradation potentially leading to TFA emissions.

2.10.1   Calcium fluoride required for fluoropolymers production and other feedstock uses

PTFE was commercialised in 1947, with a succession of fluoropolymers introduced in the following decades, summarised in Table S11 for the main fluoropolymers. By 2015, PTFE still accounted for 58% of the global fluoropolymers production. In the same year, PTFE, fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), and tetrafluoroethylene copolymers with perfluoroalkyl vinyl ethers (e.g., perfluoroalkoxy polymer, PFA), accounted for approximately 70% to 75% of the world fluoropolymer consumption (Henry et al., 2017). In addition, there are a range of fluorinated lubricants and greases, introduced from around 1960, for example based on hexafluoropropylene oxide, which is produced from hexafluoropropene. Most fluoropolymers use feedstocks, whose production quantities must be reported under the Montreal Protocol. Data are available from TEAP MCTOC reports (MCTOC, 2022) with data available from 1990 onwards.

Table S11. Main Fluoropolymers commercialised before 1980 (Teng, 2012).

Polymer	Structure	Fluoride content	Some feedstock options	Commercial introduction	Comments
PTFE	$(CF_2CF_2)_n$	76%	HCFC-22: CF_2HCl	1947	55,000 tonnes/yr in late 1990s. About 60% of the fluoropolymers market (excl. fluoroelastomers)
PCTFE	$(CF_2CFCl)_n$	49%	CFC-113: CCl_2FCClF_2	1953	
FEP	$(CF_2CF_2)_n$-$(CF_2CFCF_3)_m$	76%	HCFC-22: CF_2HCl	1960	FEP contains about 5 mol % of HFP, about 7.5 wt %
PVF	$(CH_2CHF)_n$	41%	Acetylene	1961	
PVDF	$(CH_2CF_2)_n$	59%	HCFC-142b: $CClF_2CH_3$	1961	
ECTFE	$(CH_2CH_2)_n$-$(CF2CFCl)_m$	39%		1970	
PFA	$(CF_2CF_2)_n$-$(CF_2CFOC_3F_7)_m$	~74%		1972	
ETFE	$(CH_2CH_2)_n$-$(CF_2CF_2)_m$	59%		1973	

The total production of PTFE was about 1.1 million tonnes until 1999, estimated from the global production in the late 1990s (Teng, 2012), growth rate and year of commercialisation 1947 (PTFE was used during the second world war for the Manhattan project but was made available commercially in 1947). Applying an overall fluoride efficiency of 85% (optimistic), which includes the HCFC-22 fluoride efficiency (94%), cumulative PTFE production requires the consumption of 2.0 million tonnes of CaF_2. The consumption of CaF_2 to manufacture other fluoropolymers has been estimated by two methods:

- From available PVDF production data and reported feedstock consumption under the Montreal Protocol, excluding feedstock required for PTFE and PVDF and for substances such as HFCs.
- By assuming in the period until 1999, other fluoropolymers are 25% of the cumulative total, i.e., one third of PTFE production and have a fluoride content of 60%. The fluoride content of the main fluoropolymers is shown in Table S11. An overall fluoride efficiency of 85% (optimistic) is assumed.

Both methods resulted in similar CaF_2 consumption of about 0.5 million tonnes. In total fluoropolymers account for 2.5 million tonnes of CaF_2 consumption in the period until 1999.

2.10.2 TFA emissions resulting from the production or use of feedstocks

Two feedstock substances, produced in the period until 1999, that degrade in the atmosphere to TFA are hexafluoropropene (HFP, $CF_3CF=CF_2$) and HCFC-133a (CF_3CH_2Cl).

Hexafluoropropene (HFP) is a co-product in the synthesis of TFE from HCFC-22 (chlorodifluoromethane). HFP yield can be increased, in lieu of TFE production, by altering the reaction conditions such as reduction in the pyrolysis temperature and use of steam as diluent of the reactants (Ebnesajjad, 2011). Hexafluoropropene is used for the manufacture of FEP fluoropolymer plastic introduced in 1960, for fluoroelastomers, and for production of hexafluoropropylene oxide (HFPO), an intermediate for a wide range of substances, including lubricants and greases which were introduced around 1960. HFP has an atmospheric lifetime of 5.5 days (AR6 value) and degrades in the atmosphere by reaction with hydroxyl radical giving a near quantitative yield of CF_3CFO, which then hydrolyses to TFA (Acerbonia et al., 2001). Information is not available for any emissions of HFP from its manufacture and use during the period until 1999. An estimate of TFA generated from HFP emissions is highly uncertain because emissions of HFP are very uncertain. TFA, or TFA derivatives, can be formed as co-products in the manufacture of HFPO. The extent of TFA co-product is process-dependent; some manufacturers recover the TFA for other uses.

The following assumptions are used to estimate TFA burden related to HFP production and use:

- Assume 10% yield of HFP for all TFE production (Broyer, Bekker, & Ritter, 1988).
- Assume all HFP is emitted until 1960.

