Journal of Geoscience and Environment Protection, 2023, 11, 1-16
https://www.scirp.org/journal/gep
ISSN Online: 2327-4344
ISSN Print: 2327-4336

An Inventory of Fluorspar Production, Industrial Use, and Emissions of Trifluoroacetic Acid (TFA) in the Period 1930 to 1999

Andrew A. Lindley

Consultant, Lochmaddy, UK
Email: andy.a.lindley@gmail.com

How to cite this paper: Lindley, A. A. (2023). An Inventory of Fluorspar Production, Industrial Use, and Emissions of Trifluoroacetic Acid (TFA) in the Period 1930 to 1999. *Journal of Geoscience and Environment Protection, 11,* 1-16.
https://doi.org/10.4236/gep.2023.113001

Received: January 26, 2023
Accepted: March 10, 2023
Published: March 13, 2023

Abstract

There is a generally accepted conclusion that trifluoroacetic acid (TFA) does occur naturally, in part based on the large quantities of TFA in the oceans (61 - 205 million tonnes, measured in 1998-2002). However, the recent review paper "Insufficient evidence for the existence of natural trifluoroacetic acid" concludes that "*the presence of TFA in the deep ocean and lack of closed TFA budget is not sufficient evidence that TFA occurs naturally, especially without a reasonable mechanism of formation*". Industrial sources of TFA can only result from the use of fluoride minerals in industrial processes. Major industrial uses of fluorspar started significant expansion from about the same time (1930s). Over 190 million tonnes of fluorspar have been mined in the period 1930 to 1999. An inventory has been developed (1930-1999), accounting for most of the fluorspar production (86%) and estimating emissions of TFA. Industrial emissions of TFA are estimated as 230,000 to 470,000 tonnes. Significant other industrial uses of fluorides have not been identified that could account for the large burden of TFA in the oceans. This inventory provides complementary evidence that the quantity of TFA in the oceans must include a large natural burden.

Keywords

Fluorspar, Trifluoroacetic Acid, TFA, HFCs, Pesticides, Aluminium, Steel, Anaesthetics

1. Introduction

There is a generally accepted conclusion that trifluoroacetic acid (TFA) does occur naturally, in part based on the undisputed large quantities of TFA in the oceans. However, the recent review paper “Insufficient evidence for the existence of natural trifluoroacetic acid” (Joudan, De Silva, & Young, 2021) concludes that “*the presence of TFA in the deep ocean and lack of closed TFA budget is not sufficient evidence that TFA occurs naturally, especially without a reasonable mechanism of formation.*” The large burden of TFA in the oceans (Frank et al., 2002), estimated at 61 - 205 million tonnes (Scott et al., 2005) was measured in the period 1998-2002. TFA was detected in the deep arctic ocean, with a reported ^{14}C age of about 1000 years, and oceanic TFA concentration measurements (Scott et al., 2005) included the Canadian Basin (western Arctic Ocean) deep or bottom waters. The average age of the Canadian Basin Deep Waters was concluded to be comparably high at perhaps 400 years (Rudels & Quadfasel, 1991). At 3000 m depth in the Canadian Basin of the western Arctic Ocean TFA concentration was measured as 160 ng/L similar to the concentrations measured in the Atlantic (Frank et al., 2002). A supplemental part of the oceanic measurement project for AFEAS (Alternative Fluorocarbons Environmental Acceptability Study) was a comparison of analytical results obtained using the methods employed by the two participating laboratories, the Universität Bayreuth and the University of Nevada, which carried out studies on TFA concentrations in precipitation in California and Nevada (Wujcik, Cahill, & Seiber, 1999).

In contrast to the reported TFA concentration measurements, PFAS were not found at depths below 250 m in the Arctic Ocean and the study did not include TFA (Yeung et al., 2017). “*The detection of PFASs in the four depth profiles was limited to the 150 m below the surface, except for the North Barents Sea where a PFAS was detected down to 250 m below surface.*” Samples were taken at depths down to 3000 m in the Nansen and Amundsen Basins of the Arctic Ocean “*Deep layer water samples* (*3000 m depth from 4 different stations*) *were served as field blanks and were found below limits of quantification*”. The paper states that the lifetime of tracers in Arctic Deep water is about 75 - 300 years.

Industrial sources of TFA can only result from the use of fluoride minerals in industrial processes. An inventory has been developed for the period 1930 to 1999, to account for the vast majority (86%) of fluorspar consumption by application, identify those uses that result in significant emissions of TFA, and estimate emissions of TFA. The objective of the inventory is to provide complementary evidence that the quantity of TFA in the oceans measured in the period 1998-2002 must include a large natural burden. While there are a wide range of studies for TFA emissions (Boutonnet et al., 1999; Neale et al., 2021; World Meteorological Organization, 2018), none of these studies have considered TFA emissions from all industrial sources in the period until 1999. Combining TFA emissions with an inventory of fluorspar production and consumption of other fluoride minerals provides additional confidence that significant sources of TFA have been considered, and such a study has not previously been published. However, a general background for fluorine uses has been published (Villalba, Ayres, & Schroder, 2007).

