Organofluorine Compounds in the Environment – Analysis, Sources and Fate

by

David Andrew Ellis

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Department of Chemistry
University of Toronto

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David Ellis
Department of Chemistry, University of Toronto

Abstract

An evaluation of $^{19}$F nmr as an analytical for the measurement of trifluoroacetic acid (TFA) and other fluorinated acids in the aquatic environment was conducted. A method based upon strong anionic exchange (SAX) chromatography was also optimized for the concentration of the fluoro acids prior to nmr analysis. Extraction of the analyte from the SAX column was carried out directly in the nmr solvent in the presence of the strong organic base, DBU. The method allowed the analysis of the acid without any prior clean up steps being involved. Optimal nmr sensitivity based upon $T_1$ relaxation times was investigated for seven fluorinated compounds in four different nmr solvents. The use of the relaxation agent chromium acetylacetonate, Cr(acac)$_3$, within these solvent systems was also evaluated. Results show that the optimal nmr solvent differs for each fluorinated analyte. Cr(acac)$_3$ was shown to have pronounced effects on the limits of detection of the analyte. Generally, the optimal sensitivity condition appears to be methanol-$d_4$/2M DBU in the presence of 4 mg/ml of
Cr(acac)$_3$. The method was validated through spike and recovery for five fluoro acids from environmentally relevant waters. Results are presented for the analysis of TFA in Toronto rainwater, which ranged from $<16 - 850$ ng/L. The nmr results were confirmed by GC-MS selected ion monitoring of the fluoroanalide derivative.

The lampricide 3-trifluoromethyl-4-nitrophenol (TFM) is added annually to the Great Lakes. TFM was shown to undergo photohydrolytic degradation, at 365 nm and under actinic radiation, to produce TFA. The TFA was analyzed using the $^{19}$F nmr developed. A mechanistic study for the production of TFA from TFM was conducted and the structural parameters associated with the production of TFA from trifluoromethylated phenols were investigated. It was found that the yield of TFA is clearly dependent on the nature of the trifluoromethylated phenol. The nature of the substituents, the substitution pattern, and the pH strongly affected the photolytic half life of the parent compound and the yield of TFA. The half life of TFM at 365 nm was found to be 22 hours (pH 9) and yielded 3.9 % TFA, and 54 hours at pH 7, yielding 11 % TFA. Converting the nitro- substituent of TFM to an amino- group caused a decrease in the half life to 2.3 minutes and yielded 11 % TFA. The mechanism for the production of TFA from TFM was deduced from the pH dependence and the effect of altering substituents on the trifluoromethyl phenol. Ultimately, the formation of trifluoromethylquinone led to the quantitative production of TFA.

The environmental fate of trichloro, dichloro, and monochloroacetic acids, and TFA was investigated using field aquatic microcosms and laboratory
sediment-water systems. Trifluoroacetic acid was extremely persistent and showed no degradation during a one year field study, though it appeared to undergo transient partitioning within an unknown pond phase as the temperature of the surroundings was reduced. Of the three chloroacetic acids, trichloro had the longest residence time (induction and decay) (≈40 d), dichloro the shortest (≈4 d) and monochloro an intermediate residence time (≈14 d). Laboratory studies suggest that the biodegradation of trichloro, dichloro, and monochloroacetic acids lead primarily to the formation of chloride and oxalic, glyoxalic and glycolic acids respectively.

Thermal degradation is expected to be a primary mode of destruction for highly stable fluoropolymers. The thermolysis of Teflon® and Kel-F® resulted in the production of trifluoroacetate and chlorodifluoroacetate (7.7 and 9.5% w/w respectfully) which is proposed to contribute to the atmospheric burden of both haloacetic acids. Environmental modeling suggests that this may be a significant source of TFA in Toronto rainwater (≈25 ng/L). Their thermal degradation also leads to the production of species that are known, or are suspected, to degrade to these acetates in the troposphere; both acetates are persistent environmental pollutants with no known degradation pathways. 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 and environmental impacts and are themselves being phased out of the U.S. market. The production of known greenhouse
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This thesis is dedicated to Jayne Elizabeth Ottmann -

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Chapter One

Introduction
1.0 Overview

The intention of the work presented within this thesis was to advance the current understanding and knowledge of the fate of fluorinated anthropogenic materials in the environment. Particular emphasis was placed on the analytical measurement, production, persistence, fate and prevalence of fluorinated haloacetic acids (HAAs). These are considered to be environmentally long-lived species, some of which have no known degradation pathways. This chapter is designed to give the relevant background information on the two key areas in the main body of the thesis, namely:

1) The role which fluorine imparts on the chemical and physical properties of organic molecules.
2) The use of $^{19}$F nmr spectroscopy in environmental chemistry.

Each chapter is preceded with a concise introduction dealing with the pertinent information for subsequent material.

1.1 The Incorporation of Fluorine into Anthropogenic Materials; Background and Resultant Physical and Chemical Properties

Organochlorine compounds are diverse in nature while organofluorine compounds are not. Two main reasons have been suggested to account for this observation. The first is that inorganic minerals containing fluorine are usually sparingly soluble compared with their chloro- or bromo- counterparts, leaving the fluorine biologically inaccessible. The second, and probably more importantly, is
the high redox potential required for oxidation of fluoride. This high redox potential does not permit activation of the fluoride ion by \( \text{H}_2\text{O}_2 \), thus precluding the incorporation of fluorine by the haloperoxidase reaction (Hamilton et al., 1998). The most widespread natural organofluorine compound observed is monofluoroacetate (MFA), found in the leaves and seeds of a variety of tropical plants. To date the only other fluorinated compounds that have been isolated were longer chained monofluoro acids (Gribble, 1992). All of the isolated natural products containing fluorine have only one fluorine atom. Contrastingly, nature has seen fit to introduce chlorine, bromine and iodine within a wide variety of natural products (approximately 1500 compounds).

Anthropogenic materials often contain many fluorine atoms within their structure. Perhaps due to the relative absence of fluorinated compounds in the environment, nature has a difficult time degrading anthropogenic materials which are fluorinated, especially when polyfluorinated.

Fluorine forms the strongest single bond with carbon of all the elements (103.8 - 130.5 kcal/mol depending upon the degree of carbon fluorination). In conjunction with the poor leaving group ability of fluoride (Koch, 1984; Stirling, 1974; Parker, 1963), this leads to alkyl fluorides being \( 10^2 \)-\( 10^6 \) times less reactive than the corresponding alkyl chloride in typical \( S_N1 \) solvolysis or in \( S_N2 \) displacement reactions (Hudlicky, 1976; Chambers, 1973). The very high C-F and C-C bond strengths in perfluorinated alkanes contribute to their characteristic high thermal and chemical stabilities. The thermolytic decomposition of these compounds depends only upon the length of the carbon chain, due to a
weakening of the C-C bond, cf. 1000°C required to pyrolyze \( n-C_3F_6 \) compared with 500°C for polytetrafluoroethylene (PTFE) (Banks, 1970). Although fluorine forms such strong bonds with carbon which are considerably inert toward chemical attack, the bonds can often be broken through photolytic processes (Wirz and Seiler, 1972). Carbon-fluorine bonds do not absorb energy at actinic wavelengths of light (290-700 nm) and are not broken directly. However, if the molecule to which they are connected absorbs these wavelengths then the bond can be broken through molecular excitation. For example, excitation of the molecule may result in a change in the vibrational state of the molecule. This change in the vibrational motion of the molecule may in turn change the physical properties of the carbon-fluorine bond.

Fluorine has low polarizability, is small in size, and is the most electronegative element in the periodic table (Holloway, 1995). As such, carbon-fluorine bonds are polar, \( \delta^+\text{C-F}\delta^- \), and have a relatively ionic nature. This imparts a wide variety of characteristics upon the chemical and physical properties of organofluorine compounds, which are not seen for the other halogens. In turn, this leads to organofluoro compounds having quite individual attributes. For example, benzene is reactive toward electrophiles, while hexafluorobenzene shows reactivity toward nucleophiles. When fluorine is present in highly fluorinated systems, such as PTFE, it acts to protect the carbon backbone from chemical attack. This is due to fluorine having a small atomic radius and three non-bonding electrons in its outer shell, resulting in high localized electron density, and can thus be considered as a protective sheath in the case of PTFE.
(Sandford, 2000). Fluorine atoms often impart an increased stability to organic molecules. For example, hydrocarbon radicals are extremely unstable whereas some fully fluorinated counterparts are stable enough that they can be heated for several hours (Scherer et al., 1985). Because of the small size of the fluorine atom, and thus the relatively non-sterically-demanding nature of the transition states, the influence of the fluorine substituents upon the nature of the radical is believed to derive largely from the electronic nature of the fluorine (Dolbier, 1997). Fluorine not only acts as a strong $\sigma$ inductive electron withdrawer but also is a potential strong $\pi$ donor to carbon $\pi$–systems. This includes $\pi$ donation to the semi occupied molecular orbital (SOMO) of a carbon radical. This donation is a result of the geometrically and energetically close match of the 2p orbitals of the fluorine and those of the carbon (Dolbier, 1997), a match that is not seen for the other halogens. It is these interactions which can result in the production of highly stabilized radicals, a facet which is often important in the mechanism by which thermal decomposition of a polyfluorinated species occurs, for example in the case of fluoropolymer (see Chapter 5).

The incorporation of fluorine, in comparison with the other halogens, within a molecule can have unusual and pronounced effects upon the physical properties of the molecule, for example, the effect upon boiling point, and hence vapor pressure. Homologous polyfluorinated carbons and hydrocarbons closely match each other in their boiling point despite the large differences in molecular weight (Banks, 1970). This is presumably due to the electronic repulsion of fluorinated molecules. Each fluorine within a molecule has an associated
negative dipole and also masks the positive carbon atom in the bond, therefore electrostatic repulsion would be high and thus decrease the boiling point of the compound. In the case of partially fluorinated hydrocarbons, entirely different trends are seen. (e.g., the case of fluorinated methanes (Figure 1.1)).

![Boiling points of halomethanes](image)

**Figure 1.1** Observed boiling points of fluorinated methanes.

The inclusion of additional halogen atoms to methane causes an increase in the observed boiling point, as is the case for both chlorine and bromine. In the case of fluorine, however, a maximum boiling point is observed when two fluorines are incorporated, the subsequent addition of fluorine atoms results in a suppression of the boiling point. This peculiar trend suggests that CH₂F₂ is the most polar molecule. This coincides with the observed dipole moment for these compounds. An associated intermolecular hydrogen-bonded structure, unique to the CH₂F₂ compound has been suggested (Nagel, 1990). Other hydrofluorocarbons also show correlation between their boiling point and the
dipole moment (Smart, 1994). However there are many exceptions to this rule. For example, CH$_3$CF$_3$, with a highly polar C-C bond ($\mu=2.32$ D) boils at $-47^\circ$C, considerably higher than either CH$_3$CH$_3$ (-88$^\circ$C) or CF$_3$CF$_3$ (-78$^\circ$C), but CH$_3$CHF$_2$ which has almost the same dipole moment ($\mu=2.27$ D) boils 22$^\circ$ higher at $-24.7^\circ$C. These boiling point peculiarities are often seen with fluorinated organic molecules. The boiling point and vapor pressure of a fluorinated molecule appears to be governed by a series of variables, including the degree of fluorination, the relative position of the fluorine within the molecule, and the dipole moment. Each variable can either work to raise the boiling point or decrease it.

Other similar unique properties are observed for fluorocarbons when compared with chloro- and bromocarbons. Fluorination has pronounced effects on adjacent bond strengths. $\alpha$-Fluorination always markedly increases the bond strengths of C-F and C-O bonds but does not alter the strength of C-H, C-Cl, or C-Br bonds (Smart, 1986), while $\beta$-fluorination significantly decreases C-H bond strengths but has little effect on C-F bonds. Why these trends occur is not fully understood. In order to help explain the C-F bond stabilization and length in CF$_4$ in comparison with CCl$_4$, negative hyperconjugation has been employed. This involved the use no bond – double bond resonance structures as shown in Figure 1.2(a) (Rodriquez et al., 1992), a theoretical picture that was also applied to CF$_3$ functionality on aromatic rings (Figure 1.2(b)) (Roberts et al., 1950).
Figure 1.2 (a, b). Resonance structures used to explain the observed bond strengths and lengths seen in fluoromethyl compounds.