- From 1960, assume HFP is used as a feedstock with emissions of 4% of production. Emissions can also occur from its use as a feedstock and are assumed to be 2%, towards the lower end of the 0.5% to 4% consistent with processes where conversion rates are very high. This emission factor is based on the TEAP 2020 Progress Report (TEAP, 2020), which discusses emissions from the production of feedstock *"For large scale, well designed, well operated and maintained feedstock processes, production, storage, distribution and use emissions well below 0.5% are achievable. For small-scale and/or poorly operated and maintained feedstock processes, emissions above 4% are possible."* Modern processes with improved emission control will have lower emissions.

Based on these assumptions, about 7000 tonnes of TFA could have been emitted between 1947 and 1999.

HCFC-133a (CF$_3$CH$_2$Cl) is a feedstock used to produce several fluorochemicals, including halothane. A recent paper (Vollmer et al., 2021) reports on global abundances, trends, and regional enhancements for HCFC-132b, HCFC-133a, and HCFC-31. Small European emissions of HCFC-132b and HCFC-133a, found in southeastern France, ceased in early 2017 when a fluorocarbon production facility in that area closed. The paper notes that although unreported emissive end-uses cannot be ruled out, all three chemicals are most likely emitted as intermediate by-products in chemical production pathways. According to a TEAP report (TEAP, 2021), HCFC-133a (and HCFC-133) are reported as feedstock in quantities each year between 1000 and 3000 tonnes in the period 2002 and 2009. HCFC-133a degrades in the atmosphere with an estimated 30% yield of TFA (McGillen et al., 2015; EEAP, 2022). If most HCFC-133a emissions were associated with HFC-134a production in the 1990s then TFA emissions around 240 tonnes could have occurred from HCFC-133a in the period until 1999, based on the emissions reported for 2002 and scaled to HFC-134a production, considering the atmospheric lifetime of HCFC-133a (4.6 years AR6 value).

In total about 7300 tonnes *(rounded up)* of TFA could have been emitted between 1947 and 1999 due to hexafluoropropene and HCFC-133a emissions.

2.10.3   Fluoropolymer combustion and thermolysis

Fluoropolymer degradation can result in the formation of some quantities of TFA and other fluorinated small molecules (Ellis et al., 2001). Any HFP (hexafluoropropene) generated could form TFA by reaction with oxygen as part of the high temperature degradation process (Lokhat, Starzak, & Ramjugernath, 2017), or subsequently in the atmosphere by reaction with hydroxyl radical (Acerbonia et al., 2001). According to Ellis et al., the high temperature incineration, or combustion, of fluoropolymers using a source of fuel to purposefully evoke complete decomposition is unlikely to yield environmentally significant levels of TFA, or TFA precursors, due to the high temperatures and oxidizing conditions employed, which would result in the cleavage of most carbon fluorine bonds, but lower temperature thermolysis or low temperature burning can generate TFA. The combustion of PTFE under typical waste incineration conditions has been investigated to determine if low molecular weight perfluoro-and polyfluoroalkyl substances are generated (Aleksandrov et al., 2019). The study investigates the possible generation of a wide range substances including TFA from PTFE incineration under standard municipal waste conditions. Results indicate that, within procedural quantitation limits, no statistically significant evidence was found that the PFAS studied were created during the incineration of PTFE. Therefore, municipal incineration of PTFE using best available technologies (BAT) is not a significant source of the studied PFAS and should be considered an acceptable form of waste treatment. According to a review, overall, the major share of used fluoropolymers ends up in landfills, in incineration plants or in blast furnaces. Waste incinerators can tolerate only very limited amounts of fluoropolymers owing to the high corrosiveness of the hydrofluoric acid formed during the process (Dams & Hintzer, 2016). A literature survey of emissions from incineration of fluoropolymer materials is available (Huber et al., 2009).

Experimental thermolysis studies have shown that, when some fluoropolymers are heated in the presence of air to about 500 to 600°C, which is above their maximum safe operating temperatures, TFA can be formed. The specific polymer, temperature, availability of oxygen, the physical form of the product and the residence time at elevated temperature are some of the factors determining the ultimate nature and amount of the decomposition products. Elevated and high temperature processes are potential sources of TFA emissions, but their contribution is highly uncertain.

TFA is formed from the thermolysis of PTFE at 500°C and other fluoropolymers with a yield of 7.8% from PTFE (Ellis et al., 2001). A more recent study (Cui et al., 2019) reported 1.2% yield of TFA from PTFE using a similar experimental process at 500°C or higher, proposing that the method employed is more representative of actual fluoropolymer pyrolysis processes for industrial activities and other consumer thermal applications. However, the assumption that, for example, 0.1% of global inventory of fluoropolymers can be at temperatures

above 500°C is considered to be extremely excessive, as at these extreme temperatures, the material has lost its mechanical and thermal properties. Although the experimental results may not therefore translate to the 'real world', applying the Cui methodology for global PTFE produced in the period until 1999 results in very low emissions of TFA.