2. Development of the Inventory

The inventory was developed to account for most of the fluorspar consumption by application and estimate emissions of TFA from fluorspar uses in the period 1930 to 1999, using a wide range of publicly available data sources and input from industry and academic experts. For substances emitted to atmosphere, including HCFCs and HFCs, the quantity of TFA formed from each substance in the period up to 1999 depends on the amount emitted, its atmospheric lifetime, and TFA yield. Production and emissions of the major HCFCs and HFCs are well characterized, either by atmospheric measurements (top-down) or from production, use and bottom-up emission factors (e.g., AFEAS, 2000). Some pesticides containing the CF_3 group, can generate TFA by decomposition in soil, which will enter surface and ground waters. The yield of TFA is uncertain for some pesticides and their global use in the period until 1999 is also uncertain. Therefore, a maximum generation of TFA from pesticides has been estimated. Establishing a robust estimate for the use of fluorspar (as HF) for aluminium production is important as it was a significant consumer of HF, but also used fluoride from other sources, and fluoride consumption/tonne aluminium over the period 1930-1999 was reduced. The supplementary information provides information for the TFA emission estimates and fluorspar use by application.

3. Inventory for Fluorspar Production and Emissions of TFA

The supplementary information provides details on the derivation of the fluorspar use and TFA emissions for each of the applications in **Table 1**. The inventory accounts for most of the fluorspar production (86%) by application. In addition, 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 the formation of substances that could degrade to TFA. For example, oil and gas well acid treatment may be a significant use of aqueous hydrofluoric acid. These uses are also discussed in the supplementary information. Several very minor uses of HF could be estimated but are not included in the inventory and do not result in the formation of TFA. These include the minor CFCs (e.g. CFC-13, -216, -217) and NF_3. The industrial use of other fluoride minerals is also considered, but these are relatively minor compared to fluorspar.

Industrial emissions of TFA are estimated at 84,000 tonnes until end of 1999, excluding pesticides and pharmaceuticals, and in the range 230,000 to 470,000 tonnes including pesticides and pharmaceuticals. An important conclusion from this inventory is that before 1947 extremely limited quantities (if any) of TFA were emitted from industrial sources. Steel and aluminium production are discussed in detail as both are major uses of fluorspar but are not considered to produce TFA, either based on the process conditions, by analysis or the generation of inorganic fluorides.

Significant other industrial uses of fluorides have not been identified that could account for the large burden of TFA in the oceans.

Table 1. Inventory: Summary of production and consumption of fluorspar and emissions of TFA 1930-1999.

Inventory for the period 1930-1999	**Fluorspar** (million tonnes)	**TFA emissions** (tonnes)
Global fluorspar production	191.9	
Metspar and ceramic grade production, inorganic uses	96.9	0
Acidspar grade production (at 97% minimum purity) for HF	95.0	
Losses due to HF yield from acidspar (assuming 97.5% purity)	8.9	0
Overall availability of HF as CaF_2 equivalent	**86.1**	
Identified uses of HF as CaF_2 equivalent		
CFCs (CFC-11, 12, 113, 114, 115)	14.6	0
HCFCs (non-feedstock): For CaF_2 consumption HCFC-22, 123, 124, 141b, 142b. TFA emissions: HCFC-123, 124	5.6	16,100
HFCs: For CaF_2 consumption: HFC-134a, 125, 143a. TFA emissions: HFC-134a, 227ea, 125, 143a	1.1	6700
PTFE & other fluoropolymers. TFA emissions for PTFE degradation, estimated based on Cui et al., 2019 methodology (A) and from feedstock emissions: Hexafluoropropene (HFP) & HCFC-133a (B).	2.5	60 (A) 7300 (B)
Halon 1211 (Fluoride for Halon 1301 is included in HCFC-22 F-efficiency)	0.1	0
Anaesthetics: halothane, isoflurane, sevoflurane, desflurane	0.1	23,600
Pesticides, assuming 100% yield of TFA (and assuming 90% efficiency of CaF_2 utilisation).	0.2 to 0.4 (~0.3)	140,000 to 380,000
Pharmaceuticals—example fluoxetine (Prozac) maximum TFA	trivial	5000
TFA manufacture, assumes all TFA manufactured equals TFA emissions (unlikely)	0.03	30,000
Aluminium production	25.3	0
SF_6 and SOF_2	0.3	0
Uranium processing	2.3	0
Petroleum alkylation	1.3	0
Niobium and tantalum (aqueous HF)	1.0	0
Stainless steel pickling (aqueous HF)	3.0	0
Inorganic fluorides (mainly aqueous HF) indicative estimate	1.7	0
Total uses of HF as CaF_2 equiv.	**59.2**	
Total TFA emissions Excl. pesticides & pharmaceuticals (C)		**84,000 (C)**
Incl. pesticides & pharmaceuticals (D)		**230,000 to 470,000 (D)**
TFA emissions are rounded up		
Total fluorspar production accounted for	86%	
Other HF uses as CaF_2 equivalent	26.9	

3.1. Emissions of TFA

Emissions of TFA were estimated at a maximum of 470,000 tonnes in the period 1930-1999. Significant sources of TFA are some HCFCs, some HFCs, anaesthetics, some fluorinated feedstocks, and potentially TFA manufacture, with TFA emissions from these sources estimated at 84,000 tonnes. Other sources of TFA emissions include some pharmaceuticals and potentially from incineration or thermolysis of PTFE and other fluoropolymers, although the experimental results may not translate to "real world" conditions. It is difficult to estimate the TFA generation from pesticides due to the various substances used and the uncertain or unknown yield of TFA. Pesticides containing the CF_3-group, could account for 140,000 to 380,000 tonnes of TFA, over the period until end 1999. Two methods were used to estimate the potential TFA emissions from pesticides; 1) based on published European pesticide use data and scaling this to global use, and 2) from the available trifluralin use data, as it had the greatest production volume in 1987, about 50,000 tonnes (Jordan & Frank, 1999) for these relevant pesticides, with the USA accounting for about 25% of its global use in that year. Trifluralin was the first fluoro-herbicide introduced in 1963 and is also one of the most globally used herbicides (Ogawa et al., 2020). Pesticides are most likely the largest source of TFA emissions in the period until 1999, if those pesticides containing a $-CF_3$ group and introduced before 1999, degraded to give 100% yield of TFA. The supplementary information provides details for the TFA estimates by application.