However, both the stability and the bond shortening with increasing fluorination can also be attributed to Coulombic interactions between the negatively charged fluorines and the increasing positively charged carbon (Wiberg and Rablen, 1993).

Similar trends are observed in the bond length between the carbon and the halogen atom, i.e., with increasing fluorination on the central carbon atom bond lengths decrease, a trend that is not observed with the other halogens. This is due to the nature of the molecular orbital wavefunctions (ϕ) which are formed from the atomic orbitals of the fluorine (ψ), i.e. (ϕF-C = ψF + ψC) = (ϕCl-C = ψCl + ψC).

The electron-withdrawing and donating ability of the fluorine nucleus, relative to other nuclei, has been fully studied in aromatic systems (Taft and Lewis, 1959; Jafee, 1953; Taft, 1960; Taft, 1963). The Hammet substituent
constant for fluorine when in the meta position indicates that it is a marginally worse electron-withdrawing agent than chlorine, bromine or iodine (e.g., $\sigma_{m}F - 0.34 \text{ v's } \sigma_{m}Cl - 0.37$). This is surprising due to the greater electronegativity of fluorine. However, what is most striking is the ability of fluorine to donate electrons to the benzene ring by a resonance effect when in the para position (Pross et al., 1980; Hansch et al., 1973). This results in fluorine, when para to a substituent, such as benzoic acid or a phenol, its effect is negligibly different from hydrogen on that substituent (cf. $\sigma_pF - 0.06$). This is due to the better overlap between the 2p non-bonding electrons on fluorine with the 2$\pi$ bonding of the aromatic ring. A -CF$_3$ group attached to ring does not show this effect as the total electron-withdrawing ability of the substituent is due solely to inductive effects. This point is further illustrated in the acidity of substituted phenols. For example, the O - H proton of $\rho$-fluorophenol is approximately half as acidic as that for o-fluorophenol, and $\rho$-trifluoromethylphenol is six times as acidic as $\rho$-fluorophenol (Silvestre and Topsom, 1990).

Studies have shown that fluorine has the ability to act as a hydrogen bond acceptor (Huang and Hedberg, 1989). The C(sp$^3$)–F···H–O bond is less than half the strength of C–O···H–O bond, approximately 2 kcal/mol (Huang and Hedberg, 1989). Nevertheless, this hydrogen bonding allows an increase in the water solubility of fluorinated species compared with the hydrocarbon counter parts. For example, it has been shown that the polar CF$_3$-CH$_2$ group of surfactant CF$_3$(CH$_2$)$_n$CO$_2$Na results in a doubling of the water solubility over the hydrocarbon counterpart CH$_3$(CH$_2$)$_n$CO$_2$Na (Muller and Birkitt, 1967).
As is the case for water solubility, fluorination of chemicals also effects the partition of the chemical into other phases such as lipids (Yalkowsky et al., 1979; Valvani et al., 1981; Chiou et al., 1982). However, the generalization that fluorination always decreases the hydrophobicity of a compound is incorrect. Aromatic fluorination and fluorination adjacent to atoms or groups which contain \( \pi \)-electrons does indeed invariably decrease hydrophobicity (Hansch and Leo, 1979; Sangster, 1989). It is reported that fluorination of alcohols results in a decrease in hydrophobicity, e.g. \( \text{CF}_3(\text{CH}_2)_m\text{OH} \) partitions significantly less into octanol than \( \text{CH}_3(\text{CH}_2)_m\text{OH} \) \((m=4,5)\) (Muller, 1986). Smart et al. suggests that as a general trend it would appear that mono- and trifluorination results in a increase in hydrophobicity, as long as the fluorination occurs at a position within the molecule which is removed from any \( \pi \)-electrons (Smart, 1994).

1.1.1 The Utilization of Fluorine in Commercial Products – Fluorinated Polymers, Pesticides, Drugs, Refrigerants and Surfactants

Fluorine is contained in an ever increasing number of household and industrial products. Fluoropolymers are found in a gamut of uses, to mention but just a few; waterproof clothing, gaskets, car engines, artificial veins, and non-stick coatings. Smaller fully fluorinated molecules such as perfluorobutane find uses in ultrasound contrast imaging agents for visualizing heart disease and liver damage (Carmichael, 1998). Perfluorocarbon fluids (PFCs) possess the unique property of being able to dissolve large amounts of oxygen. As such they are now being implemented in uses such as filling the deflated lungs of premature
babies. The world of anaesthesiology has been revolutionized by the development of fluorinated analogues, such as halothane, to replace more hazardous alternatives (e.g., ether and chloroform).

Many pharmaceuticals that owe their bio-activity to the incorporation of single fluorine atoms or trifluoromethyl groups have been developed. They find use in many areas of medicinal chemistry such as antibiotics, anticancer, antiviral, and antidepressants. Several representative examples are shown in Figure 1.3.

![Representative pharmaceuticals that contain fluorine within their structure.](Image)

**Figure 1.3** Representative pharmaceuticals that contain fluorine within their structure.

Floxacillin (1) is an orally active antibacterial which has been shown to have improved activity over the nonfluorinated product (cloxacillin) (Filler and Kobayashi, 1982). 5-fluorouracil (2) was first used in landmark breakthroughs in
the field of cancer research by Heidelberger et al. (Duschinsky et al., 1957).

When uracil is incorporated within DNA it first must undergo a thymidylate synthase-catalyzed methylation of the deoxyuridine monophosphate (dUMP) at the C-5 position to produce thymidine monophosphate. The introduction of fluorine in place of the hydrogen in the C-5 position, producing fl<sup>5</sup> dUMP alters the chemical reactivity at that site. Thus the essential C-5 methylation is prevented as fluorine is unreactive toward formate. As (2) and its anabolities are concentrated in cancer cells, this enzymatic blockade inhibits tumor growth by causing "thymineless death" of malignant cells. Erythro-4-fluoro-DL-glutamic acid (3) is a non-competitive inhibitor of glutamine synthase due to the incorporation of fluorine, an enzyme that catalyzes the synthesis of glutamine from L-glutamic acid and ammonia. This inhibition helps explain the antitumor and antiviral activities of the molecule (Firsova et al., 1986). Flunoxaprofen (4) was introduced as a nonstereoidal anti-inflammatory agent. It is a lipoxygenase inhibitor which shows considerably less severe gastric disturbance over the non-fluorinated analogue (Quaglia et al., 1986). Monoamine oxidase (MAO) inactivates serotonergic and catecholaminergic neurotransmitters. 5-Fluoro-α-methyltryptamine (5) is an important MAO selective inhibitor, and as such exhibits mood-elevating properties. Similar activities are observed for 4-fluorotranylcypromine (6), which is 10 times more potent than the non-fluorinated analogue (Coutts et al., 1987). It is believed that the enhanced activity may be due to the increased hydrophobicity of the fluorinated compound and/or the blockade of metabolic para-hydroxylation.
The incorporation of CF$_3$ within amino acids has resulted in a stabilization of peptides (Koksch et al., 1996). The trifluoromethyl group imposes considerable polarization effects and important conformational restrictions on the neighboring residues when incorporated. These properties result in an increased proteolytic stability of peptides depending upon the relative position of the $\alpha$-trifluoromethyl group to the predominant cleavage site of the protease used. This results in the peptides being more available for application as pharmaceuticals.

The number of fluorinated agrochemicals that contain fluorine continues to grow. Presently, nearly half of all the molecules undergoing field trials as plant protection products contain fluorine (Sandford, 2000). The ever growing interest in the incorporation of fluorine within these molecules is due mainly to the fact that strategic placement of the fluorine can greatly alter the physicochemical properties and thus the biological activity of the pesticide (Lang, 1995). Undoubtedly fluorine also adds several other secondary features to the molecule. For example, due to the strength of the C-F bond it would be expected that the chemical, or metabolite would have a longer half-life in the environment. As pointed out in section 1.1, the incorporation of fluorine leads to an alteration in the physical properties of the chemical. This will result in a change in fate of the chemical, for example, in transport phenomena and partitioning coefficients. There are no globally defining rules and as such the addition of fluorine can cause these properties to either be enhanced or reduced and thus the prediction of the fate of the chemical is a complex task and compound specific. These features may be either beneficial or detrimental depending upon the requisites of
the agrochemical. Some examples illustrating the structural diversity, and hence physical variance, of fluorinated agrochemicals are given in Figure 1.4.

![Figure 1.4 The structural diversity of fluorinated agrochemicals.](image-url)
Fluorine has been incorporated into dyes as perfluoroalkyl groups resulting in an increase in the solubility, in organic solvents, in certain instances. This increase in solubility can be attributed to weak intermolecular interactions between molecules (Matsui, 1999). The solubility was observed to increase with chain length, with a maximum solubility observed for the perfluorohexyl derivative, at which point it tapered off with the perfluoroctyl derivative becoming much less soluble. This may be due to an increase in the rigidity of the chain. The stability and light absorption – relaxation phenomena of the dyes are also observed to change with the degree of fluorination.

Fluorine has been incorporated into many refrigeration gases. Traditionally these molecules were small hydrocarbons in which all of the hydrogen atoms were replaced with either chlorine and fluorine, hence they were given the acronym CFCs – chlorofluorocarbons. Due to overwhelming evidence that they were involved in the breakdown of stratospheric ozone they are being phased out of use in accordance with the Montreal Protocol. It was observed that the photochemical production of Cl radicals were the direct species responsible for the ozone depletion. Fluorine radicals are also produced photolytically, however it is believed that their impact upon ozone is negligible. In the upper stratosphere both fluorine and chlorine radicals can react with water, abstracting a proton. Due to the strength of the F – H bond (135.9 Kcal/mol) in comparison to that for Cl – H (103.2 Kcal/mol) results in this reaction being a sink for the fluorine radicals. Contrastingly, Cl – H can re-undergo photolysis to reproduce Cl radicals (Abbatt, 2001).
Surfactants that contain fluorine atoms can have remarkable characteristics which include extreme resistance to oxidation, water and oil repellency, thermal resistance (fluorosulphonates <350°C and carboxylic acids 175-250°C (Bryce, 1964)), chemical resistance (Pabon and Corpart, 1999), and lubricating action (Abe, 1999). The good thermal and chemical stability lends itself well to the use of fluorinated surfactants as fire fighting foams (Pabon and Corpart, 1999). The replacement of hydrogen with fluorine within the tail of a surfactant results in a change in the molecular geometry of the molecule. Hydrocarbon chains tend to take on a zigzag structure while fluorocarbon chains tend to have a rigid rod-like shape with a period twist of 13 carbon atoms (Figure 1.5) (Abe, 1999).

![Molecular structure of perfluorinated carbon chains compared with that seen for the hydrocarbon counterpart.](image)

**Figure 1.5** Molecular structure of perfluorinated carbon chains compared with that seen for the hydrocarbon counterpart.
Changes in the molecular structure of the fluorosurfactant can have pronounced effects upon the mode of action. For example the introduction of two hydrophobic groups increases the fluorosurfactants ability to solubilize large amounts of oil. Hybrid surfactants which contain both hydrocarbon and fluorocarbon chains show a large degree of functionality due to their extremely good surface and interfacial tension lowering ability.

In 1991 it was estimated that the commercial value of all products available which contain fluorine was approximately $1622 billion dollars (US) per year (Holloway, 2000). By 1996 this figure had rapidly increased and was extrapolated to $2000 billion. A further example of this trend is seen in the fluoropolymer industry with a base consumption of $1100 million in the USA alone in 1997, a figure which is expected to grow at a rate of 8% per annum.

1.2 The Utility of $^{19}$F nmr Spectroscopy in the Study of Environmental Processes; Fluorine as an nmr Nucleus

Usually, although not always, analytes of environmental interest are at relatively low concentration. They often occur within complex matrices leading to possible analytical interferences. These problems must be addressed when developing an analytical method of study, in particular when direct measurement without further sample purification or concentration is to be conducted. Although nmr is a relatively low sensitivity technique, if certain other aspects can be met it has several advantages over other methods of analysis, which often can outweigh the problems associated with sensitivity. The context of the present
studies is limited to dealing with the aspects of fluorine as an nmr nucleus. It should also be noted that $^{19}$F nmr has been extensively applied to the study of biological systems, such as in medicinal chemistry. This field has largely been omitted in the following discussions, except in the cases where there is direct overlap with environmental chemistry.