The experimental thermolysis study for China by Cui et al. used decomposition for 5 years of polymer production from 2010 to 2014 as the base value and three scenarios for the proportion of fluoropolymers that underwent thermolysis each year: 0.5% (high); 0.1% (medium); and 0.05% (low). Similarly, Ellis et al. estimated the quantity of fluoropolymers used over 5 years, assumed that 0.1% of that total underwent thermolysis each year. Applying the Cui experimental generation rate of TFA for PTFE (1.2%) and Cui et al. medium scenario (0.1%) results in theoretically about 60 tonnes emissions of TFA over the period until end 1999 from the estimated global PTFE production. It must be emphasised that this is theoretical and highly uncertain but provides an indication of potential emissions of TFA from PTFE, if thermolysis were to occur at a 0.1% rate (unlikely).

2.11 Fluorotelomer alcohols

Fluorotelomer alcohols are reported to degrade in the environment to potentially produce low yields of TFA, either by atmospheric or biological degradation. Atmospheric chemistry experiments resulted in some TFA formation from Cl atom initiated oxidation of 8:2FTOH, which yielded the entire suite of PFCAs ranging from trifluoroacetic acid (TFA) to PFOA (Ellis et al., 2004). Another paper reported that TFA is formed in low yields from 6:2FTOH and 4:2FTOH by a landfill soil microbial culture. The authors estimate global emissions of 3.9 to 47.3 tonnes of TFA in the period from 1961 to 2019, via the pathway of 4:2 and 6:2 FTOH biodegradation (Sun et al., 2020). Fluorotelomer alcohols are not considered to be significant sources of TFA in the period until end 1999.

2.12 Aluminium production

With thanks to Stephen J Lindsay, formerly of Alcoa, for providing valuable advice, data, information, and review editing for this section. Also, Linlin Wu of the International Aluminium Institute for AlF_3 consumption data and historical texts on aluminium production.

2.12.1 Fluorspar consumption

Aluminium production was reported as 272,000 tonnes in 1930 reaching about 10 million tonnes in 1970 and 23.6 million tonnes in 1999 (U.S. Geological Survey, 2022). Cumulatively this is 594.5 million tonnes globally in the period from 1930 to 1999. Aluminium fluoride (AlF_3) and cryolite (Na_3AlF_6) form the electrolyte for the aluminium smelting process from alumina allowing the process to operate at about 960°C. One of the uses of aluminium fluoride or cryolite is to replace lost fluoride, which is consumed (Welch, 2000) by emissions, as gaseous fluoride mainly HF, fluoride particulates, PFCs (Tabereaux & Peterson, 2014), and by absorption of fluoride into the pot linings (Samec, Mikša, & Kokalj, 2004). The primary use of aluminium fluoride in modern reduction cells is to neutralize the inputs of sodium oxide and calcium oxide in alumina to a target ratio of sodium fluoride to aluminium fluoride in the electrolytic bath. This is shown in Figure S2, which is representative of the typical modern primary aluminium industry. Since the 1970s, Spent Pot Linings (SPL) have been recognised as a valuable resource for other industries, including as a feedstock in the cement, mineral wool and steel production processes (International Aluminium Institute, 2022a).

Modern technology recycles most of the fluoride minimising the fluoride consumption. Aluminium smelting until the 1940s primarily used natural cryolite for the electrolyte. It was somewhat modified by additions of calcium fluoride (Bradbury, Finger, & Major, 1968) and a little aluminium fluoride. Consumption of natural cryolite (70-90% purity imported into the USA) in this period is reported as 100 kg/tonne aluminium produced (Hamrick & Voskuil, 1949). Modern technology consumes considerably less fluoride, reported as 16 kg AlF_3/ tonne aluminium produced globally in 2005 (International Aluminium Institute, 2022b). Since the 1940s, the dominant source of fluoride for synthetic cryolite or aluminium fluoride is from fluorspar (CaF_2). From the 1950s, aluminium fluoride has also been produced from fluorosilicic acid (H_2SiF_6), a by-product from processing of phosphate minerals, contributing about 10% to the fluoride used. Fluorapatite ($Ca_5(PO_4)_3F$) is mined along with other apatites for its phosphate content and is used mostly for fertilizer production.
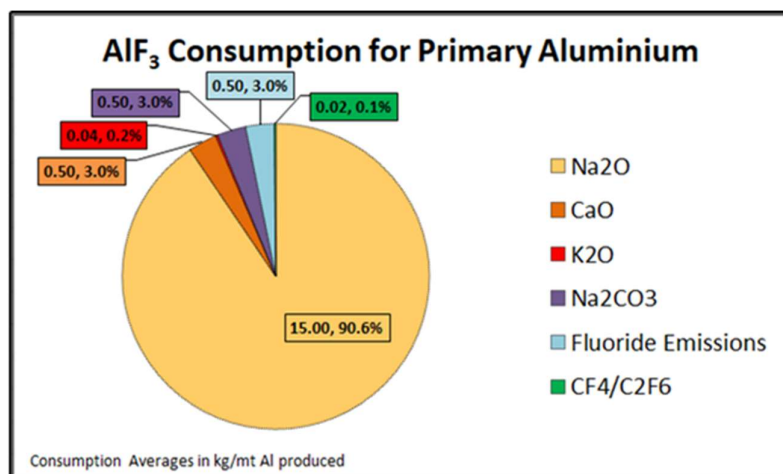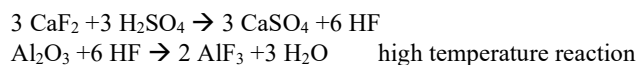
Figure S4. AlF$_3$ Consumption for typical modern day primary aluminium production (Chart provided by Stephen J Lindsay, formerly of Alcoa)