The UNEP Environmental Effects Assessment Panel (EEAP, 2022, 2023) gives estimated yields and upper limits for TFA generated from degradation of HFCs, HCFCs, and anaesthetics. Applying upper limits of TFA yields has minimal effect on the total TFA emissions until end of 1999, resulting in an increase of about 8500 tonnes. TFA from pesticides is already an indicative maximum estimate.

Estimated annual TFA emissions from HCFCs, HFCs, feedstock emissions (hexafluoropropene and HCFC-133a), anaesthetics, and pesticides are shown in **Figure 1**. This shows insignificant emissions of TFA (<100 tonnes/year) before 1950. According to a 1968 USA industry report (Bradbury, Finger, & Major, 1968), fluorinated aromatics were of minor importance "*Although still of minor importance among fluorochemicals, the fluorinated aromatic, alicyclic, and heterocyclic compounds and their derivatives are receiving increased attention in academic and industrial laboratories. Because of their limited application thus far, no production or dollar value data are available.*"

3.2. Production of Fluorspar and Other Fluoride Minerals

In the period 1930-1999 cumulative reported fluorspar production was 191.9 million tonnes (British Geological Survey, 2014). Complete data are not available for production of acidspar grade (used for HF production) from 1930, but the US Minerals Yearbook (United States Bureau of Mines, 1993; National Minerals

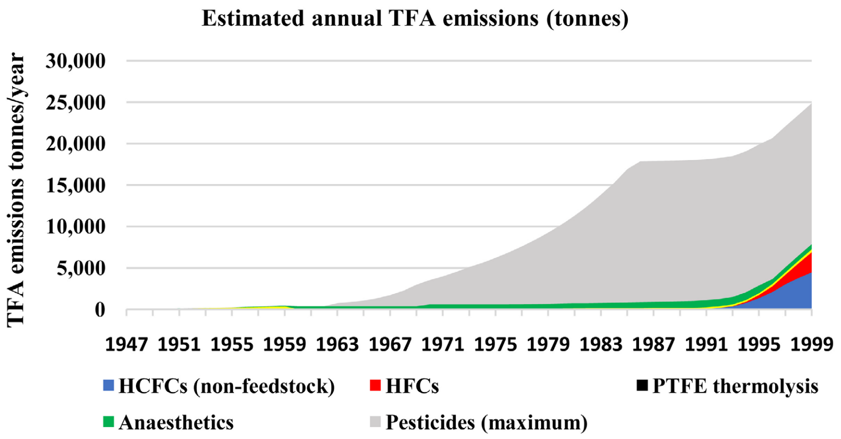

Figure 1. Estimated annual TFA emissions (tonnes) from significant sources. *Explanatory note: Pesticides is an indicative maximum estimate based on an estimate of trifluralin consumption, and assuming degradation to give 100% yield of TFA, which may not occur.*

Information Center, 2022) reports global production from 1970, although some production by country is not segregated by grade. World production of fluorspar by grade is also available for more recent years (Clarke & Huxtable, 2017). Prior to 1970, the US Minerals Yearbook data for domestic US acidspar used for HF production is assumed to be a good proxy for global acidspar production. Over the period 1930 to 1999, acidspar production is estimated as 95 million tonnes, about 50% of the total fluorspar production, and metspar (metallurgical)/ceramic grade is estimated as 96.9 million tonnes, used for inorganic processes, mainly steel production. The use of fluorspar by the ceramics industry is relatively minor, accounting for about 10% of total annual fluorspar consumption in the United States in the early 1960s (Bradbury, Finger, & Major, 1968), reducing to about 1% in 1980 (United States Bureau of Mines, 1981).

Cryolite and fluorapatite are other relatively minor sources of fluoride used industrially. Cryolite mineral (sodium hexafluoroaluminate, Na_3AlF_6) was commercially mined in Greenland from 1854 to 1987 resulting in 3.7 million tonnes of ore with an average content of 58% cryolite in the ore (Geological Survey of Denmark and Greenland, 2002). Cryolite has been found in small quantities in other locations, but the only large commercial deposit of cryolite was in Greenland. It was originally used in the production of soda, and later for iron enamelling and the production of opaque glass. Until 1900, cryolite was used to produce soda (cryolite soda), with peak consumption in the period 1865-1870, when about 44,000 tonnes of cryolite were consumed annually for this use (Kruse, 2016). Natural cryolite was used for aluminium production.

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, although some recovered fluorosilicic acid was used for water fluoridation, AlF_3 production for aluminium production, and other uses (Agency for Toxic Substances and Disease Registry, 2003).

3.3. Production and Use of HF

Anhydrous HF is produced from acidspar (minimum purity of 97%) by reaction with concentrated sulphuric acid. There are stringent limits on the sulphur, arsenic, and phosphorus contents (British Geological Survey, 2011). The yield of HF from acidspar has increased since the 1930s as the manufacturing process has improved. Fluoride inefficiency results in some CaF_2 lost in solid synthetic anhydrite ($CaSO_4$). For many years, this was considered as a waste, but much of it is now dried in a kiln and used as a raw material for producing cement, plaster, and flooring. It is also used as a filler in the production of plastics and paper products (Chemical Book, 2022). Some fluoride is lost as H_2SiF_6, although this can be used for a range of applications if recovered. In the 1990s/2000s fluoride recovery systems were introduced for HF production.