Of all the nmr nuclei $^{19}$F may be the most attractive one for investigations within environmental chemistry. The $^{19}$F nucleus has a relatively high sensitivity, approximately 81% that of a proton. Due to the absence of naturally occurring fluorinated compounds background noise is usually minimal. This leads to good signal to noise ratios being observed, an aspect directly related to sensitivity in the experiment. Sensitivity can also be enhanced, usually four to five times, through the addition of paramagnetic relaxation agents. The nucleus has a spin value of $\frac{1}{2}$ leading to relatively simple splitting patterns and as the nucleus has a zero quadrupolar moment leads to signals that are often sharp and well resolved in homogeneous solutions. The $^{19}$F isotope is 100% abundant in nature. There is a large spectral window associated with the nucleus (for organofluorine compounds this is typically 500 ppm, cf., $^{1}$H 15 ppm and $^{13}$C 250 ppm), thus leading to low probability of spectral overlap. This is further reinforced with the virtual absence of naturally occurring fluorinated species (section 1.1) resulting in few matrix interferences. Important information is often contained within the change in chemical shift for a given medium as is shown in equation 1.

$$\Delta \delta_{\text{medium}} = \Delta \delta_b + \Delta \delta_a + \Delta \delta_w + \Delta \delta_e + \Delta \delta_c$$
The term $\Delta \delta_b$ is the contribution of bulk magnetic susceptibility differences to $\Delta \delta_{\text{medium}}$. The magnetic anisotropy term, $\Delta \delta_a$, is important for anisotropic solvents such as rod-shaped CS$_2$ or planar benzene, which have anisotropic diamagnetic susceptibilities. The magnitudes of $\Delta \delta_b$ and $\Delta \delta_a$ depend only on the shape and magnetic susceptibility of the surrounding medium, not upon solute properties, and thus should be the same for any nucleus in a sample. The contribution of van der Waals dispersion interactions, $\Delta \delta_w$, depends upon solute size as well as on the polarizability and ionization potential of the solvent. Finally, $\Delta \delta_E$ is the effect of electric dipolar interactions on chemical shifts, and $\Delta \delta_c$ is the contribution from hydrogen bonding, charge transfer, ion-pair, or other complexes. As can be seen, if certain of these contributing parameters are eliminated by virtue of experimental or theoretical considerations, key information can be attained from the resultant chemical shifts. This leads to details pertaining to the analytes interaction with other solution-phase constituents (such as dissolved organic carbon (DOC)) and with solid-phase sorbants (such as sediments and soils). This topic is dealt with in more detail in sections 1.2.3 and 1.2.5.

A change in chemical shift is also a useful tool in the elucidation of bio-, physical and chemical degradation process of fluorinated compounds, as it often reveals structural information pertaining to the identity of intermediates. Due to the sensitivity of the fluorine nucleus, observable chemical shift changes can occur with only minor molecular alterations.

Techniques involving two-dimensional nmr offer an attractive tool for structural identification of unknown analytes. These techniques (of which there
are many) can often yield information about the connectivity of atoms within a molecule, thus allowing exact peak identification to be made in relation to the structure of the molecule. An often insurmountable obstruction in the use of these pulse sequences is the requirement of a large mass of sample. Thus 2D nmr experiments have been limited in their usefulness to the environmental chemist (section 1.2.4).

The line width of a peak, a function of the $T_2$, or the time taken for the magnetization to return to equilibrium in the $x-y$ plane, or more commonly expressed as the $T_2^*$ relaxation time to include magnet inhomogeneities, can also yield valuable information about the molecular mechanism of interaction of an analyte with a particular environment. For example there are several types of molecular interactions that can contribute to line broadening, including 1) fast chemical exchange between different environments, 2) interaction with a continuum of sites, 3) reduced molecular mobility caused by sorption or by increased solution viscosity, 4) interaction with paramagnetic sites. A cleverly designed experiment can allow information to be gathered to give a clearer understanding of any one of these phenomena.

1.2.1 $^{19}$F nmr Applied to Metabolic Processes in the Environment

The *in vivo* study of a fluorinated chemical and its metabolites, or biosynthetic products, within plants has certain distinct advantages (Ratcliffe, 1998). These include, removing the necessity for tissue extraction and subsequent work up and that there is no pre-selection of compounds by the
investigator sometimes which may result in the observation of unexpected information. Thirdly, that it is a non-evasive technique yielding information such as intercellular activity and compartmentation of metabolites. $^{19}$F nmr can be used to probe xenobiotic mechanisms, and is possibly the most useful nmr nucleus for this type of study due to lack of naturally occurring interferences.

For example, Serre et al. (Serre et al., 1997) applied this technique in the study of the metabolism of a fluorinated fungicide [N-ethyl-N-methyl-4-(trifluoromethyl)-2-(trifluoromethyl)-2-(3,4-dimethoxyphenyl)benzamide (Figure 1.6)] by Acer pseudoplatanus.

![Figure 1.6](image)

**Figure 1.6** The fluorinated fungicide N-ethyl-N-methyl-4-(trifluoromethyl)-2-(trifluoromethyl)-2-(3,4-dimethoxyphenyl)benzamide.

In this study 10 fluoro-metabolites were observed, five of which were positively identified, in which demethoxylation and N-dealkylation were the most predominant metabolic pathways. The signals for all of the metabolites were resolvable, reinforcing the advantageously large spectral window associated with
The study also sought to examine potential interferences of which none could be found. The concentrations of all of the major metabolites were quantifiable within the limitations of sensitivity imposed by the $^{19}$F nmr experiment.

A clear mechanistic understanding of the biosynthetic processes involved in the production of a natural product within a plant is often of considerable interest. Of the limited examples fluoroacetate (MFA) is the most common organofluorinated compound produced by plants. This highly toxic natural product was first identified from plant extracts in 1943 (Marais, 1943). Until recently the biosynthetic origins of this compound have remained entirely speculative and proposed without evidence (Marais, 1943; Mead and Segal, 1972; Meyer and O'Hagen, 1992a; Meyer and O'Hagen, 1992b; Peters et al., 1965; Vickery et al., 1979). The use of $^{19}$F nmr has aided in establishing a biosynthetic route for the compound (Hamilton et al., 1998; Tamura et al., 1995).

It was shown that inorganic fluoride is directly utilized in the production of MFA by Steptomyces cattleya. Fluoride was added to the culture broth and the production of MFA and a secondary metabolite, 4-flourothreonine, were monitored (Figure 1.7).

![Figure 1.7](image.png)  
*Figure 1.7* Fluorinated compounds produced by *Steptomyces cattleya*. 

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The use of direct $^{19}$F nmr, the measurement of $J(^{13}$C - $^{19}$F) coupling constants through the addition of labeled compounds such as [2-$^{13}$C] glycerol to the system, and other analytical techniques allowed the complete deciphering of the *Streptomyces cattleya* biosynthetic pathway leading to MFA (Tamura *et al*., 1995; Hamilton *et al*., 1998). It was shown that the glycerol was solely incorporated as the carboxylate carbon of the MFA (Figure 1.8). Results indicated that one enzyme was solely responsible for fluorination.
Figure 1.8  Partial reaction mechanism showing principle mechanisms by which MFA and 4-fluorothreonine are produced in *Streptomyces cattleya*.

In 1998 it was reported that 10% of all pesticides that were being commercially produced contained fluorine within their structure, and in most cases incorporation was as a CF$_3$ unit (Reinscheid et al., 1998). Despite this fact there are only a limited number of reports of their microbial degradation, of which the tests were only conducted to a point where the CF$_3$ remained intact. The
ultimate fate of fluorine has typically not been established (Abernethy and Walker, 1993; Gennari et al., 1994; Golab, et al., 1979; Kulowski et al., 1997; Zayed et al., 1983; Zeyer and Kearny, 1983). The degradation of pesticides can lead to the production of intermediates with greater toxicity to the environment than their parent compounds. Furthermore, these metabolites can enter into the environment facilitating non-metabolic degradation processes, such as thermal and photochemical reactions, to take part in their transformation. A recent study has attempted to tackle such a problem (Reinscheid et al., 1998). Using $^{19}$F nmr the researchers showed that ring hydroxylation of 2-trifluoromethylphenol is induced by *Bacillus thermoleovorans*, to produce the 3-trifluoromethylcatechol. The aromatic ring of the catechol is then cleaved by 2,3-dioxygenase to yield 2-hydroxy-6-oxo-7,7,7-trifluorohepta-2,4-dienoate (7-TFHOD)(Figure 1.9).

![Figure 1.9 Biodegradation of 2-trifluoromethylphenol by *Bacillus thermoleovorans*.](image)

As it is possible that 7-TFHOD is a metabolite that may be deposited in the environment, it was subjected to photochemical experiments. Upon disappearance of the fluorine signal for 7-TFHOD no new signals were produced in the $^{19}$F nmr spectra. This led to the postulation that $\alpha$-cleavage occurred to
give a CF₃ radical, which was lost from solution as fluoroform, a reaction which is not supported by evidence within the literature. It was also noted that the starting material was prone to chemical hydrolysis to produce fluoride. This was a result that the authors felt was inexplicable given the normally inert nature of the CF₃ group. Experiments herein (Chapter 3) help to further explain this observation.

¹⁹F nmr has been used in several studies to aid investigations toward understanding and elucidating the mechanisms by which the microbial degradation of fluorophenols occurs (Boersma et al., 1998; Bondar et al., 1998; Finkelstein et al., 2000). In the degradation of 2-fluorophenol by whole cells and cell extracts of *E. jeanselmei* three primary metabolites were observed by nmr (Boersma et al., 1998). The presence of a signal corresponding to fluoride indicated that biodehalogenation had occurred. It was suggested that this was through the action of a phenol hydroxalase as the production of a catechol was observed. The other two metabolites were identified as 3-fluorocatechol and 2-fluoromuconate, the latter being formed via ring cleavage of the 3-fluorocatechol by a catechol 1,2-dioxygenase. The identity of these metabolites was established on the bases of their chemical shift when compared to authentic standards. Further studies were made in order to determine the metabolic pathways for a series of di-, tri-, tetra- and penta- fluorophenols. The muconates produced (Figure 1.10) were identified by chemical shift and also through the coupling constants of nuclei, J(F-H) and J(F-F).
Figure 1.10. The production of 2,3-difluoromuconate through the reaction of catechol 1,2-dioxygenase with 2,3-difluorophenol.

In a study conducted using various *Rhodococcus* species in order to invoke metabolism of fluorophenol, similar products were observed by $^{19}$F nmr (Bondar et al., 1998). However, a fourth previously unidentified metabolite was also observed, tentatively assigned as 5-fluoromaleylacetate. The utility of the method was stressed as this product had gone unnoticed using other methods such as HPLC. In a concurrent study by Finkelstein *et al.* (2000) another metabolite, also produced through degradation by *Rhodococcus opacus* 1cp, and was characterized as 2-pyrone-4-fluoro-6-carboxylate, a fluoropyrogallol. The products, which have been positively or tentatively assigned by $^{19}$F nmr resulting from the metabolic breakdown of fluorophenols, is ever expanding. A summary of these results is shown in Figure 1.11.
Figure 1.11 Reaction mechanisms observed in the biodegradation of fluorophenols.

The microbial degradation of pollutants directly in soils is of importance, through both an understanding of the mechanisms that govern degradation and also the products that are formed. $^{19}$F nmr has also been employed in this field, albeit to a small degree. Fluorinated biphenyls are often produced as byproducts in the production of chlorinated biphenyls (Jaffé and Hites, 1985). Their degradation within soils was studied using nmr in conjunction with $^{14}$C labeling by Green et al. (Green et al., 1999a; Green et al., 1999b). In these studies they
solvent extracted the treated soils and analyzed by $^{19}$F nmr. The results indicated no degradation of the fluorobiphenyls over a 60 day period.

1.2.2 Non-Biologically Mediated Pesticide Degradation

The utility of $^{19}$F nmr in the analysis of fluorinated pesticide residues was first studied by Mazzola et al (1984). At that time limitations in the size of the magnetic field available to the researchers resulted in the need for large sample masses (100g) in order to achieve reasonable levels of sensitivity (0.1 mg/kg) over long acquisition times (8 h). However, the idea was revisited in 1991 by Mortimer et al. (1991). As a result of larger magnetic fields they were able to demonstrate the utility of the technique in trace fluorinated pesticide analysis for foods. The technique was optimized for in order to obtain maximum sensitivity. Spin-lattice ($T_1$) relaxation times were measured for the materials in order to reduce acquisition times. Furthermore the inclusion of relaxation agents was investigated in order to further reduce the $T_1$ times. This was done through the addition of Cr(acac)$_3$. Although Cr(acac)$_3$ reduces the $T_1$ time it also causes peak broadening resulting in a loss of resolution. After optimization, the method was applied to pesticides in matrices such as vegetable oil and wine, where limits of detection were found to be $\geq 1$mg/L for a 3C min acquisition time.