The production of AlF$_3$ from CaF$_2$ is via anhydrous HF and requires at least 1.5 moles CaF$_2$ for each mole of AlF$_3$.

$$3\ CaF_2 + 3\ H_2SO_4 \rightarrow 3\ CaSO_4 + 6\ HF$$
$$Al_2O_3 + 6\ HF \rightarrow 2\ AlF_3 + 3\ H_2O \qquad \text{high temperature reaction}$$

Whereas open electrolysis cells were historically used, modern technology makes use of a super-structure to contain the gases and dust produced during smelting. Modern cell technologies and improved cell operating practices were introduced mainly in the period 1960 -1965 (Tabereaux & Peterson, 2014). The first full application of dry scrubbing technology was on two new smelting lines at Massena, NY in 1958. In the early 1970s, scrubbing technology, making use of primary alumina to clean the off-gases, was established (Aarhaug & Ratvik, 2019). Even in the 1990s, for some smelters, the total fluoride consumption in cells varied from 20 to 50 kg per tonne of aluminium produced (UNCTAD, 1995). In the late 1990s there were more than 130 smelters located in more than 30 countries using different technology vintages (Gagné & Nappi, 2000).

Due to the relative complexity of the changing pattern of fluoride consumption and limited available historical data, an estimation of calcium fluoride consumption for aluminium smelting in the period 1930 to 1999 requires several assumptions:

- The US Minerals Yearbook (United States Bureau of Mines, 1993a) provides data on fluoride consumption for aluminium smelting, these together with other sources and expert input from the aluminium industry allowed fluoride consumption by year to be estimated.
- The US Minerals Yearbook also reports natural cryolite imports and their estimated purity, the timing for the use of synthetic cryolite from fluorspar, and aluminium fluoride from H$_2$SiF$_6$.
- From the introduction of the use of H$_2$SiF$_6$ as a source of fluoride, it has been assumed that this contributes 10% of the fluoride consumption each year (Dreveton, 2012). This may be an overestimate. Purity of AlF$_3$ from H$_2$SiF$_6$ or calcium fluoride (Lindsay, 2013) is not considered.
- Some recycling of fluoride occurred from the 1940s. However, the Minerals Yearbook reports actual fluoride consumption for some years so this may have been considered.
- The quantities of natural cryolite imported into the USA after 1968 were small and irregular. These have been ignored.
- Due to the lack of availability of similar data for other regions, the consumption data set developed for the US has been scaled for global aluminium production. Technology improvements were adopted globally at roughly the same time.

Figure 3 in the paper shows the consumption of fluoride minerals and primary aluminium production by year for the period 1930 - 1999. This also shows the reduction in relative use of fluoride minerals as aluminium production technology improved.

The estimated consumption of calcium fluoride (fluorspar), natural cryolite and aluminium fluoride from H_2SiF_6 are in Table S12.

Table S12. Estimated consumption of fluoride minerals for aluminium production 1930-1999

Calcium fluoride	25.3 million tonnes
Natural cryolite (80% purity) (1930-1968)	1.9 million tonnes
AlF_3 from H_2SiF_6 (from phosphate minerals)	1.8 million tonnes

2.12.2   Natural cryolite consumption for aluminium production

The consumption for aluminium production in the period 1930-1968 is estimated as 1.9 million tonnes of 80% purity, accounting for about 70% of the cryolite mined in Greenland, considering purity equates to 3.7 million tonnes at an average content of 58% cryolite (Geological Survey of Denmark and Greenland, 2002). The imports of natural cryolite into the USA, reported in the US Bureau of Mines Minerals Yearbook in the period 1930 to 1940, match the required demand over the period, based on 100 kg natural cryolite/tonne aluminium production and the reported US aluminium primary production. At the very beginning of the primary aluminium industry natural cryolite was also used to produce alumina (Al_2O_3) as feedstock for aluminium reduction (Von Wagner, 1892).
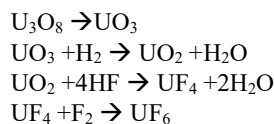
2.13 SF_6, SOF_2, and NF_3

Sulphur hexafluoride (SF_6) is produced commercially by direct fluorination of sulphur using elemental fluorine (obtained by electrolysis). During process of producing of this gas, other by-products like SF_4, SF_2, S_2F_2, S_2F_{10} are also produced in small percentages (Electrical4U, 2020). Data on the production of SF_6 by year until 1999 is available with reported cumulative production of 136,172 tonnes between 1961 and 1999 (Smythe, 2001). Assuming an overall fluoride efficiency of 90% results in the consumption of 242,000 tonnes of CaF_2.

Sulfuryl fluoride (SOF_2) global emissions (Jones, Robinson, & Eibeck, 1975) have been reported and the paper includes industry data for global production. About 24,000 tonnes of SOF_2 were produced in the period from 1960 to 1999. This would require about 35,000 tonnes of CaF_2 assuming a fluoride efficiency of 95%. According to a 1977 patent (Jones, 1975), the most common method at that time employed for the commercial production of sulfuryl fluoride involved the gas phase reaction of sulphur dioxide, chlorine, and hydrogen fluoride.