Anhydrous HF is normally produced with a concentration of 99% - 99.9%, and aqueous HF (hydrofluoric acid) is primarily produced as a 70% solution, although a range of other strengths are then prepared for a wide range of applications (U.S. EPA, 1993). In 1944, in the USA, the total HF production was 43,000 tonnes, with about 50% of was earmarked as anhydrous acid and a similar quantity as aqueous hydrofluoric acid. By 1948 more anhydrous acid was being generated than aqueous. By then the industrial trend was to produce anhydrous HF with subsequent dilution to the desired aqueous strengths. In earlier years aqueous hydrofluoric acid was made directly and not by dilution of anhydrous HF (Hamrick & Voskuil, 1949). The organic fluorochemicals industry and aluminium production use anhydrous HF, with aqueous hydrofluoric acid mainly being used for a wide range of inorganic applications.

The use of HF (as CaF_2 equivalent) can be estimated by year when there is production and usage data for the specific application. **Figure 2** shows the consumption CaF_2 for more significant uses of HF. AFEAS compiled annual production data for reporting companies from 1931 for the main CFCs: 11, 12, 113,

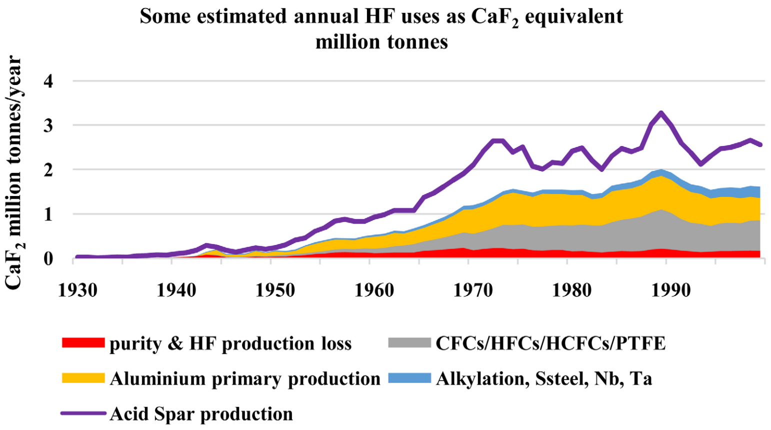

Figure 2. Some uses of HF as CaF_2 equivalents in million tonnes annually.

114 and 115 (AFEAS, 2000, 2003). AFEAS production data are available for most of the major commercial HCFCs, except HCFC-123, and in 2000 is thought to represent about 98% of global HFC-134a production. The AFEAS data excludes Chinese production. Fluoride efficiencies, provided by industry experts, are used to account for consumption of HF for production of these substances. PTFE was commercialised in 1947, with a succession of fluoropolymers introduced in the following decades. 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 commercialization in 1947. The HF alkylation process for motor and aviation fuel production takes place in the presence of anhydrous HF catalyst. Developed during the late 1930s and early 1940s, alkylation was a major consumer of HF from the early 1940s, initially due to the demand for aviation fuel (Hamrick & Voskuil, 1949). Pickling of stainless steel 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 surface in a clean, passivated condition (Speciality Steel Industry of North America, 2022). 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. Fluorides are prepared by the initial reaction of the oxides with aqueous hydrofluoric acid (Ayanda & Adekola, 2011).

Before 1944 any other uses of HF are most likely to be as aqueous hydrofluoric acid for inorganic applications based on the USA aqueous hydrofluoric acid consumption for 1944. Although uranium processing is a significant use of anhydrous HF, 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). It is clear from **Figure 2** that, prior to 1950, only a minor proportion of HF (as CaF_2 equivalent) is not accounted for and most likely is predominantly used in aqueous hydrofluoric acid applications. There are a wide range of other uses for aqueous hydrofluoric acid which are not easily estimated. One of these, which may be a significant use, is the acid treatment of oil and gas wells and geothermal wells. Oil and gas operators have used acid treatment (acidizing) to improve well productivity for almost 120 years. 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 (American Petroleum Institute, 2014).

3.4. Production of Aluminium

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, 2022a). 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 (Hyland et al., 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).

Since the 1940s, the dominant source of fluoride for synthetic cryolite or aluminium fluoride is fluorspar (CaF_2). It is estimated that 25.3 million tonnes of fluorspar have been used by for aluminium production in the period 1930 to 1999. In addition, an estimated 1.9 million tonnes of natural cryolite and 1.8 million tonnes of AlF_3 from H_2SiF_6 (from phosphate minerals) have been used. The derivation of the estimate is described in detail in the supplementary information. **Figure 3** 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.

From the 1970s, Spent Pot Linings (SPL) has 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, 2022). 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. Small quantities of perfluorocarbons (PFCs) are produced at the anode; this occurs during the anode effect condition. The formation of fluorocarbons in primary aluminium production occurs at the anode when the local consumption of alumina becomes higher than the supply, reducing the local concentration of alumina to allow competitive anode reactions (Aarhaug & Ratvik, 2019). The emission factors for