In a further study by Mortimer et al. (1994) $^{19}$F nmr was compared with the more conventional GC-ECD technique. In this study analysis was carried out on soil and carrot extracts containing the herbicide trifluralin. It was found that when

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samples contained 10 (or greater) ppb of the pesticide the two techniques were comparable.

Mabury and Crosby (1995) used $^{13}\text{F} \text{nmr}$ in the study of the sunlight photodegradation of the trifluoromethylated pesticide, Trifluralin. The utility of the technique was emphasized in the lack of requirement for extraction, cleanup, concentration, or chromatographic separation. The rate of degradation of the parent molecule could be quantitatively measured as a function of time, along with numerous key degradation intermediates. Due to the large spectral window associated with $^{19}\text{F} \text{nmr}$ very good separation of the products was achieved (Figure 1.12).

Figure 1.12 Spectrum of the sample taken after 120 min irradiation of the aqueous trifluralin.
1.2.3 $^{19}$F nmr Studies on the Processes of Phase Interaction

Natural humic substances, or dissolved organic matter (DOC), can affect the fate and transport of organic pollutants in the aqueous environment through the binding of the chemicals with the substrate. As such, an understanding of this interaction is of importance. The measurement of $^1$H and $^{19}$F chemical shifts and line widths has been used in order to better understand the interaction between fluorobenzenes and DOC in aqueous solution (Herbert and Bertsch, 1997). A strong hydrogen bonding interaction was observed between the solute and charged groups on the DOC. These results are similar to other researchers who also used $^{19}$F nmr to investigate such interactions (Chien and Bleam, 1997; Anderson, 1997). Dixon et al. (1999) used $^{19}$F nmr to investigate the interaction of 4'-fluoro-1'-acetophenone and Suwannee River fulvic acid. The measurement of $T_1$ and $T_2$ relaxation times, and $^{19}$F nuclear Overhauser effect (NOE) were used in conjunction with chemical shift and diffusion coefficient measurements to establish the binding mechanisms present. It was shown that both $T_1$ and $T_2$ relaxation times decrease upon increasing concentration of DOC suggesting sorption is taking place. Molecular correlation times, which were calculated from these relaxation times, suggest a decreased mobility of the $^{19}$F nucleus due to hydrogen bonding. This was further supported by evidence obtained from chemical shift changes. Increasing DOC concentration resulted in a downfield shift of the fluorine nuclei as a result of a decrease in electron shielding. A pH dependence upon the relaxation times suggested that at neutral pHs hydrophobic association was more prominent than hydrogen bonding. $^{19}$F NOE
measurements indicated that interactions are not limited to the aromatic regions of the acetophenone and that the molecules are strongly enough associated with the DOC for sufficiently long periods of time to allow for the NOE to build up. Diffusion experiments, however, suggested that only a small fraction of the material is bound at any moment in time. Competition experiments indicated that fluorobenzene will displace the fluoroacetophenone and that non-fluorinated acetophenone cannot compete for the binding sites on the DOC when in the presence of the fluorinated analogue.

In a separate study the association of fluorobenzene with DOC was also investigated using $^{19}$F nmr (Hinedi et al., 1997). The association of the fluorobenzene was examined by pulsed field gradient spin echo nmr. Using this technique in conjunction with two fractions of DOC differing in the average atomic mass units (amu) present it was shown that fluorobenzene remained unbound when the DOC had a low amu ($<1000$) and was found to associate at higher amu ($<8000$). The use of solid state $^{19}$F nmr to investigate the sorption of fluorobenzene is outlined in section 1.25.

1.2.4 1D and 2D $^{19}$F nmr in Quantitative and Structural Identification in Environmental Chemistry

Lignin is a naturally formed organic material, and possess a random structure of non-repeating units and it contains active sites within its structure which allow foreign molecules, such as pesticides, to bind to it. For example, it is known to contain a small amount of carbonyl groups that are structurally diverse,
and can act to complex with pollutants (Alder and Ellmer, 1948). It is therefore of importance to understand the nature of these binding sites. Several early attempts were made to determine the carbonyl content of lignin using derivatization with a fluorinated reagent followed by $^{19}$F nmr (Barelle, 1993; Lachenal et al., 1995). Unfortunately the derivatizing agents that were chosen resulted in the production of species with very little difference in chemical shift. As a result quantitative and qualitative reliability was reduced. Ahvazi et al. (1999) later showed that using the correct choice in derivatizing agent, namely trifluoromethyltrimethylsilane in the presence of tetramethylammonium fluoride, good separation could be seen for distinct classes of carbonyl groups, for example between different types of aldehydes, terminal ketones and internal ketones. Further, the spectral identity of moieties could be established through $^{19}$F - $^1$H coupling and the use of two dimensional $^{19}$F - $^{13}$C heteronuclear nmr experiments such as HMQC. However, these 2D techniques proved to be fruitless in situations were the carbonyl content was very low. Further carbonyl spectral assignments could be made through the selective reduction of specific types. For example, when the lignin was reduced with sodium hydrosulphite, quinones were selectively reduced over aldehydes or ketones. In the case of reduction with sodium borohydride reduction of all ketones, aldehydes and esters was accomplished. By comparing spectra obtained with and without these reductions to those obtained by neat derivatization the absence and presence of certain peaks allowed further spectral assignment. Quantitation, with careful consideration of $T_1$ relaxation times, of the total amount of carbonyls present was
also carried out using nmr by comparison of the total derivatized signal with the internal standard 3,3'-bis(trifluoromethyl)benzophenone. A good correlation was seen when the nmr results were compared to those obtained by UV spectroscopy.

Long chain perfluorinated alkanes appear to be ubiquitous in the environment (Moody and Field, 2000). As such the development of nmr techniques to study these compounds would be advantageous (Hagen et al., 1981). Compounds of this nature add a considerable challenge to the $^{19}$F spectroscopist (Ribeiro, 1994; Ribeiro, 1997). These challenges arise from the fact that in the absence of fluorine decoupling $^{13}$C spectra are very complex with the chemical shift of the nuclei being very close to one another, resulting in the complex overlap of signals. Further, the chemical shift of the fluorine nuclei are often not predictable. Due to these complications several 1D and 2D must be employed in order to positively identify a structure such as that shown in Figure 1.13.

![Figure 1.13](image)

**Figure 1.13** The chemical shifts observed for a polyfluorinated alcohol. Values given are in ppm.
In order to fully discern a structure of this nature $^{19}$F, $^{13}$C HMQC, HMBC along with $^{19}$F, $^{19}$F COSY and TOCSY were employed.

1.2.5 The Use of Solid State $^{19}$F nmr in Environmental Analysis

Magic angle spinning solid state $^{19}$F nmr has been employed to investigate the sorption of hexafluorobenzene (HFB) to sediments (Cornelissen et al., 2000). Changes in chemical shift indicate that the HFB is bound to structurally different parts of the organic matter or that the parent molecule is bound in an altered manner. Unfortunately, it was difficult to assign the exact physical or chemical processes that were taking place to result in such pronounced changes in chemical shift. Inferences could be made as to the electronic nature of the sites at which adsorption was occurring. That is, chemical shifts which were down field could be assigned to HFB molecules that were close to areas of increasing electron density, thus producing a deshielding effect. However, the research does indicate that there is the possibility to use solid state $^{19}$F nmr as a tool to investigate the interactions of organic species and organic matter within sediments.
1.2.6 Miscellaneous Techniques

Fluorinated surfactants, long chain polyfluorinated chemicals similar to those discussed in section 1.24, have been found in various compartments within the environment. In aqueous solution these chemicals form assemblies known as micelles above a critical concentration. These formations have a hydrophilic exterior and a hydrophobic interior. It is known that the surfactant molecules will undergo exchange between monomeric units and the micelles. An understanding of the rate at which this exchange occurs is important in gaining insight toward an understanding of the fate and physical identity of surfactant in the environment. It was found that $^{19}$F nmr could be used to establish this rate due to the difference in chemical shifts between the monomeric and aggregated states (Guo et al., 1991). The method was applied to the free salts, the acids and amides of the acid. Further, it was suggested based upon the characteristics of the nmr that the surfactants aggregate to form a cubic phase.

1.3 Summary

The field of organofluorine chemistry is an ever-expanding one. Fluorine finds itself incorporated in an increasing number of chemical roles. These chemicals have very diverse applications, from space shuttle polymers to pharmaceuticals. Fluorine often imparts unique properties upon the molecule, properties that are frequently unpredictable when the established rules that have been developed for the other halogens are employed. $^{19}$F nmr offers itself as an attractive method for the study of these compounds and their fluorinated degradation products. Researchers have shown that the technique can be
applied to a gamut of practical problems, such as metabolic and environmental degradation processes, and the partitioning fluorinated species within the environment. The technique can be employed for both quantitative and qualitative problems.
1.4 References

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Chapter Two

The Development of an $^{19}$F NMR Method for the Analysis of Fluorinated Acids in Environmental Water Samples

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2.1 Introduction

The number of anthropogenically produced fluorinated compounds has increased dramatically over the past few years. For example, the sales of fluoropolymers were projected to rise from $1.35 to $1.76 billion dollars over the past 5 years (Business Communications Company, 1995). Since the Montreal protocol of 1987, which called for a worldwide reduction of chlorofluorocarbons (CFCs), the use of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) has become more prevalent. Both HCFCs and HFCs are more “ozone friendly” because they undergo tropospheric oxidative degradation processes, which is believed to be the major sink for these compounds (Francisco and Maricq, 1996).

Much of the degradation of fluoroorganics in the atmosphere has yet to be investigated, however it is known that HCFCs 123 and 124, along with HFC 134a, degrade to produce TFA (Franklin, 1993; Hayman et al., 1994; Wallington et al., 1992). A large number of studies have shown TFA to be ubiquitous in surface and rain waters, ranging in concentrations of 40 to 630 ng/l (Frank, 1996). It has been observed that TFA concentrations were 4-13 times higher in terminal lake systems, suggesting that TFA may accumulate over time (Wujcik et al., 1999). More recently, chlorodifluoroacetic acid has also been observed in Ontario rainwaters, using GC-MS in selected ion mode (SIM) (Martin et al., 2000). Although not fully established, it is believed that the primary source of this acid is through the degradation of HCFC-142b and CFC-113. It has been suggested that the combustion of fluorinated polymers may also lead to the
production of TFA (Jordan and Frank, 1999). Other fluorinated acids have also been detected in aqueous environments, including monofluoroacetic acid (Ogilvie et al., 1998) and the trifluoromethylated acids, which are produced through the degradation of bifenthrin and tefluthrin (Ruzo et al., 1998; Heath and Leahey, 1989; Bewick et al., 1986). Several methods exist for the measurement of TFA, such as GC-ECD or ion chromatography (Both and Jermal, 1992; Frank et al., 1995; Zehavi and Seiber, 1996; Simonzadeh, 1993). These methods generally require arduous concentration steps, the use of deleterious derivatizing agents, or are only appropriate for TFA. In this study a novel method for the detection of fluorinated acids using $^{19}$F NMR was developed to avoid these impediments. $^{19}$F NMR has been previously used to investigate the production of TFA from the metabolism of 1,1,1,2-tetrafluoroethane (Monté et al., 1994), to measure TFA cell membrane potential (London and Gabel, 1989), and to monitor the uptake of TFA in stems and leaves of the plant L. esculentum (Rollins et al., 1989). The use of SAX extraction has been employed by several groups for the concentration of haloacetic acids (Wujcik et al., 1998; Reimann et al., 1996). These methods typically involve elution of TFA under strongly acidic conditions and esterification with a small alcohol to yield a suitably volatile derivative for GC analysis. The presence of competing species toward active sites on the SAX column can often lead to reduced recoveries in the analyte (Slingsby and Pohl, 1996). These species include sulphate and DOC, which can be successfully removed using IC-Ba and C-18 cartridges respectfully. Our objective was to remove deleterious sample clean up steps, to have the analyte in an organic
solvent system that would allow direct measurement, and to have a method of
detection and quantification of the fluoro acids irrespective of the plethora of
other chemicals present in the rain water samples. Due to the limited quantity of
fluorinated compounds observed in rainwater, it was decided that a method
which was specific to only fluorine and transparent to all other compounds should
be employed.