Nitrogen trifluoride production is a minor use of fluoride and are not included in this inventory (Arnold et al., 2013).

2.14   Uranium processing

Enrichment of uranium for nuclear energy requires the production of UF_6 that enables the enrichment of the U^{235} isotope. The process requires mining and milling of U_3O_8 which is then converted to UF_6 by a multi-step process (Hardy, 2008; Alfaro, Torres, & Thiele, 2015).

$$U_3O_8 \rightarrow UO_3$$
$$UO_3 + H_2 \rightarrow UO_2 + H_2O$$
$$UO_2 + 4HF \rightarrow UF_4 + 2H_2O$$
$$UF_4 + F_2 \rightarrow UF_6$$

According to the 1972 U.S. Minerals Yearbook, 1.5 to 1.66 tonnes of acid spar are required per tonne of UF_6, significantly more than the theoretical quantity, about 1 tonne of acid spar (United States Bureau of Mines, 1974). The global stock of depleted uranium at the end of 1999 was 1,028,204 tonnes of U as UF_6 (WISE Uranium Project, 2008), equivalent to 1,520,705 tonnes UF_6. Taking the average of 1.5 and 1.66 tonnes acid spar (1.54 tonnes CaF_2 per tonne of UF_6) and acid spar purity of 97.5%, it requires 2.3 million tonnes of CaF_2 to produce the 1999 global stock. Some depleted uranium was also stored as U_3O_8 and uranium metal, but these are not included in the CaF_2 requirement, which means that consumption up to the end of 1999 could have been higher. The production of U_3O_8 by mining cannot be used to determine CaF_2 consumption by year as stocks were created and processing to UF_6 depended on demand (Nuclear Energy Agency, 2016). Recovering usable fluoride from depleted UF_6 is problematic (Borgard et al., 2015).

2.15   Petroleum alkylation and production of Linear Alkyl Benzenes

The HF Alkylation process for motor and aviation fuel production catalytically combines light olefins, which are usually mixtures of propylene and butylenes, with isobutane to produce a branched-chain paraffinic fuel.

The HF alkylation reaction takes place in the presence of anhydrous HF under conditions selected to maximize alkylate yield and quality. The HF Alkylation process was developed during the late 1930s and early 1940s. The process was initially used to produce high-octane aviation fuels from butylenes and isobutane. Alkylation was a major consumer of HF in the early 1940s due to the demand for aviation fuel (Hamrick & Voskuil, 1949). Alkylation experienced tremendous growth during the 1940s because of the demand for high-octane aviation fuel. Capacity remained relatively flat during the 1950s and 1960s due to the comparative cost of other blending components (Stratford Engineering, 2023). By the early 1960s, the HF Alkylation process had virtually displaced motor fuel polymerization units for new installations, and refiners had begun to gradually phase out the operation of existing polymerization plants (Meyers, 2006). The U.S. Environmental Protection Agency's lead phase-down program in the 1970s and 1980s further increased the demand for alkylate as a blending component for motor fuel. A different alkylation process uses sulphuric acid as catalyst and more recently other catalyst are used.

In the HF Alkylation process, HF acid is the catalyst that promotes the isoparaffin-olefin reaction. Improved processes (internal acid regeneration) technique has virtually eliminated the need for an acid regenerator and, as a result, acid consumption has been greatly reduced in more modern processes. Acid neutralisation of effluents results in the formation of CaF_2 which is a waste. In the past, this was traditionally disposed of in a landfill after analysis to ensure appropriate properties are met.

$HF + KOH \rightarrow KF + H_2O$
$2KF + Ca(OH)_2 \rightarrow CaF_2 + KOH$
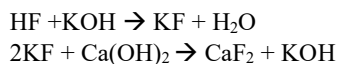
According to a 1993 report, approximately 0.1 to 0.2 lb (about 0.05 to 0.1 kg) of HF were consumed per barrel of alkylate produced (U.S. EPA, 1993). However, 2001 Petroleum Refining states that 0.3 lb (about 0.15 kg) HF is consumed per barrel of alkylate (Gary & Handwerk, 2001), and, according to another source (Meshri, 2000), the consumption of hydrofluoric acid per barrel of alkylate varies from 0.09 to 0.23 kg. The total HF consumption rate was higher in earlier years. The US Minerals Yearbook reports HF consumption for some years and US alkylation capacity is also available. In the early 1990s, HF alkylation units accounted for 52% of the alkylate produced in the United States and also operated at more than 90% of capacity (Felten, Bradshaw, McCarthy, 1994). For the USA, a 52% share for HF alkylate production in 1991, and 90% alkylation capacity utilisation, results in about 0.07 kg/barrel alkylate, based on the reported HF consumption (16,200 metric tonnes) and the reported installed alkylation capacity, which is available for the U.S. from 1982 (U.S Energy Information Administration, 2022). This is within the range stated in the 1993 report, 0.05 to 0.1 kg/barrel (U.S. EPA, 1993).