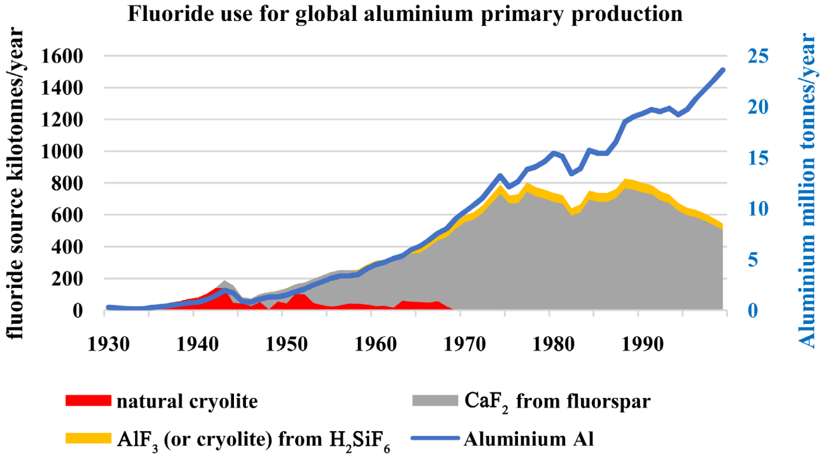

Figure 3. Calcium fluoride and other mineral consumption for aluminium production.

PFCs have decreased from around 2.1 - 4.4 kg/tonne for CF_4, 0.49 - 0.72 kg/tonne for C_2F_6 and 0.004 - 0.05 kg/tonne for C_3F_8 in 1940 to about 0.04, 0.003 and 0.0001 kg/tonne in recent years. Over the period 1930 to 1999, total PFC emissions from primary aluminium production are estimated as CF_4: 560 kilotonnes, C_2F_6: 70 kilotonnes and C_3F_8: 9 kilotonnes (Trudinger et al., 2016).

The formation of other fluorinated organic species has been investigated (Aarhaug & Ratvik, 2019), "*While formation of COF_2 is favourable thermodynamically, this species has only been reported once in laboratory-scale experiments with inert gas. An attempt to reproduce this experiment was not successful. It has been suggested that COF_2 is unstable and will either react with carbon to form PFCs or self-disproportionate to form CF_4 and CO_2.*" The potential formation of TFA has been investigated (Jordan & Frank, 1999), and concluded. "*Formation of TFA or trifluoroacetyl fluoride was also considered possible, but analysis of a stack gas sample of an aluminium production site did not reveal any TFA. An upper limit of 0.25 g of TFA emitted per ton aluminium as derived from the limit of determination would result in a maximum annual global release of 5 tes/yr from this source, assuming a global annual aluminium production of 20 million tons. However, these are preliminary results which warrant more detailed investigations.*"

3.5. Production of Steel

Metallurgical-grade fluorspar is consumed mainly in steelmaking but is also used in making Portland cement and casting iron and steel (Miller, 2018). Fluorspar use for cast iron was reported in the 19th century (Henderson, 1871). Most of the 96.9 million tonnes of metspar/ceramic grade fluorspar in the period 1930 to 1999 was used by the iron and steel industry, which is by far the largest single industrial use of fluoride. Metallurgical grade fluorspar has a calcium fluoride content typically > 80%, but it can be as low as 60%, depending on the requirement. Steel production uses metspar as a flux to lower the melting temperature, reduce viscosity, and increase the chemical reactivity to help the absorption and removal of sulphur, phosphorus, carbon, and other impurities in the slag (Critical Raw Materials Alliance EU, 2022). Fluoride-containing slag modifiers have been widely used for decades in industry (Schrama et al., 2020). Raw steel production processes in the period 1930 to 1999, initially open hearth, then replaced by the basic oxygen process, and electric arc, used fluorspar as a flux, at a rate of 2 - 10 kg/tonne in 1982. Steel slags can be recycled for use in iron blast furnaces (Kokal & Ranade, 1994). The basic oxygen process is the main process for raw steel manufacture accounting for about 70% of global production in 2021 (World Steel Association, 2022). Around 160 - 250 million tonnes of steel slag were generated in 2014 (van Oss, 2015). Slag is widely used as aggregate and in other applications (Zulhan, 2013). The electroslag remelting (ESR) process is used to remelt and refine steels and various super-alloys, resulting in high-quality ingots, and conventional commercial ESR slag contains a large amount of CaF_2 (typically 50 - 70 mass %), to reduce the melting temperature and viscosity of the slag (Zheng, Li, & Shi, 2020). Where fluorspar is used as a flux, electric arc furnace (EAF) steel slag typically contains < 1% fluoride (Teo et al., 2020). If this was typical of steel slags generally, then 0.5% fluoride content for 160 - 250 million tonnes of slag would be equivalent to 1.5 - 2.5 million tonnes of calcium fluoride, in the range expected for fluorspar use. In 2019, 6.5 million tonnes of fluorspar were produced, and 40% as metspar at a minimum of 80% purity would be about 2 million tonnes of calcium fluoride.

The basic oxygen process for raw steel production uses molten iron (melting point 1538˚C) and the hot metal is treated by blowing oxygen to remove carbon and other elements that have a high affinity to oxygen. When the reaction process is complete, molten crude steel collects on the bottom of the furnace and the liquid slag floats on top of it. The crude steel and the slag are tapped into separate ladles/pots at temperatures typically above 1600˚C (Euroslag, 2022). Open hearth was the most widely used steel production process until the 1960s, being replaced by the basic oxygen process. The open-hearth process achieves similar temperatures to the basic oxygen process. Scrap is charged to the furnace through doors in the furnace front. Hot metal from the blast furnace is added by pouring from a ladle through a trough positioned in the door. Melting heat is provided by gas burners above and at the side of the furnace. The most significant emissions from the basic oxygen process occur during the oxygen blow period. The predominant compounds emitted are iron oxides, although heavy metals and fluorides are usually present. Particulate emissions from an open-hearth furnace vary considerably during the process but are mostly iron oxides (U.S. EPA, 1986).