$^{19}$F NMR spectroscopy has a large spectral window associated with it.
Typically organofluorine nuclei lie within a window of 300 ppm, resulting in a
small probability of peak overlap between molecules. Furthermore, the spin $\frac{1}{2}$
$^{19}$F isotope is 100% abundant and has a sensitivity which is 81% of a $^1$H
nucleus. The technique can be used for spectral identification of an analyte and
for quantification, when an internal standard of known concentration is included
(Komoroski, 1994; Mabury and Crosby, 2000; Ellis and Mabury, 2000). One
drawback of the NMR technique is that, relative to other techniques, it is an
inherently low sensitivity form of spectroscopy as a result of a small population
difference between ground and excited states. Thus, for the low concentrations
of fluorinated acids seen in the aqueous environment key factors influencing the
sensitivity of the experiment must be optimised. One of the parameters which is
routinely open to the spectroscopist for optimising sensitivity is the recycling
delay time (D1) which is related to the spin lattice relaxation time (T1) of the
nuclei. Prior to the measurement of the T1 time the exact 90° pulse must be
established. The optimal spectrometer conditions will vary depending on the
specific analyte. A precise measurement of the T1 duration allows for the
maximum number of transients to be obtained in a given time. The T1 relaxation time for chemically different fluorines is dependent upon such factors as the solvent, temperature and the presence of paramagnetic materials in the solution. Through the purposeful inclusion of a paramagnetic material, such as $\text{Cr(acac)}_3$ within the sample, relaxation times can be reduced (Mortimer and Dawson, 1991). However, this can be to the detriment of observed line widths. By optimising each of these parameters a maximum signal to noise ratio can be established. Since the overall relaxation time is dependent upon a multivariant system, predicting the optimal conditions for an analyte becomes a complex operation. Mapping out the effect of each of these parameters for a suite of compounds, provides a useful tool for predicting a starting point for a new target analyte. The apparent sensitivity of the NMR experiment can be further enhanced by post free induction decay (FID) manipulations. An example of this is the mathematical manipulation by the multiplication of the FID with an exponential factor.

2.2 Materials and Methods

2.2.1 Chemicals

Sodium monofluoroacetate (MFA), difluoroacetic acid (DFA), chlorodifluoroacetic acid (CDFA), 4'-(trifluoromethoxy)acetanalide (TFMAA), hexafluorobenzene (HFB), $\text{Cr(acac)}_3$ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) which were purchased from Aldrich Chemical Company (Mississauga, Canada). Trifluoroacetic acid (TFA) was purchased from Caledon (Georgetown,
3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylic acid (TEF) was prepared through the hydrolysis of Tefluthrin, which was kindly given to us by Dr. Joel Coats. The NMR solvents used were chloroform-d, dimethyl-d₆ sulfoxide (DMSO), acetone-d₆ from Cambridge Isotope Laboratories, Inc. (Andover, MA) and methyl-d₄ alcohol from Isotech Inc. (Miamisburg, OH).

### 2.2.2 NMR Spectrometer Parameters

An overview of the generic parameters used in individual experiments are given in Tables 2.1 and 2.2. All spectra were obtained at 25°C on a Varian Unity 500, 3 channel spectrometer operating at 470.297 MHz and equipped with a 5-mm Nalorac ¹⁹F proton decoupling probe. Free induction decays (FID) were zero filled by making the fourier number equal to twice the number of data points. Chemical shifts were recorded relative to CFCl₃ (0.000 ppm).
Table 2.1  Overview of NMR parameters used in solvent and Cr(acac)$_3$ T1 experiments

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pw=90°x pulse width (11.5), p1=180°y pulse, d1=initial delay time, d2=delay time between pulses, sw=spectral window, at=acquisition time, np=number of points, tof=transmitter offset, and ct=completed transients.
Table 2.2  Overview of NMR parameters associated with the spike and recovery experiment. Please see Table 2.2 for acronym explanation

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2.2.3 SAX Extraction of Fluorinated Acids

For the analysis of aqueous environmental samples with low concentrations of the fluoro acids (< 1 μg/L), a preconcentration step was employed. Aqueous samples (≤ 1L) were filtered using a 0.45 μm filter paper. They were then passed sequentially through a C-18 and an IC-Ba cartridge (Alltech, Geulph, Canada) and two 500 mg SAX columns (Varian, Mississauga, Canada). The SAX columns were centrifuged at 3400 rpm for 10 min, to remove any residual water and then eluted using 800 μl of the deuterated solvent/2M DBU mixture. This solution was transferred to a 1 ml volumetric cylinder, which
included 4 mg of Cr(acac)₃. To this was added 50 µl of the deuterated solvent containing the internal standards TFMAA and HFB. The solution was then diluted to the mark using deuterated solvent, and sonicated until all of the Cr(acac)₃ had dissolved. The NMR spectra were recorded using the appropriate established parameters (in particular d₁=5*T₁) for the analyte and the internal standards. The minimum d₁ value was set to the maximum T₁ for either the analyte or for the internal standard. External calibration was performed using standards of known concentration in both the analyte and the internal standard, in same matrix as for the samples. Care was taken to ensure that all the NMR parameters were the same for the samples as they were for the standards.

2.2.4 Spin-Lattice Relaxation Time as a Function of Solvent

All T₁ relaxation times were recorded using an inversion recovery method (Dermone, 1997). All samples were made using the following procedure. A stock solution of deuterated solvent (chloroform, methanol, DMSO, and acetone) containing 2 M DBU, was prepared. This solution was degassed to remove as much molecular oxygen as possible for 5 mins using a diffusion vacuum pump operating at ~600.04 mm Hg. 1 mg of the analyte was dissolved in 1 ml of this solution in a 528-PP NMR tube (Willmad Glass Co., Buena, NJ). The 90° pulse was established for the fluorine nuclei and then the T₁ time recorded. It should be noted that the minimal spectral window required for each analyte was used.
2.2.5 Spin-Lattice Relaxation Time as a Function of Cr(acac)$_3$ and Solvent

Separate deuterated solvent/2M DBU solutions containing 1, 2 and 4 mg/ml of Cr(acac)$_3$ were prepared. The solutions were then sonicated until the Cr(acac)$_3$ had completely dissolved. The seven fluorinated compounds were individually dissolved in four separate solvent mixtures, to avoid relaxation due to analyte interaction. Each of these experiments was repeated at the three Cr(acac)$_3$ concentrations. The T1 values for the fluorine were then recorded and compared.

2.2.6 Effect of Cr(acac)$_3$ on Peak Resolution

Solutions were prepared for all of the analytes (1 mg/ml) in the four solvent systems which were 4 mg/ml in Cr(acac)$_3$. The NMR spectra were then recorded and the peak width noted.

2.2.7 Optimal NMR Solvent for Spike and Recovery of Fluorinated Acids from Lake Huron Water and Toronto Rainwater

In order to establish the optimal NMR solvent for the extraction of the fluoro acids from the SAX column, all of the analytes were spiked into Lake Huron water (120 μg/L), passed through the SAX extraction procedure and eluted with the four NMR solvents containing 2M DBU. The NMR spectra were then recorded using the appropriate parameters for the analyte in question, the internal standard pertaining to that analyte, and the solvent matrix. The experiment also provided information on the overall performance of the
procedure. A spike and recovery of TFA from Toronto rainwater was also conducted at environmentally relevant concentrations. 500 mL aliquots of Toronto rainwater were spiked with 50, 250 and 300 ng/L of TFA (n=3). The solutions were passed through the SAX system and analysed by $^{19}$F NMR. The concentration of TFA, which was naturally present in the rainwater sample used in the spike and recovery, was recorded and subtracted from the total concentration.

2.2.8 NMR Time limits and Determination of MDL

The S/N ratio for a peak in the NMR experiment increases with time as the $\sqrt{S/N}$. A limitation was therefore placed on the time frame of the NMR experiment depending on the analyte of interest. The time limit was set to one hour for TFA and the time limit for other analytes was based on their comparative relaxation times with TFA. For example, the $T_1$ time for CDFA was found to be approximately twice that of TFA, therefore CDFA acquisition times were two hours. Employing these time constraints, the MDL for each of the analytes was established based upon the minimum concentration that would allow a signal to be observed that was $\geq 3*S/N$.

2.2.9 Measurement TFA in Toronto Rainwater using $^{19}$F NMR

Toronto rainwater samples were collected on the roof of the Gage Institute (University of Toronto, 223 College Street), a four story building, in downtown Toronto. Samples were collected using an automated (wet only) rain
collector (MCI Company, Thornhill, Ontario). On an event basis, sample volumes ranged from 0.5 to 4 L. Nine sampling dates were used, spanning all four seasons. The SAX extraction and concentration method was applied to a 500 ml aliquot of the rainwater collected; SAX columns were eluted using the 2M DBU/methanol-d$_4$ solvent system. NMR samples were prepared with the inclusion of the internal standard TFMAA and 4 mg/ml Cr(acac)$_3$. Calibration was performed using external standards that were matrix matched. The NMR conditions were held constant for each of the samples and standards. The smallest possible spectral window and relaxation time that would allow quantitative detection of TFMAA and TFA was employed.

2.2.10 Measurement TFA in Toronto Rain water using GC-MS-SIM

Rainwaters were passed through glass microfibre filters (Whatman GF/C). To the aqueous phase was added ethyl acetate containing 2,4-difluoroaniline and dicyclohexycarbodiimide to produce the acid anilide of TFA as described by Scott and Alaee (Scott and Alaee, 1998). Analysis was performed on a gas chromatograph (HP Model 5890 Series II) interfaced to a quadrupole mass selective detector (HP Model 5971A) operating in single ion mode, and equipped with a 70 eV electron ionization source. GC separation was performed on a fused silica capillary column coated with cross linked 5 % phenyl methyl siloxane (HP-5MS, 30m x 0.25mm, film thickness 0.25 μm), using helium as a carrier gas. The injector temperature was 220°C and the initial oven temperature was 50°C.
for 2 minutes, increasing at a rate of 5°C min\(^{-1}\) to 250°C. A procedural blank was run with each sample set.

2.3 Results and Discussion

2.3.1 Spin-Lattice Relaxation Time as a Function of Solvent

The T1 relaxation time for a fluorine atom contained within a molecule can be affected by multiple parameters. Since the relaxation of the nuclei involves the transfer of excess energy to the surrounding lattice, one of these parameters is the deuterated NMR solvent. TEF had the overall shortest relaxation time of all seven fluorinated compounds investigated in all solvents (Table 2.3). The reduction or gain in T1 times for each analyte in shifting from one solvent system to another was not comparable. In other words, the optimal solvent for analysis for a given analyte was dependent on the nature of the analyte itself and not the solvent. Furthermore, the optimal solvent system for the analysis of MFA is acetone, while for DFA it is chloroform. The sensitivity of the NMR experiment for an analyte is dependent upon the total number of acquired transients, and the number of transients acquired is dependent upon the T1 relaxation time. It is apparent that for an analysis that requires optimal spectrometer sensitivity the choice of solvent is imperative and would have to be made after the careful screening of several solvents. It should also be noted that, for quantitative analysis, the time of the NMR experiment, and hence sensitivity, is restricted by the T1 relaxation time of the internal standard in that solvent when it is higher in value than the analyte.
Table 2.3 The comparison of T1 relaxation times (seconds) for seven fluorinated compounds in the solvents; dimethylsulphoxide, acetone, chloroform and methanol. T1 relaxation times are given for varied concentrations of the relaxation agent Cr(acac)$_3$. The effect of Cr(acac)$_3$ on peak resolution (line width, Hz) is given for all of the compounds at a Cr(acac)$_3$ concentration of 4 mg/ml.