In 2004, it was reported that 2% (22,000 tonnes) of global HF consumption was used for alkylation (Will, 2007). Globally, about 60% of the installed alkylation capacity used HF as catalyst in the mid-1990s (Oil & Gas Journal, 1996), but, by 2014, HF alkylation had reduced to about 40% of the total installed capacity as more recent installed capacity used other catalysts (Norton Engineering, 2016). The USA still had a 78% share of global total alkylation capacity in 2010. Reported HF consumption for alkylation is in Table S13.

From the available data, it is estimated that over 640,000 tonnes of HF were consumed for alkylation in the period to 1999, equivalent to 1.3 million tonnes of CaF_2.

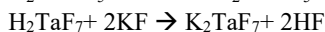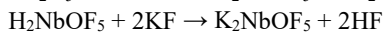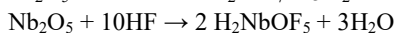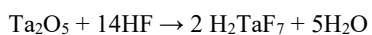**Table S13.** Reported HF consumption for Alkylation

	HF metric tonnes USA	Data Source
1957	5500	US Minerals Yearbook
1966	11,000	US Minerals Yearbook
1972	13,500	US Minerals Yearbook
1977	11,000	US Minerals Yearbook
1991	16,000	US EPA hydrogen fluoride study 1993, (U.S. EPA, 1993).
2001	14,000	Fluorides, hydrogen fluoride, and fluorine; Chapter 5, 2003 (Agency for Toxic Substances and Disease Registry, 2003)
2004	22,000 (global)	Will, 2007

The reported USA data are rounded in short tons or tons, the metric equivalents here are also rounded.

Linear Alkyl Benzenes (LAB) were introduced in the mid-1960s as a raw material for detergents. They replaced branched chain alkyl benzene derived detergents in most applications due to improved biodegradation. Global demand for LAB was 1987: 1514 kilotonnes; 1992: 1873 kilotonnes; and 1995: 2364 kilotonnes. Almost two thirds of LAB was produced using HF as catalyst, using a similar process to petroleum alkylation (de Almeida, 1994). By 2005 75% of the installed LAB capacity used HF (Environmental Risk Assessment, 2013). The HF consumption for LAB production in the period until the end of 1999 is estimated at less than 20,000 tonnes.

2.16 Niobium and Tantalum (aqueous HF)

Niobium and tantalum are chemically similar and are associated with each other in nature which makes it very difficult to separate. For many years, the separation of tantalum from niobium involved the fractional crystallization of potassium heptafluorotantalate away from potassium oxypentafluoroniobate monohydrate. The mixed oxides of tantalum Ta_2O_5 and niobium Nb_2O_5 are obtained from ore by various processes. Fluorides are prepared by the initial reaction of the oxides with aqueous hydrofluoric acid, with one process route being reaction with KF. Newer processes use the liquid extraction of the fluorides from aqueous solution by organic solvents (Ayanda & Adekola, 2011).

$Ta_2O_5 + 14HF \rightarrow 2\ H_2TaF_7 + 5H_2O$
$Nb_2O_5 + 10HF \rightarrow 2\ H_2NbOF_5 + 3H_2O$
$H_2NbOF_5 + 2KF \rightarrow K_2NbOF_5 + 2HF$
$H_2TaF_7 + 2KF \rightarrow K_2TaF_7 + 2HF$

Global production of niobium is available for 1943 to 1999 and tantalum from 1970 to 1999 in the U.S Minerals Yearbook (United States Bureau of Mines, 1993a). Tantalum production is minor compared to niobium, in 1999 tantalum was 495 tonnes and niobium 24,500 tonnes. Reported production of niobium was 396 metric tonnes in 1943. Assuming 95% fluoride efficiency the use of HF and CaF_2 equivalents can be estimated for each year. This is calculated from the HF use, and does not include fluoride from KF, as alternative processes are possible that do not use KF. The total HF consumption over the period to 1999 is estimated at about 0.5 million tonnes equivalent to 1 million tonnes CaF_2.

2.17 Stainless Steel Pickling (aqueous HF)

Pickling is the most common chemical procedure used to remove oxides and iron contamination. Besides removing the surface layer by controlled corrosion, pickling also selectively removes the least corrosion-resistant areas such as the chromium-depleted zones. The most common pickling solution is 10 to 15% nitric acid plus 1 to 3% hydrofluoric acid. The treatment leaves the stainless-steel (StS) surface in a clean, passivated condition (Speciality Steel Industry of North America, 2022). During the pickling process the concentration of metals in the bath grows and the content of the free acid falls accordingly. The pickling effect decreases with use and the pickling bath has to be renewed or strengthened (Brown, 2002). Pickling requirement and HF concentration depends on the stainless-steel type and surface to be cleaned. The total HF use depends on the surface area per tonne and percentage of stainless steel pickled. Data are available for HF consumption for stainless steel pickling for some years in the USA in the period 1944 to 1999 (United States Bureau of Mines, 1993), and for 2001 (Agency for Toxic Substances and Disease Registry, 2003; U.S. Geological Survey, 2001), shown in Table S14. Stainless steel production data are also available for the USA (1944 -1999) from the Minerals Yearbook and globally for 1950-1999 (World Stainless, 2020). From the US consumption of HF and production of stainless steel, the HF use per tonne of stainless steel can be estimated. Although the global pickling requirement may be different to the USA, applying the USA HF use/tonne provides an estimate for the potential global HF consumption.