The most difficult fluorinated organic compound to decompose is CF_4, requiring temperatures over 1400˚C. Limited studies on the thermal destructibility of fluorotelomer-based polymers found no detectable levels of perfluorooctanoic acid after 2 second residence time and 1000˚C (U.S. EPA, 2019). Generation of TFA by the iron and steel industry is not expected and fluoride used as a flux for steel production remains as an inorganic substance predominantly in the slag. It is worth noting that some chlorinated hydrocarbons (mainly C_1 and C_2) are formed during iron and steel production, and these may be attributable to incomplete combustion of chlorinated fuel and raw coal. The emission factor for Cl_{VOCs} is reported as 0.08 g Cl/tonne for steel making (Ding et al., 2020). In 1999, the world production of steel was 784 million tonnes (U.S. Geological Survey, 2022b). Applying the reported Cl_{VOCs} emission factor to this production quantity, equates to about 63 tonnes of chlorine as VOCs.

4. Conclusion

Industrial sources of TFA can only result from the use of fluoride minerals in industrial processes. Major industrial uses of fluorspar started significant expansion from about the same time (1930s). The inventory accounts for most of the fluorspar production (86%) of the 191.9 million tonnes of fluorspar that has been mined in the period 1930 to 1999. In addition, 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. Other fluoride minerals were only a minor source of fluoride used for industrial processes in this period, mainly for aluminium production.

Industrial emissions of TFA are estimated at 84,000 tonnes until end of 1999, excluding pesticides and pharmaceuticals, and in the range 230,000 to 470,000 tonnes including pesticides and pharmaceuticals. It is difficult to estimate the TFA generation from pesticides due to the various substances used and the uncertain or unknown yield of TFA. Pesticides are most likely the largest source of TFA emissions in the period until 1999, if those pesticides containing a CF_3-group and introduced before 1999, degraded to give 100% yield of TFA. Steel and aluminium production were the two largest consumers of fluoride minerals, predominantly fluorspar, but are not considered to produce TFA, either based on the process conditions, by analysis or the generation of inorganic fluorides. Significant other industrial uses of fluorides have not been identified, in the period 1930-1999, that could account for the large burden of TFA in the oceans. An important conclusion from this inventory is that before 1947 extremely limited quantities (if any) of TFA were emitted from industrial sources. However, TFA was detected in the deep Arctic Ocean in waters with a reported ^{14}C age of about 1000 years, with a different study concluding that the waters have a comparably high average age at perhaps 400 years.

The inventory for the period 1930-1999 provides complementary evidence that the quantity of TFA (61 - 205 million tonnes) measured in the oceans in the period 1998-2002 must include a large natural burden.

Acknowledgements

This work was supported financially by EFCTC trade association and by helpful discussions with its member companies' industry experts. Also, Archie McCulloch for discussions about fluorochemical production and data sources. In particular, the use of fluorspar for aluminium production benefitted from extensive dialogue with Stephen J Lindsay, formerly of Alcoa, for providing valuable advice, data, information, and review editing for this section and the more detailed data in the supplementary information. Also, Linlin Wu of the International Aluminium Institute for AlF_3 consumption data and historical texts on aluminium production.

Supporting Information

The derivation of all the data in the paper Table 1. Inventory: Summary of production and consumption of fluorspar and TFA emissions 1930-1999 is in the 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 supporting information is available to download at https://www.fluorocarbons.org/wp-content/uploads/2023/02/Supporting-Information-Inventory-of-fluorspar-production-and-TFA-emissions-1930-to1999-FINAL.pdf.

Funding and Conflict of Interest Statement

The author is a science consultant to EFCTC (European Fluorocarbons Technical Committee). This is a review paper, and data and information are referenced. The work was supported financially by EFCTC trade association and by helpful discussions with its member companies' industry experts. EFCTC trade association members produce HFCs and HCFCs (discussed in this inventory), and some of the substances EFCTC members produce degrade to TFA, which is the subject of this review paper.

References

Aarhaug, T. A., & Ratvik, A. P. (2019). Aluminium Primary Production Off-Gas Composition and Emissions: An Overview. *JOM, 71,* 2966-2977. https://doi.org/10.1007/s11837-019-03370-6

AFEAS (2000). *Alternative Fluorocarbons Environmental Acceptability Study. Introduction to AFEAS, Production, Sales and Atmospheric Release of Fluorocarbons through 2000.*

AFEAS (2003). *Expanded Data.* https://agage.mit.edu/sites/default/files/documents/em-cfc-11.pdf

Agency for Toxic Substances and Disease Registry (2003). Chapter 5. Production, Import/Export, Use, and Disposal. In *Fluorides, Hydrogen Fluoride, and Fluorine.* https://www.atsdr.cdc.gov/toxprofiles/tp11-c5.pdf

American Petroleum Institute (2014). *Acidizing: Treatment in Oil and Gas Operators.* https://www.api.org/oil-and-natural-gas/wells-to-consumer/exploration-and-production/hydraulic-fracturing/acidizing-treatment-in-oil-and-gas-opera

Ayanda, O. S., & Adekola, F. A. (2011). A Review of Niobium-Tantalum Separation in Hydrometallurgy. *Journal of Minerals and Materials Characterization and Engineering, 10,* 245-256. https://doi.org/10.4236/jmmce.2011.103016

Boutonnet, J. C., Bingham, P., Calamari, D., de Rooij, C., Franklin, J., Kawano, T. et al. (1999). Environmental Risk Assessment of Trifluoroacetic Acid. *Human and Ecological Risk Assessment, 5,* 59-124. https://doi.org/10.1080/10807039991289644

Bradbury, J. G., Finger, G. C., & Major, R. L. (1968). *Fluorspar in Illinois.* Illinois State Geological Survey, Circular 420, ISGS.