### DMSO

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<td>6.23</td>
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<td>6.32</td>
<td>6.69</td>
<td>5.60</td>
<td>6.84</td>
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Methanol

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<th>[Cr(acac)_3]</th>
<th>MFA</th>
<th>DFA</th>
<th>TFA</th>
<th>CDFA</th>
<th>TEF</th>
<th>HFB</th>
<th>TFMAA</th>
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<tr>
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<td>1.51</td>
<td>2.05</td>
<td>1.27</td>
<td>1.71</td>
<td>0.85</td>
<td>1.98</td>
<td>1.30</td>
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<tr>
<td>1</td>
<td>0.73</td>
<td>1.49</td>
<td>0.59</td>
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<td>0.67</td>
<td>0.87</td>
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<td>2</td>
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<td>0.34</td>
<td>0.41</td>
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<td>5.41</td>
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<td>6.85</td>
<td>11.86</td>
<td>5.89</td>
<td>4.74</td>
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</tbody>
</table>

2.3.2 Spin-Lattice Relaxation Time as a Function of Cr(acac)_3 and Solvent

The T1 relaxation times for each of the fluorinated compounds were measured as a function of the concentration of the relaxation agent Cr(acac)_3. Measurements were made for three different concentrations of Cr(acac)_3, for each of the compounds, in four different solvents (Table 2.3). The overall trend in the reduction of T1 for each compound is a 1/x function with increasing Cr(acac)_3 concentration, applicable for each of the solvents investigated. However, the value assigned to x differs for each compound and differs between
solvents for that compound; the enhancement in T1 is not as pronounced for particular compounds. For example the T1 relaxation time of MFA in acetone, in going from 1 mg/ml to 2 mg/ml Cr(acac)$_3$, shows a decrease in T1 by factor of 0.6, while under the same conditions TFA's T1 is only decreased by a factor of 0.4. The sensitivity of all compounds investigated in the NMR experiment can be enhanced by the inclusion of Cr(acac)$_3$ in each solvent system, for which the optimal concentration is 4 mg/ml. All T1 measurements showed < 1% standard deviation.

2.3.3 Effect of Cr(acac)$_3$ on Peak Resolution

Interference in the $^{19}$F NMR experiment due to peak overlap may present a problem. This is especially true for analytes that are very similar in structure. In these cases careful selection of the NMR solvent system must be made on the basis of lowest peak linewidth. Cr(acac)$_3$, along with the solvent, can have a marked effect on the resolution. It should be noted that the concentration, the NMR tube and magnetic inhomogeneities can also have detrimental effects on the linewidth, and thus every effort was made to minimise these problems. A comparison of the effect of Cr(acac)$_3$ on linewidth for each compound in the four solvent systems is given in Table 2.3. As can be seen, there is a general trend of increasing linewidths with the following solvent series; DMSO > acetone > chloroform > methanol. This is in part due to ability of the nuclei to transfer excess energy to the surrounding lattice. The most pronounced deviation from
2.3.5 SAX Extraction of Fluorinated Acids

All five acids studied could be analysed from the same sample due to their differing chemical shift values (Figure 2.1).

Figure 2.1 Chemical structures and acronyms of fluorinated acids used in $^{19}$F NMR studies. The chemical shift of the fluorinated moiety is given in ppm, relative to CFCI$_3$ (0.000 ppm), in methanol-d$_4$/2M DBU.

Chemical shifts of multiplets are given as the central line.
this is for TEF, which shows a similar trend excluding methanol. In general, the optimal solvent system for peak resolution is methanol-d₄/2M DBU.

### 2.3.4 NMR Time Limits and Determination of MDL

The method detection limit for each of the fluoro acids in methanol-d₄/2M DBU, for a defined total NMR acquisition time (based upon their T1 values), is shown in Table 2.4. The length of the NMR experiment to obtain comparable sensitivity between analytes was quite variable. Furthermore, the sensitivity of the experiment was dependent upon the total number of equivalent fluorine atoms giving rise to the signal.

**Table 2.4** NMR experiment time restraints as based upon T1 values, and MDL for fluorinated compounds in methanol-d₄/2M DBU and 4 mg/ml

<table>
<thead>
<tr>
<th>Compound</th>
<th>T1 (sec)</th>
<th>Total Acquisition Time (min)</th>
<th>MDL (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFA</td>
<td>0.220</td>
<td>100</td>
<td>84</td>
</tr>
<tr>
<td>DFA</td>
<td>0.353</td>
<td>120</td>
<td>66</td>
</tr>
<tr>
<td>TFA</td>
<td>0.134</td>
<td>60</td>
<td>16</td>
</tr>
<tr>
<td>CDFA</td>
<td>0.362</td>
<td>150</td>
<td>42</td>
</tr>
<tr>
<td>TEF</td>
<td>0.261</td>
<td>120</td>
<td>56</td>
</tr>
<tr>
<td>TFMAA</td>
<td>0.153</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>HFB</td>
<td>0.335</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

N/A=Not Applicable.
The results for the spike and recovery of the five fluoro acids, MFA, DFA, TFA, CDFA, and TEF from Lake Huron water are shown in Figure 2.2.

![Bar graph showing % Recovery of fluorinated acids with optimal NMR solvent system.](image)

**Figure 2.2** Spike and recovery of five fluorinated acids from Lake Huron waters. Optimal NMR solvent for extraction of each of the acids from a SAX column.

The optimal solvent system for all the acids was methanol-d$_4$/2M DBU. The general order of solvent suitability for extraction is methanol$>$acetone$>$DMSO$>$chloroform. Quantitative recovery of all the acids were observed when methanol-d$_4$/2M DBU was used as the eluting solvent. Recoveries were 94.3±6.2 % (n=8). Quantitative recovery of TFA can also be obtained using the acetone-d$_6$ and DMSO-d$_6$ solvent systems. The general order of recovery with respect to the acids is TFA $>$ CDFA $>$ DFA $>$ TEF $>>$ MFA. The elution of MFA was not observed in chloroform. It is believed that this may be
due to a combination of the acid pKₐ and the solvation power of the eluting solvent. DBU being a soft base would have a higher affinity toward soft acids, thus MFA being the hardest acid would have the least affinity. It appears that the percentage recovery decreases as the pKₐ decreases, MFA having the lowest recovery and TFA the largest. There is also a direct correlation between the percentage recovery and the polarity of the solvent. The mechanism for the elution of the acid, which is bound to the quaternary amine within the SAX stationary phase, may occur by complexation with the protonated form of DBU. This hypothesis is further supported by the solvent elution series, that is DBU would be protonated to a smaller degree in chloroform than it would be in methanol. Furthermore, the methanol would thermodynamically support an ion pair such as analyte*⁺DBU more effectively than chloroform would. Presumably the percentage recovery could be further enhanced for each of the analytes by increasing the concentration of the DBU. This would however result in a decrease in the ability to obtain magnetic homogeneity (shimming) because of a decrease in deuterated solvent concentration for the sample, ultimately resulting in a decrease in the sensitivity of the experiment. This method of elution and analysis of fluoro acids from SAX columns enhances the currently available techniques (Wujcik et al., 1998; Reimann et al., 1996), as the analyte is contained with in an organic matrix and further derivatization is not required.
2.2.6 Spike and recovery of TFA from Toronto Rainwater

The recovery of TFA from Toronto rainwater (n=3) using the SAX method, employing methanol-d$_4$/2M DBU as the eluent, was 104.3±6.2% for 50 ng/L, 100.9±3.7% for 250 ng/L, and 100.7±3.7% for 300 ng/L. These results indicate good accuracy and precision for the method compared with the currently available methods, which involve several additional steps.

2.2.7 Measurement TFA in Toronto Rain water using $^{19}$F NMR and GC-MS-SIM

The concentration of TFA was measured in Toronto rainwater using $^{19}$F NMR. Four time points were also measured using GC-MS-SIM. As can be seen through comparison of the data (Table 3), the $^{19}$F NMR data are in close agreement with results obtained from the accepted published procedure. A typical $^{19}$F NMR spectrum is shown in Figure 2.3 indicating the presence of TFA and CDFA in Toronto rain water.
Figure 2.3  $^{19}$F NMR showing TFA relative to the internal standard TFMAA, shown in the inset. The measured concentration of TFA was 343 ng/L. The results are obtained from Toronto rain water, dated January 26th 1999. The fluoroacetic acid CDFA, also observed in rainwater, is shown.
There are no indications of interferences observed. This results in short sample preparation times for the NMR. The results show that there was considerable variance in the measured amount of TFA in Toronto rainfall (74-850 ng/L). These results suggest that the degradation of HCFCs 123 and 124, along with HFC 134a is not solely responsible for the production of TFA. This is in accord with results for the concentration of CDFA in Toronto rainwater which shows an inverse relationship with the sample volume of the rain event (Martin et al., 2000).

2.4 Conclusions

A method based upon SAX extraction and $^{19}$F NMR has been developed which permits the determination of TFA and other fluorinated acids at ng/L levels. Fluorinated acids can be concentrated from natural waters using SAX column chromatography at environmentally realistic concentrations. The acids can then be quantitatively eluted using an appropriate NMR solvent in the presence of the strong organic base DBU. Given the large chemical shift range, all of the fluoroacids could be analysed from the same sample. The choice of NMR solvent used can have a significant effect on the sensitivity of the NMR experiment. The inclusion of Cr(acac)$_3$ in the NMR solvent allows the sensitivity to be increased by as much as 80%. Of the four solvents used in the present study, methanol was the optimal solvent for elution and for peak resolution in the presence of Cr(acac)$_3$. The limits for quantification using $^{19}$F NMR spectroscopy
are strongly influenced by the T1 relaxation times of the nuclei, which in turn are
effected by the choice of solvent matrix.
2.5 References


Chapter Three

The Aqueous Photolysis of TFM and Related Trifluoromethylphenols. An Alternate Source of Trifluoroacetic Acid in the Environment

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3.1 Introduction

Fluorinated chemicals are rarely observed in nature (Peters and Hall, 1960). However, the incorporation of fluorine in anthropogenic products is expanding, with fluorine present in many different types of organic materials, including agrochemicals, polymers and pharmaceuticals (Key et al., 1997). The ultimate fate of the fluorine contained within these molecules is of considerable interest. From 1958 the chemical 3-trifluoromethyl-4-nitrophenol (TFM) has been used to control the sea lamprey (Petromyzon marinus) in four of the Great Lakes (Superior, Michigan, Huron, and Ontario). By 1988, more than one million kilograms of TFM had been applied to these lakes, and usage since has been approximately 50,000 kg/year (Hewitt et al., 1996). TFM has also been introduced in order to control tadpole infestations in warm water ornamental fish ponds (Gabbadon and Chapman, 1996).

A possible loss mechanism for lampricides is through adsorption onto bottom sediments (Allen et al., 1986). However, studies have shown microbial degradation is not significant within this medium (Thingvold and Lee, 1981; Scott et al., 1984). The enzymatic biodegradation of TFM was investigated under aerobic conditions in natural water sediments (Thingvold and Lee, 1981). No degradation of TFM was observed over a 2.5 month period. It was assumed that the trifluoromethyl substituent of the aromatic ring remained intact as no fluoride production was observed. Under anaerobic conditions, partial reduction of the TFM nitro- group to an amine has been observed (Lui and Fox, 1979). TFM is
almost completely ionized in most natural waters, so this is unlikely to be an important loss mechanism due to the lack of adsorption on such sediments.

It has been reported (Liotta et al., 1972; Kozachuk et al., 1973) that the trifluoromethyl group contained within a phenolic ring is susceptible to hydrolytic degradation when in the ortho- or para- positions relative to a hydroxyl group. Conversely, when in the meta- position, the trifluoromethyl group is inert to alkaline or acidic hydrolysis even at elevated temperatures. However, a photoinduced excited state may allow the cleavage of the carbon-fluorine bonds (Wirz and Seiler, 1972).

Trifluoromethyl aromatics, which do not contain an electron withdrawing substituent, have been shown to undergo bacterial metabolism to produce trifluoroacetic acid (TFA) (Engesser et al., 1988). This is an unlikely mechanism for the degradation of TFM, or the subsequent production of TFA due to the electron withdrawing nitro group.

The major source of TFA in the environment is believed to be the degradation of the HCFC's 123, 124, and 134a, which occurs primarily through reaction with a hydroxy radical followed by subsequent hydrolysis (Scientific Assessment of Stratospheric Ozone, 1989). From this source alone, the projected concentrations have been calculated to be >100 μg L\(^{-1}\) by the year 2010 in seasonal wetlands. However, the concentrations which have been measured in the environment cannot be accounted for based on current atmospheric sources (Boutonnet et al., 1999). These levels have been shown to inhibit plant growth (Tromp et al., 1995). TFA has also been shown to be a biliary excretion
metabolite of haloethane anesthetics in infants younger than five months, but at
greater than five months it has been shown to be completely retained in an
enterohepatic circulation (Wark et al., 1991).