In 1944, stainless steel production in the US was 0.43 million tonnes. Global stainless steel production was 1 million tonnes in 1950, increasing to about 16 million tonnes in 1999. The total HF consumption over the period to 1999 is estimated as 1.5 million tonnes equivalent to 3 million tonnes CaF_2.

Table S14. HF use per tonne for stainless steel pickling estimated from reported US use and stainless steel production

	HF kg/tonne StS
1944	6.7
1957	6.7
1966	7.5
1972	8.0
1976	5.2
1985	5.1
1986	5.2
2001	9.6

2.18 Inorganic fluorides (mainly aqueous HF)

The use of aqueous HF for the recovery of niobium and tantalum, and uranium are discussed in separate sections, as global production data and recovery processes are known. According to a 1993 survey (U.S. EPA, 1993), a range of other inorganic fluorides were produced using anhydrous or aqueous HF, shown in Table S15.

Table S15. Some inorganic fluorides and their uses (1993)

From anhydrous HF	
Boron trifluoride	Catalyst, nuclear technology, preparation of boranes
Stannous fluoride	Toothpaste additive
Ammonium bifluoride (NH_4HF_2)	Neutralisation of alkalis for laundry/textiles, metal fluorides → beryllium fluoride → beryllium, acid dips for steel
From aqueous HF	
Fluoroboric acid	Heavy metal fluoroborates (catalysts, electroplating, metallurgy) electropolishing aluminium, metal cleaning
Alkali metal and ammonium fluoroborates	High temperature fluxing in metal processing
Lithium fluoride	Ceramics, flux compositions for metal joining
Magnesium fluoride	Fluxing in magnesium metallurgy, ceramics
Potassium bifluoride (KHF_2)	Fluorine
Sodium fluoride	Fluoridation of drinking water, flux for steel, aluminium re-smelting

According to a 1968 report (Bradbury, Finger, & Major, 1968), in 1958 in the USA, about 13100 tonnes of inorganic fluorides were produced, which were mainly sodium, ammonium and boron fluorides (11,300 tonnes). The report comments that it is reasonable to assume increased production by 1968, although available data are fragmentary. If the USA represents 50% of global inorganic fluoride production and assuming that production doubled between 1958 and 1999 allows an estimate of the hydrogen fluoride (and calcium fluoride) used for production, see Table S16. Alternatively, assuming 2% of total global HF production up to 1999 is used to produce inorganic fluorides results in the same quantity of hydrogen fluoride.

Table S16. Estimated calcium fluoride consumption for inorganic fluoride production

Inorganic Fluorides F-content %	
NaF	45
NH_4HF_2	67
BF_3	84
Assumed average F-content	50%
Global production of inorganic fluorides tonnes	
1958	26,300
1999	52,600
total production 1958 to 1999, tonnes	1,620,000
as HF equivalent	850,000
as CaF_2 equivalent	1,700,000

3   Other uses of HF not resulting in TFA formation

There are many other uses of fluorspar (as HF) that are not as easily estimated but would also not result in the formation of TFA, as these uses are aqueous HF, inorganic, catalysis, solvent or uses that do not result in substances that could degrade to TFA.

3.1   Uses of anhydrous hydrogen fluoride

A review in 1982 *Reactions in anhydrous hydrogen fluoride* (Baasner & Klauke, 1982) stated that anhydrous hydrogen fluoride (AHF) serves as an excellent agent for introducing fluorine into organic compounds, as a solvent, and a catalyst. There are a wide range of organic compounds that contain fluorine but do not contain CF_3-C groups, required for the potential formation of TFA. Some examples are:

- Anhydrous HF is a catalyst and solvent for the production of an intermediate in the manufacture of acetaminophen (paracetamol), and according to this report (U.S. EPA, 1993), the use of AHF is relatively small at one production unit in the USA in the 1990s, about 20 tonnes/year. AHF is used for its reaction selectivity. Globally by 2002 about 75,000 to 80,000 tonnes of this analgesic were produced annually (S&P Global, 2002).
- PEEK Polymer (Polyether ether ketone) and other polyaryletherketones are high performance engineering thermoplastics. The production route uses 4,4'-difluorobenzonephenone as one of the monomers, with elimination of fluoride. The polymer was introduced commercially in the early 1980s (Victrex, 2018).
- Fluorobenzene is used to control carbon content in steel manufacturing, as an identification reagent for plastic and resin polymers, and as an intermediate for pharmaceuticals, pesticides, and other organic compounds (PubChem, 2022). The first successful fluoro-pharmaceutical, florinef acetate, containing a single F- group was introduced in 1954 (Ogawa et al., 2020).

3.2   Uses of aqueous hydrofluoric acid

There are a wide range of uses for aqueous hydrofluoric acid which have been reported over the period until 1999 for the USA. Some may no longer be used. These are in addition to the use of the aqueous acid to make inorganic fluorides, and niobium and tantalum production.