British Geological Survey (2011). *Fluorspar Profile, Fluorspar Mineral Profiel.* British Geological Survey.

British Geological Survey (2014). *World Mineral Production 2008-2012 Centenary Edition.* http://www.bgs.ac.uk/mineralsuk/statistics/worldStatistics.html

Chemical Book (2022). *Synthesis and Uses of Anhydrite.* Chemical Book.

Clarke, G., & Huxtable, P. (2017). Fluorspar to 2018 and Beyond. In *Fluorine Forum 2017.* IMFORMED.

Critical Raw Materials Alliance EU (2022). *Fluorspar.* CRM Alliance.

Cui, J., Guo, J., Zhai Z., & Zhang, J. (2019). The Contribution of Fluoropolymer Thermolysis to Trifluoroacetic Acid (TFA) in Environmental Media. *Chemosphere, 222,* 637-644. https://doi.org/10.1016/j.chemosphere.2019.01.174

Ding, X., Li, Q., Wu, D., Huo, Y., Liang, Y., Wang, H. et al. (2020). Gaseous and Particulate Chlorine Emissions from Typical Iron and Steel Industry in China. *Journal of Geophysical Research: Atmospheres, 125,* e2020JD032729. https://doi.org/10.1029/2020JD032729

EEAP (2022). Environmental Effects Assessment Panel, Presentation Assessment 2022, Environmental Effects of Stratospheric Ozone Depletion, UV Radiation, and Interactions with Climate Change. In *34th Meeting of the Parties to the Montreal Protocol (2022).* EEAP.

EEAP (2023). *Environmental Effects Assessment Panel, Assessment Report 2022.* When Published Is Expected to Provide an Update on TFA Emissions and Sources, Environmental Effects Assessment Panel (EEAP). Ozone Secretariat.

Euroslag (2022). *The European Association Representing Metallurgical Slag Producers and Processors Basic Oxygen Furnace Slag.* Euroslag.

Frank, H., Christoph, E. H., Holm-Hansen, O., & Bullister, J. L. (2002). Trifluoroacetate in Ocean Waters. *Environmental Science & Technology, 36,* 12-15. https://doi.org/10.1021/es0101532

Geological Survey of Denmark and Greenland (2002). Early Mining Activities in South Greenland. Exploration and Mining in Greenland, Fact Sheet No. 2.

Hamrick, N. T., & Voskuil, W. H. (1949). *Fluorspar and Fluorine Chemicals: Part I-Economic Aspects of the Fluorspar Industry. Part II-Fluorine Chemicals in Industry.* State of Illinois, Division of the State Geological Survey, Urbana, Report of Investigations-No. 141. https://ia600301.us.archive.org/28/items/fluorsparfluorin141hamr/fluorsparfluorin141hamr.pdf

Henderson, J. (1871). The Action of Fluorspar on Different Qualities of Cast Iron. *Nature, 3,* 435. https://doi.org/10.1038/003435a0

Hyland, M. M., Patterson, E. C., Stevens-McFadden, F., & Welch, B. J. (2000). Aluminium Fluoride Consumption and Control in Smelting Cells. In *6th Molten Slags, Fluxes and Salts Conference.* High Temperature Materials and Processing Group, The University of Auckland.

International Aluminium Institute (2022). *Spent Pot Lining: An Introduction Fact Sheet Spent Pot Lining: An Introduction Factsheet.* International Aluminium Institute.

Jordan, A., & Frank, H. (1999). Trifluoroacetate in the Environment. Evidence for Sources Other than HFC/HCFCs. *Environmental Science & Technology, 33,* 522-527. https://doi.org/10.1021/es980674y

Joudan, S., De Silva, A. O., & Young, C. J. (2021). Insufficient Evidence for the Existence of Natural Trifluoroacetic Acid. *Environmental Science: Processes & Impacts, 23*, 1641-1649. https://doi.org/10.1039/D1EM00306B

Kokal, H. R., & Ranade, M. G. (1994) *Metallurgical Uses: Fluxes for Metallurgy. Industrial Minerals and Rocks, 15,* 661-675.

Kruse, F. (2016). Historical Perspectives—The European Commercial Exploitation of Arctic Mineral Resources after 1500 AD. *Polarforschung, 86,* 15-26.

Miller, M. M. (2018). *Mineral Resource of the Month: Fluorspar.* American Geosciences Institute.

National Minerals Information Center (2022). *Fluorspar Statistics and Information*. http://www.usgs.gov/centers/national-minerals-information-center/fluorspar-statistics

-and-information

Neale, R. E., Barnes, P. W., Robson, T. M., Neale, P. J., Williamson, C. E., Zepp, R. G. et al. (2021). Environmental Effects of Stratospheric Ozone Depletion, UV Radiation, and Interactions with Climate Change: UNEP Environmental Effects Assessment Panel, Update 2020. *Photochemical & Photobiological Sciences, 20,* 1-67. https://doi.org/10.1007/s43630-020-00001-x

Nuclear Energy Agency (2016). *Uranium 2016: Resources, Production and Demand.* Nuclear Energy Agency (NEA).