To date there is little evidence for the degradation of TFA. It was reported
that trifluoroacetic acid was observed to degrade in both oxic and anoxic
sediments (Visscher et al., 1994), although this observation has yet to be
reproduced (Oremland et al., 1995).

The aqueous photolytic fate of TFM has been investigated by Carey et al.
(Carey et al., 1988; Carey and Fox, 1981). In the present investigation particular
attention has been paid to certain key intermediates proposed by Carey et al.,
specifically the formation of the trifluoromethylhydroquinone, from which it was
postulated that there were two competing loss mechanisms: the production of the
trifluoromethylquinone or a reaction which produces the corresponding acid
fluoride (2,5-dihydroxybenzoyl fluoride). Furthermore, Carey et al. hypothesized
that this acid fluoride in turn leads to the formation of gentisic acid (2,5-
dihydroxybenzoic acid) and hydrogen fluoride. Investigations within our
laboratory have indicated that the fate of the trifluoromethyl substituent was as
fluoride or trifluoroacetic acid (TFA), which had not been previously observed.

Due to the absence of naturally occurring fluorinated materials and the
large spectral windows associated with fluorine, $^{19}$F NMR provides a very
powerful method for the direct analysis of fluorinated materials, reaction
intermediates and degradation products (Xu and Kuchel, 1993). Therefore this
technique was adopted in the characterization of TFM degradation.
It was our hypothesis that the production of trifluoromethylquinone is of key importance to the production of TFA. Our objectives were to investigate the role of phenolic substitution patterns in the rate of degradation of the parent compound, the mechanism of TFA formation, and the influence of aromatic substituents on the yield of TFA.

3.2 Materials and Methods

3.2.1 Chemicals

The chemicals 3-trifluoromethyl-4-nitrophenol (99%), 2-nitro-4-(trifluoromethyl)phenol (99%), 2-(trifluoromethyl)phenol (97%), 3-(trifluoromethyl)phenol (99%), 4-(trifluoromethyl)phenol (99%) were purchased from the Aldrich (Mississauga, Canada). Trifluoroacetic acid (98%) was purchased from Caledon (Georgetown, Canada). All other solvents and reagents were analytical purity grade or better. All chemicals were used without further purification.

3.2.2 Synthesis

Trifluoromethylquinone was synthesized through the oxidation of 2-(trifluoromethyl)phenol using Fremy’s radical in a procedure similar to that used by Zimmer et al. (Zimmer et al., 1970) for the oxidation of phenols. Synthesis of 4-hydroxy-3-trifluoromethylphenol was carried out directly using the method of Feiring et al. (Feiring and Shepard, 1975) in which the 3-(trifluoromethyl)phenol was oxidized using potassium persulphate. The 4-amino-3-trifluoromethylphenol
was synthesized via the reduction of the 4-nitro-3-trifluoromethylphenol using zinc metal in hydrochloric acid according to a standard procedure (Furniss et al., 1978). All products were verified by IR, NMR, and MS.

3.2.3 Photolysis Experiments

Photolysis experiments were carried out at 365 nm (Rayonette bulbs), which also show minor lines at 334 and 313 nm. Photolysis was also confirmed under actinic radiation in a solar simulator (Suntest CPS Solar Simulator). All analytes were dissolved in buffered deionized water (borax buffer (pH 9) and potassium dihydrogen phosphate (pH 7)) to a concentration typically in the range of 5 - 10 \times 10^{-5} \text{M} and irradiated in sealed, 100 mL, quartz vessels. Samples were obtained at appropriate time intervals, and analyzed using the pertinent analysis equipment.

3.2.4 NMR Analysis

$^{19}\text{F}$, $^1\text{H}$, and $^{13}\text{C}$ NMR spectra were obtained for synthesized and degradation products when appropriate, on a Gemini 500 MHz spectrometer operating at 470.596 MHz with a broad band probe tuned to fluorine, on a Varian VXR-S 400 MHz spectrometer operating at 376.289 MHz with a Nalorac 4N probe tunable to H, F, H, Si. Chemical shifts were reported relative to CFCl$_3$ (0.00 ppm). The internal standard 4’-(trifluoromethoxy)acetanalide (TFMAA) was used for quantification.
3.2.5 Chromatographic Analysis

HPLC analysis was carried out using either a Waters 600 pump equipped with a 486 UV/Visible tunable detector, a Waters 616 pump equipped with a 996 photodiode array detector, or on a Perkin-Elmer instrument equipped with a series 200-IC pump and a diode array detector 235 C. Separation was achieved using an Alltech Econosphere C18 5U column. Mobile phases were generally AcCN/buffered water mixtures. Fluoride, Nitrite, Nitrate, and TFA were analyzed using a Perkin Elmer Series 200 IC pump equipped with a Dionex Ionpac AS14 column, and an Alltech 1000 HP conductivity suppresser and conductivity detector; the mobile phase used was generally borax buffered water. Fluoride was analyzed using an Orion ISE. High Resolution Mass Spectra were obtained using a Micromass 70-250S (double focusing) spectrometer in negative El mode. Data were obtained at 10,000 (10 % Valley) resolution. For GC-MS analysis aqueous samples were acidified and extracted with ethyl acetate. Derivatisation, if required, was carried out using diazomethane. Samples were run on a Perkin-Elmer GC Auto System XL equipped with a Q-Mass 910 quadrupole mass spectrometer, run in El mode, with a 30 m, 0.25 μm Simplicity 5 column. The carrier gas was helium at a flow rate of 0.5 mL/min.

3.2.6 UV/Vis Spectroscopy

Molar extinction coefficients and UV/Vis spectra were obtained for the analytes using an HP-diode array model 8452 spectrometer.
3.2.7 Analysis of Trifluoroacetic acid

A new method was developed for the analysis of TFA to overcome problems such as unreliable liquid-liquid extractions and derivatisation required for currently accepted procedures (Zehavi and Seiber, 1996; Wujcik et al., 1998; Frank et al., 1995; Both and Jemal, 1992). Aqueous samples (100 - 1500 mL) of TFA (10^{-6} to 10^{-5} M) were passed through a strong anionic exchange column (SAX) at a flow rate of 5 ml min^{-1}. Elution was carried out using 1 mL of 2 M NaOH, or alternatively with acetone, methanol, or DMSO containing the organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The eluents were then spiked with 300 µl of deuterated acetonitrile containing the internal standard (TFMAA) and TFA was measured directly using ^{19}F NMR (117 ± 13 % for a 500 ppb solution, and 101 ± 6 % for a 120 ppb solution, n=3).

3.3 Results and Discussion

3.3.1 Compounds used and Molar Extinction Coefficients

Trifluoromethylated compounds used to investigate the mechanistic pathway and structural requirements for the production TFA from TFM are shown in Figure 3.1.
The trifluoromethylhydroquinone (II) was selected since it is observed in the environment as a degradation product of TFM (I). Carey et al. (1981) postulated that the trifluoromethylquinone (III) is formed from (II), thus the degradation of this species was also investigated. The aminotrifluoromethylphenol (IV) and the trifluoromethylphenols (V) were used to investigate the influence of the nitro- substituent in TFM, on the production of TFA. Finally, an isomeric form of TFM (VI) was studied in order to determine the substitution pattern required for the production of TFA. Molar extinction coefficients for the compounds at 365 nm and their half-lives are presented in Table 3.1.

The figures are labeled as follows:

**Figure 3.1** Chemical structures used in the mechanistic fate of TFM.

- **TFM (I)**
- **Trifluoromethyl-p-hydroquinone (II)**
- **Trifluoromethylbenzoquinone (III)**
- **4-Amino-3-trifluoromethylphenol (IV)**
- **Trifluoromethylphenol (V)**
- **2-Nitro-4-trifluoromethylphenol (VI)**
Table 3.1  Molar extinction coefficients and observed half lives of trifluoromethyl aromatics.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar Extinction Coefficient, $\varepsilon_0$, liter mole$^{-1}$ cm$^{-1}$, 365 nm, pH 9</th>
<th>Maximum Actinic Absorption Wavelength</th>
<th>Half Life, hours (365 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>6675</td>
<td>394 nm</td>
<td>22.4</td>
</tr>
<tr>
<td>(II)</td>
<td>0.0123</td>
<td>310 nm</td>
<td>0.5</td>
</tr>
<tr>
<td>(IV)</td>
<td>0.00495</td>
<td>308 nm</td>
<td>0.04</td>
</tr>
<tr>
<td>(V)</td>
<td>0.0261</td>
<td>298 nm</td>
<td>0.4</td>
</tr>
<tr>
<td>(VI)</td>
<td>565</td>
<td>500 nm</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

From Table 3.1 it can be seen that the rate of degradation of the parent compound is not solely dependent upon the amount of light absorbed at 365 nm. It is also dependent upon the quantum yield of the molecule. For example compound (IV) has a lower absorption at 365 nm, but degrades more rapidly than (I), indicating that it has a higher quantum yield.

3.3.2  Photolysis of TFM (I)

Figure 3.2 shows the photolysis of TFM (pH 9, 365 nm). The concentration of products fluoride and TFA are shown as a function of time; nitrite was also observed as a product.
Figure 3.2 The photolysis of TFM (I) at pH 9.2. Loss of TFM and the production of fluoride and TFA. No observable loss of TFM in the absence of light.

Trifluoromethylhydroquinone (II) was observed as a short lived intermediate based upon HPLC/UV spectral comparison with an authentic sample. These results are in concordance with work carried out by Carey et al (1981, 1988), in which aqueous field samples that had contained TFM, were analyzed using mass spectroscopy. Evidence was presented for an initial photoinduced nucleophilic hydroxyl displacement of the nitro group, which led to the tentative assignment of trifluoromethylhydroquinone and a trifluoromethylquinone, the latter considered to have been produced through thermal or photochemical oxidation of the hydroquinone precursor. This postulated mechanism is further supported by the observation that
heteroaromatics containing a trifluoromethyl substituent undergo enhanced nucleophilic substitution (Kobayashi and Kumadaki, 1977).

In the present studies the observed pseudo first order half-life for TFM was 22.4 hours. Nitrite and fluoride were produced at the time of initial irradiation, suggesting they were produced directly from TFM. Observable TFA production occurred only after irradiation for 10 hours, suggesting that TFA was produced from an intermediate, rather than directly from TFM. The yield of TFA was approximately 3.9 % when 76 % of the parent molecule had undergone photolysis. Figure 3.3 shows the time-dependent $^{19}$F NMR obtained over the course of irradiation at 365 nm. The production of TFA relative to the internal standard TFMAA is shown.
Figure 3.3 Time dependent $^{19}$F NMR for the production of TFA (-71.2 ppm) from TFM (-56.3 ppm). The concentration is relative to the internal standard TFMAA (-54.3 ppm).

Photolysis of TFM using actinic radiation yielded the same photodegradation products as those observed at 365 nm. The half-life of the TFM under these conditions was observed to be 10.7 hrs.

TFM photolysis was also conducted at pH 7, and identical products were observed (Figure 3.4). TFM was more persistent at pH 7, with a half-life of 91.7 hours.
Figure 3.4 Photolysis of TFM at pH 7. Loss of TFM and the production of nitrite, TFA, and fluoride. No observable loss of TFM in the absence of light.

The yield of TFA at this lower pH was 22%, when 50% of the parent molecule had undergone photolysis. At a lower pH there is a shift in the equilibrium toward the protonated form of TFM, overall producing a greater yield of TFA. It is hypothesized that degradation of TFM, through an excited state of the deprotonated anion occurs more readily at higher pH and does not lead to the production of TFA. At lower pH, this type of degradation is reduced due to an increase in concentration of the protonated form. Given that the pKₐ of TFM is 6.1 (Scott et al., 1984), structure (Ib) (Figure 3.5), would be in a 100 fold excess at pH 9 relative to pH 7.
Degradation (no TFA)

Figure 3.5 Mechanism for the enhanced production of TFA from TFM by altering the pH. Shift in equilibrium at higher pH from the production of a hydroquinone (II) toward (Ib) which does not lead to the production of TFA.