1940s and 1960s: The aqueous acid finds use for: frosting, etching, and polishing of glass; as an antiseptic in breweries and distilleries; electroplating; cleaning of copper and brass; in the making of filter paper and carbon electrodes; and for the removal of silica from graphite; in the removal of efflorescence from stone and brick; and galvanizing metals. Occasionally hydrofluoric acid is used in acidizing oil wells to increase oil production.

1990s: Glass etching and polishing; cleaning including aircraft paint stripping; manufacture of semiconductor chips, where the ultra-high purity aq. HF may be mixed with ammonium fluoride (U.S. EPA. 1993), and oil and gas well treatment reported in Minerals Yearbook 1993 (United States Bureau of Mines,1993b).

Acid treatment of oil and gas wells and geothermal wells: Oil and gas well acid treatment may be a significant use of aqueous HF. Oil and gas operators have used acid treatment (acidizing) to improve well productivity for almost 120 years (American Petroleum Institute, 2014). Acidizing predates all other well stimulation techniques, including hydraulic fracturing which was not developed until the late 1940s. Commercial use of aqueous HF for acid treatment started in 1940. Today, acidizing is one of the most widely used and effective means available to oil and gas operators for improving productivity (stimulation) of wells. Acidizing is commonly performed on new wells to maximize their initial productivity and on aging wells to restore productivity and maximize the recovery of the energy resources. Two types of acids are most commonly used; hydrochloric acid is the most widely used acid in all formation types and, if necessary, hydrofluoric acid in sandstones and certain shales. Since geologic formations are never homogeneous, blends (particularly for sandstone formations) of HCl and HF are usually pumped with the blend ratios based on the formation mineralogy. When the acid reacts with formation materials it is largely consumed and neutralized. If HF is used, typically it is as a HCl/HF aqueous solution ("mud acid"), however other HF mixtures are also used (Shafiq & Mahmud, 2017). The trend in HF acid concentration is away from the previous standard 3% HF + 12% HCl with 1.5% HF + 13.5% HCl becoming the normal choice. The American Petroleum Institute, 2014 reports that up to 500 gallons per foot can be used. The Trends in matrix acidizing for one simulated 2 stage treatment reports 68.2 +55.6 [oil] barrels of 3% HF mud acid, equivalent to 19684 litres or about 590 kg of 100 % HF. Therefore, at 3% HF the reported HF use per treatment (Crowe et al., 1995) is up to about 500 kg. According to one report there are over 3 million abandoned oil and gas wells in the USA alone (NRDC, 2021).

Globally even if a very small percentage of abandoned wells globally had used aqueous HF, then the overall consumption may be a significant use of aqueous HF in the period until end 1999.

The acidification of geothermal wells (Portier, André, & Vuataz, 2007) is not frequently used but the operations were borrowed from the treatments performed on oil or gas wells. Hydrochloric acid (HCl), hydrofluoric acid (HF) or both have been used since the 1980's in hydrothermal wells. These two acids are considered the most effective ones. HCl was selected to treat limestone, dolomite and calcareous zones whereas HF was used to dissolve clay minerals and silica.

4   Metallurgical and ceramic grade and other inorganic uses of fluorspar

The use of fluorspar as a flux for steel production is discussed in the paper.

4.1   Use of ceramic grade fluorspar

The use of fluorspar by the ceramics industry is inorganic. During the 1940s, in the USA, the ceramic industry was the third largest user of fluorspar (Hamrick & Voskuil, 1949). It was used in glass manufacture where opaque, coloured, and clear glass is desired. Manufacturers of enamel and vitrolite used it as a fluxing and opacifying agent. In the 1960s, about 27,000 tonnes/year of fluorspar was used as a flux or opacifier. During this period about 85% of the fluorspar was ceramic grade with the remainder almost all acid grade fluorspar. In the same period, about 4500 tonnes of mainly ceramics grade fluorspar were used for enamels and glazes, with the fluorspar reducing the melting point of the glass melt. Fluorspar content of the enamels and glazes is in the range 0 -15% (Bradbury, Finger, & Major, 1968) By 1980, in the USA fluorspar used for glass and enamel had reduced to about 10,000 tonnes (United States Bureau of Mines, 1981).

4.2   Other inorganic uses of fluorspar

There are a range of other smaller inorganic uses of fluorspar which have been reported over the period until 1999 for the USA. Some may no longer be used.

1940s: Magnesium industry, cement manufacturing, rock wool industry, paint pigment, binder in abrasives, carbon electrode manufacture, welding fluxes and rods, heat resistant brick, optical spar.

1960s: In addition to magnesium, minor amounts are used in the smelting of metals including zinc, antimony, copper, chromium, gold, lead, tin, silver, nickel and other metals. Excluding magnesium, consumption of fluorspar for these non-ferrous metals production was about 9000 tonnes in 1963, with metallurgical grade usually specified. Special fluxes used in refractory, aircraft and welding industries with about 4500 tonnes used in 1963.

1980s and 1990s: Fluorspar was reported to be used by fiberglass, cement and brick manufacturers and for welding rod coatings (United States Bureau of Mines, 1993b).

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