Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment

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Following the introduction of hydrochlorofluorocarbon (HCFCs) and hydrofluorocarbon (HFCs) gases as replacements for the ozone-destroying chlorofluorocarbons (CFCs), it has been discovered that HCFCs/HFCs can degrade in the atmosphere to produce trifluoroacetic acid[1], a compound with no known loss mechanisms in the environment[2,3], and higher concentrations in natural waters[4] have been shown to be mildly phytotoxic[5]. Present environmental levels of trifluooracetic acid are not accounted by HCFC/HFC degradation alone[8–10]. Here we report that thermolysis of fluorinated polymers, such as the commercial polymers Teflon and Kel-F, can also produce trifluoroacetate and the similar compound chlorodifluoroacetate. This can occur either directly, or indirectly via products that are known to degrade to these haloacetates in the atmosphere[11]. The environmental significance of these findings is confirmed by modelling, which indicates that the thermolysis of fluoropolymers in industrial and consumer high-temperature applications (ovens, non-stick cooking utensils and combustion engines) is likely to be a significant source of trifluoroacetate in urban rain water (~25 ng l^{-1}, as estimated for Toronto). Thermolysis also leads to longer chain polyfluoro- and/or polychlorofluoro- (C3–C14) carboxylic acids which may be equally persistent. Some of these products have recently been linked with possible adverse health[6] and environmental impacts and are being phased out of the US market[7]. Furthermore, we detected CFCs and fluorocarbons—groups that can destroy ozone and act as greenhouse gases, respectively—among the other thermal degradation products, suggesting that continued use of fluoropolymers may also exacerbate stratospheric ozone-depletion and global warming.

The replacement CFC gases HCFC-123 (CF_3CHCl_2), HCFC-124 (CF_3CHClF) and HFC-134a (CF_3CH_2F) are known to degrade in the troposphere, through reaction with hydroxyl radicals, to trifluoroacetate, TFA[1]. TFA is expected to be a long-lived environmental species, and has no known significant loss mechanism[3]. Studies have suggested that at higher concentrations, such as those observed in surface waters with seasonal evaporation–concentration cycles[4], TFA will exhibit mild phytotoxicity[5]. Environmental modelling calculations conducted for TFA predict a concentration of 100–120 ng l^{-1} in rain water between the years 2010 and 2020[2]: these predictions were based on the assumption that TFA originates from the CFC replacement gases. Environmental measurements[8–10] of TFA have shown that current levels cannot be accounted for by these sources alone. In certain regions, concentrations of TFA in rainwater now average 120 ng l^{-1} (ref. 8), and no major alternative source has been identified to explain these observations. Although there is some controversy within the literature, it seems that the TFA observed in precipitation is largely a result of urban activities. For example, TFA concentrations of <2–92 ng l^{-1} have been found at remote sites, compared with 50–1,100 ng l^{-1} for industrialized urban sites[12,13]. The unidentified source of TFA is likely to be anthropogenic in origin, as there are no known naturally occurring trifluoromethylated compounds. A second long-lived fluorinated acetic acid, chlorodifluoroacetic acid (CDFA) has recently been identified in rain water[3]. Direct evidence of a source responsible for its production has yet to be established, although CFC-113 ($CF_2ClCFCl_2$) may contribute.

Agrochemicals, anaesthetics and fluoropolymers are the three main, distinct, categories into which environmental emissions of fluorine-containing anthropogenic organic compounds can be subdivided. Both agrochemicals[14] and anaesthetics[8] have been shown to produce TFA, but they can be eliminated as major contributors due to the quantities that are currently being emitted into the atmosphere[8]. Fluoropolymers, such as polytetrafluoroethylene (PTFE), are potential sources, due to their heavy usage in urban and industrial areas. In 1988 the average annual global consumption of fluorinated polymers was 40,000 tonnes (ref. 15) and by 1997 this figure had risen by almost 220% based upon sales[16], with a projected annual increase of 7%.

In order to produce the CF_3– or CF_2Cl– unit required for the formation of haloacetic acid, the polymer would have to undergo decomposition and subsequent rearrangement. Fluoropolymers are being designed and modified specifically for use in areas of high thermal stress, such as ovens, cookware, industrial and car engines, heat exchangers, high-temperature circuits and a wide variety of other thermal applications. In 1997, 1% of all polymers were used in areas of elevated temperature, a grouping composed primarily of fluoropolymers[17]. The subcategory of plastics known as engineering plastics, in particular fluoropolymers, operate at the extreme of polymers' temperature performance[17]. PTFE, for instance, will endure 260 °C for ~2.3 years (ref. 18) until failure due to degradation[19]. Fluoropolymers are, largely, either recycled or degrade *in situ*[19], resulting in research on the toxicity of the decomposition products[20]. The onset of thermal degradation of fluoropolymers is known to initiate cleavage of the backbone and

Table 1 Positively identified species produced in the thermal decomposition of fluoropolymers

Polymer	Thermal product identified	Per cent produced
PTFE	TFE*†	–
	HFP*‡	10.8§
	TFA*†	7.8‡§
	c-OFB†	–
	$CF_3(CF_2)_nCOOH$†	>0.01‡
	$CF_3O(CF_2)_mCOOH$†	–
	DFA†	>0.01‡
	MFA†	>0.01‡
CPTFE	CTFE*†	–
	CPFP*‡	13.1§
	CDFA*†	9.5‡§
	TFA*†	>0.1‡§
	DCHB*†	–
	DCHFCB*	–
	TCTFE*	–
	1,3-DCTFP*†	–
	1,1,3-TCTFP*†	–
	$CCl_xF_y(CCl_{x-1}F_2)_zCOOH$†	–
ECTFE	TFA*†	6.3‡§
	CDFA*†	7.2‡§
	HFP*	–
	CPFP*	–
PFEPE	TFA*†	2.5*†
	HFP*	–

A dash indicated that the analyte was positively identified but not quantified. Acronyms used which are not in the body of the text: MFA, monofluoroacetic acid; DFA, difluoroacetic acid; FDCA, fluorodichloroacetic acid; DCFP, dichloroperfluoropentanoic acid; DCFB, dichloroperfluorobutanoic acid; DCHFCB, 1,2-dichlorohexafluorocyclobutane; TCTFE, 1,1,2-trichloro-1,2,2-trifluoroethane; 1,3-DCTFP, 1,3-dichlorotetrafluoropropene; 1,1,3-TCTFP, 1,1,3-trichlorotrifluoropropene; ECTFE, ethylene-chlorotrifluoroethylene; PFEPE, polytetrafluoroethylene-*co*-tetrafluoroethylene perfluoropropylether. For the long-chain acids, $n = 1$–12, $m = 1$–7, $x = 0$–2, $y = 1$–3, $z = 1$–2, $p = 9$–13.
* Identified by NMR.
† Identified by MS.
‡ Quantified by NMR.
§ Quantified by MS.