Ogawa, Y., Tokunaga, E., Kobayashi, O., Hirai, K., & Shibata, N. (2020). Current Contributions of Organofluorine Compounds to the Agrochemical Industry. *iScience, 23,* Article ID: 101467. https://doi.org/10.1016/j.isci.2020.101467

Rudels, B., & Quadfasel, D. (1991). *The Arctic Ocean Component in the Greenland-Scotland Overflow.* International Council for the Exploration of the Sea.

Samec, N., Mikša, D., & Kokalj, F. (2004). Recycling Possibilities of Spent Potlining from the Aluminium Industry. In V. Popov, H. Itoh, C. A. Brebbia, & S. Kungolos (Eds.), *Waste Management and the Environment II.* WIT Press. https://www.witpress.com/

Schrama, F. N. H., Ji, F., Hunt, A., Beunder, E. M., Woolf, R., Tuling, A. et al. (2020). Lowering Iron Losses during Slag Removal in Hot Metal Desulphurisation without Using Fluoride. *Ironmaking & Steelmaking, 47,* 464-472. https://doi.org/10.1080/03019233.2020.1747778

Scott, B. F., Macdonald, R. W., Kannan, K., Fisk, A., Witter, A., Yamashita, N., Durham, L., Spencer C., & Muir, D. C. G. (2005). Trifluoroacetate Profiles in the Arctic, Atlantic, and Pacific Oceans. *Environmental Science & Technology, 39,* 6555-6560. https://doi.org/10.1021/es047975u

Speciality Steel Industry of North America (2022). *Descaling Stainless Steel.* SSINA

Tabereaux, A. T., & Peterson, R. D. (2014). Aluminum Production. In S. Seetharaman (Ed.), *Treatise on Process Metallurgy: Volume 3: Industrial Processes* (pp. 839-917). Elsevier. https://www.sciencedirect.com/topics/engineering/aluminum-production https://doi.org/10.1016/B978-0-08-096988-6.00023-7

Teng, H. (2012). Overview of the Development of the Fluoropolymer Industry. *Applied Sciences, 2,* 496-512. https://doi.org/10.3390/app2020496

Teo, P. T., Zakaria, S. K., Salleh, S. Z., Taib, M. A. A., Sharif, N. M., Seman, A. A. et al. (2020). Assessment of Electric Arc Furnace (EAF) Steel Slag Waste's Recycling Options into Value Added Green Products: A Review. *Metals, 10,* Article No. 1347. https://doi.org/10.3390/met10101347

Trudinger, C. M., Fraser, P. J., Etheridge, D. M., Sturges, W T., Vollmer, M. K., Rigby, M. et al. (2016). Atmospheric Abundance and Global Emissions of Perfluorocarbons CF_4, C_2F_6 and C_3F_8 since 1800 Inferred from Ice Core, Firn, Air, Archive and in Situ Measurements. *Atmospheric Chemistry and Physics, 16,* 11733-11754. https://doi.org/10.5194/acp-16-11733-2016

U.S. Geological Survey (2022a). *Aluminium Statistics.* USGS. http://minerals.usgs.gov/minerals/pubs/historical-statistics/

U.S. Geological Survey (2022b). *Iron and Steel Statistics and Information.* USGS.

U.S. EPA (1986). *AP-42, CH 12. 5: Iron and Steel Production.* U.S. EPA.

U.S. EPA (1993). *Hydrogen Fluoride Study: Report to Congress.* Document Displa, NEPIS, U.S. EPA. https://search.library.wisc.edu/digital/APPYAWXJZXOESO8L

U.S. EPA (2019). Technical Brief: Per- and Polyfluoroalkyl Substances (PFAS): Incineration to Manage PFAS Waste Streams. U.S. EPA.

United States Bureau of Mines (1981). *Minerals Yearbook. Vol. I. Metals and Minerals.* UWDC, 341 p.

United States Bureau of Mines (1993). *Minerals Yearbook 1932-1993.* |Minerals Yearbook (172 Issues). UWDC-UW-Madison Libraries. (wisc.edu)

van Oss, H. G. (2015). *Mineral Resource of the Month: Iron and Steel Slag.* U.S. Geological Survey.

Villalba, G., Ayres, R. U., & Schroder H. (2007). Accounting for Fluorine: Production, Use, and Loss. *Journal of Industrial Ecology, 11,* 85-101. https://doi.org/10.1162/jiec.2007.1075

World Meteorological Organization (2018). *Scientific Assessment of Ozone Depletion: 2018* (588 p.). Global Ozone Research and Monitoring Project, Report No. 58. World Meteorological Organization.

World Steel Association (2022). *#steelFacts.* World Steel Association. https://worldsteel.org/about-steel/steel-facts/

Wujcik, C. E., Cahill, T. M., & Seiber, J. N. (1999). Determination of Trifluoroacetic Acid in 1996-1997 Precipitation and Surface Waters in California and Nevada. *Environmental Science & Technology, 33,* 1747-1751. https://doi.org/10.1021/es980697c

Yeung, L. W. Y., Dassuncao, C., Mabury, S., Sunderland, E. M., Zhang, X., & Lohmann, R. (2017). Vertical Profiles, Sources, and Transport of PFASs in the Arctic Ocean. *Environmental Science & Technology, 51,* 6735-6744. https://doi.org/10.1021/acs.est.7b00788

Zheng, D., Li, J., & Shi, C. (2020). Development of Low-Fluoride Slag for Electroslag Remelting: Role of Li_2O on the Crystallization and Evaporation of the Slag. *ISIJ International, 60,* 840-847. https://doi.org/10.2355/isijinternational.ISIJINT-2019-575

Zulhan, Z. (2013). *Iron and Steelmaking Slags: Are They Hazardous Waste?* ASEAN Iron and Steel Sustainability Forum.