This hypothesis is further supported by the observation that TFM absorption shifts from 297 nm to 394 nm as pH is changed from 7 to 9. This leads to photonucleophilic substitution occurring to a greater extent at pH 7, and producing the trifluoromethylhydroquinone intermediate (II), followed by subsequent degradation to TFA. It follows that, since the production of TFA is proposed to occur from the intermediate (II), the TFA yield would increase at lower pH. This hypothesis also supported by the observation that there is an enhanced production of nitrite at pH 7 relative to pH 9. All dark control experiments showed no loss of TFM.
The photolysis of TFM was also carried out in the presence of equimolar 4-tert-butyl phenol. The rate of reaction was observed to be identical to that in the absence of the phenol. It is known that radicals react with aromatic rings in a manner that superficially resembles that of a nucleophilic substitution (Perkins, 1973), thus kinetically resembling an Sn2 type reaction. If the degradation of TFM had occurred through a radical reaction, the rate would be expected to change in the presence of the phenol due to its radical capturing ability (Evens, 1975).

The structural isomer of TFM, 2-nitro-4-trifluoromethylphenol (Figure 3.1, structure VI) was photolysed under the same conditions. No observable degradation of the isomer was observed over time periods up to 4 times greater than the half-life of TFM, presumably due to the stabilizing formation of an ortho-methylene.

3.3.3 Photolysis of trifluoromethylhydroquinone (II)

Figure 3.6 shows the photolysis of trifluoromethylhydroquinone (pH 9, 365 nm). The rate of production of gentisic acid, fluoride and trifluoroacetic acid are indicated. The half-life of the parent compound was observed to be 31 minutes.
Figure 3.6  The photolysis of trifluoromethylhydroquinone (II) and the production of gentisic acid (VIII), fluoride and TFA.

When complete degradation of the parent molecule had occurred, the yield of TFA was 6% and the yield of fluoride was 82%; the remaining fluoride can be accounted for in residual starting material. No degradation of the parent compound was observed in the dark. $^{19}$F NMR of the photolysate indicated the presence of a short lived trifluoromethylquinone ($\delta = -59$ ppm).

3.3.4 Photolysis/hydrolysis of the trifluoromethylquinone (III)

Trifluoromethylquinone appeared to degrade rapidly (< 5 mins) and quantitatively at pH 9 (observed from HPLC), to TFA. In order to investigate the mechanism for the production of the TFA from (III), the aqueous samples were
extracted and derivatised with diazomethane. From mass spectral evidence the
degradation structures shown in (Figure 3.7) were tentatively assigned.

Figure 3.7 Degradation products observed from the hydrolysis
trifluoromethylquinone. Parent ion mass is indicated in parenthesis
for the methylated product.

It would appear that initial hydroxylation of the quinone occurs to produce (1), or
the 3,6 dihydroxyquinone isomer. This is followed by cleavage of the quinone
ring at the 3,4 bond (2). The ring is then further cleaved at the 1,2 bond to yield
dihydroxymaleic acid (3) and trifluoromethylglyoxal (4). Compound 4 is then
presumed to decarboxylate to produce TFA, in a manner similar to that published
for pyruvic acid (Nord, 1940).
3.3.5 Proposed mechanism for the production of TFA from TFM

The proposed mechanism for the production of TFA from TFM is outlined in Figure 3.8.

![Proposed mechanism for the production of TFA from TFM](image)

**Figure 3.8** Proposed mechanism for the production of TFA from TFM(I). The alternate pathways for the degradation of TFM are also indicated.

The initial steps of this mechanism are similar to that suggested by Carey *et al.* (1981). The results suggest the overall photolytic degradation of TFM occurs through the hydrolysis of the nitro- substituent via a photonucleophilic aromatic substitution to produce a nitrite anion; fluoride can also be lost from the excited state of the TFM (Figure 3.6). The nucleophilic substitution results in the production of a trifluoromethylhydroquinone, which would then appear to undergo...
two competing reactions. One possibility is the production of an acid fluoride through the expulsion of two moles of fluoride. This is then followed by loss of hydrofluoric acid leading to the formation of the genistic acid. The second possibility is a photochemical oxidation of the hydroquinone to a trifluoromethyl quinone. The trifluoromethyl quinone then undergoes what would appear to be a hydrolytic degradation to produce trifluoroacetic acid. The mechanism of this degradation appears to be complicated due to the numerous products observed in the GC-MS. A mechanistic postulation is presented on the basis of certain key intermediates that were observed. The rate of degradation of TFM is strongly dependent upon the degree to which the compound is ionized. This is evident from the observed four fold increase in the half live of TFM from pH 9 to pH 7. As previously indicated, the production of TFA by the photonucleophilic hydroxyl substitution of the nitro- group is further supported by the increased production of TFA at lower pH values due to the shift in equilibrium toward the production of the hydroquinone (Figure 3.5).

3.3.6 Possible structural requirements for the production of TFA

Trifluoroacetic acid is produced from 3-trifluoromethyl-4-nitrophenol (I). An investigation toward discovering the structural requirements within the phenol ring was carried out. An aromatic nitro group is a very strong electron withdrawing substituent that results in a pKa of 4.91 for a phenol (Maskill, 1985). The role of this substituent on the production of TFA was investigated; the
amount of TFA produced in the absence of this group and when it is replaced with a strong electron-donating group.

3.3.7 Photolysis of 4-amino-3-trifluoromethylphenol (IV)

The strong nitro electron withdrawing substituent of the TFM was replaced with a strong electron donating amino group. Figure 3.9 shows the loss of the parent compound (IV) through photolysis and the production of fluoride, 2,5-dihydroxybenzoic acid (VIII), and TFA.

![Figure 3.9](image)

**Figure 3.9** Photolysis of 4-amino-3-trifluoromethylphenol (IV). Loss of the parent compound, production of TFA, fluoride, and gentisic acid (VII).

Approximately 11 % of the expected amount of TFA was produced from the parent compound, when the parent molecule had undergone 100 % photolysis.
The half life of the parent compound was 2.3 minutes. Mechanistically the production of TFA from the 4-amino-3-trifluoromethylphenol appears to be complicated as seen from the numerous peaks that arise in the HPLC chromatogram.

3.3.8 Photolysis of trifluoromethylphenols (V)

The photolysis of the three isomers ortho, meta, and para-trifluoromethylphenol, at 365 nm was executed. The relative rates of degradation, based upon the amount of fluoride that is produced, are shown in Figure 3.10(a-c)
Figure 3.10 (a-c) The photolysis of 2,3, and 4-(trifluoromethyl)phenols (V) and the production of fluoride. The reaction mechanism for the hydrolysis of each of the compounds in the dark is given, along with the relative rates.

As can be seen from the figure the meta isomer is stable in the dark. Both the ortho and the para isomers are not. A strong electrical interaction of electron donating substituents was initially proposed by Roberts et al. (1950). The para-isomer produces 33% fluoride immediately, after which little change is seen over
time. These results are consistent with the loss of hydrogen fluoride through hydrolysis of the ortho and the para isomers to produce the methylenes, 2-(difluoromethylene)-2,5-cyclohexadien-1-one and 4-(difluoromethylene)-2,5-cyclohexadien-1-one respectively. The rate of hydrolysis of the para isomer is greater than the ortho isomer due to the linear conjugation produced as opposed to cross conjugation. The para-isomer is then presumed to undergo polymerization as observed by Kozachuk et al. (1973). The aqueous solution became opaque over time due to the formation of an insoluble polymer. A methylene is not observed for the meta isomer and, hence, is stable in the dark (Figure 3.10).

Further investigation into the mechanism for the degradation of 3-(trifluoromethyl)phenol is shown in Figure 3.11 (pH 9, 365 nm).
Figure 3.11 Photolysis of 3-(trifluoromethyl)phenol and the production of fluoride, 3-hydroxybenzoyl fluoride (IX), 3-hydroxybenzoic acid (X), and fluoride.

Photolysis is observed to initiate the loss of two moles of fluoride to produce the acid fluoride, 3-hydroxybenzoyl fluoride (IX). Assignment of this compound was based upon an $^{19}$F NMR signal at +44 ppm, which is highly indicative of an acid fluoride. The acid fluoride (IX) then undergoes further hydrolysis to produce 3-hydroxybenzoic acid (X). The half life of the phenol was 22 mins.

Concentration of 500 mL of the photolysed sample was carried out by passing it through a SAX column. $^{19}$F NMR and ion chromatography showed no observable TFA.
3.4 Summary

The photolysis of TFM under light intensities and wavelengths which would be equivalent to those found on a typical summers day in the Great Lakes region, leads to the production of TFA. Based on TFM concentrations of approximately 4.6 ppm in Lake Ontario tributaries, and that the photodegradation is the primary loss mode (Carey and Fox, 1981), the average concentration of TFA produced from this source alone would be 500 ppb. Typical environmental water samples have shown a concentration in the order of 10-100 ppt (Scott and Alaee, 1998), indicating that this might be an important source of TFA in the aqueous environment surrounding Lake Ontario.

It would appear that the type and sequence of substitution on a trifluoromethyl phenol are of importance to the fate of the fluorine; ultimately yielding fluoride or TFA. The pH also strongly affects the production of TFA, for compounds that contain the correct structural parameters. In addition, the degree of electron donating/withdrawing of the substituent ortho to the trifluoromethyl group defines the yield of TFA. The results also indicate that the rate of decay and the nature of the products produced for trifluoromethyl phenols is dependent upon the substituents of the aromatic ring and their relative substitution.
3.5 References


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Chapter Four

The Fate and Persistence of Trifluoroacetic and Chloroacetic Acids in Pond Waters

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4.1 Introduction

Recent field monitoring studies (Frank et al., 1996 and Jordan and Frank, 1999a) indicate that haloacetic acids (HAAs) are widespread in the environment and have generated interest in investigating their sources, environmental fate, persistence, and disposition. Since the $pK_a$ of the acids are low, the HAAs are expected to be associated with the aqueous phase when deposited in the environment.

Although other sources of trifluoroacetic acid (TFA) have been proposed (Jordan and Frank, 1999b), until recently (Ellis and Mabury, 2000a) the primary source of TFA in the environment was believed to be through the atmospheric oxidation of the CFC replacement gases, HCFC-123 and HFC-134a (Tromp et al., 1995). Modelling calculations for the behaviour of TFA in the environment depend upon a knowledge of the fate of the compound in the aqueous phase, which in turn requires environmental measurements. Although TFA is being dispersed widely within the biosphere, its ecological fate is largely unknown. TFA has been shown to exhibit phytotoxicity at concentrations $>100 \mu g l^{-1}$ (Berends et al., 1999). Little translocation of TFA was observed when applied to an experimental forest; however, it was observed to accumulate in wetland areas (Likens et al., 1997).

It has been reported that chlorinated solvents degrade to chloroacetic acids (CAAs) in the atmosphere, although this has been disputed (Sidebottom and Franklin, 1996). Naturally produced TCA has been observed as a result of the reaction between chloroperoxidase and humic materials, such as acetic,
malic and fumaric acids (Haiber et al., 1996). All of the chloro-HAAs have been detected as bioproducts from the red alga *Asparagopsis taxiformis* (Woolard et al., 1979). The action of chlorine on organic materials in the process of disinfection of drinking water leads to the production of DCA and TCA, which are reportedly the major chlorinated by-products (Williams et al. 1997). TCA was used as a herbicide for the control of monocotyledonous weeds in the late 1940s (Ashton et al., 1973). Many European countries have banned its use; apparently it is not widely used in North America, although in Canada, TCA is still approved as a weed killer against annual and quack grasses as well as conifers, and is used on crops such as barley, oats, red beets and non crop land (Ontario Ministry of Agriculture, Food, & Rural Affairs, 1998). TCA was even observed to be produced from the chlorination of instant tea through the reaction of residual chlorine used as a disinfectant in drinking water (Wu et al., 1998). It has been found to be ubiquitous in the environment (Juuti and Hoekstra, 1998) and measured in a variety of media including, conifer needles (Frank et al., 1990) (180 μg Kg⁻¹), urban air (Frank et al., 1995) (3 ng/m³), and rain water (Frank, 1996) (6.4 μg l⁻¹).

DCA is directly deposited into the environment by several processes including the use of disinfectants and surfactants (Cetinkaya, 1996; Sugita, 1987). Derivitives of DCA are found in many anthropogenic materials, such as flame retardants, hair growth tonics, skin ageing-preventing cosmetics, drugs (florfenicol), medical polymers, and dichloroacetamide antidotes for benzoate type herbicides (Hasunuma et al., 1996; Hikima, 1994; Miller and Bussler, 1990;
Myamoto, 1988; Myamoto and Nakagawa, 1997; Parr and Hope, 1989; Schumacher et al., 1990; Yamamoto and Mori, 1990). Hydrolysis and/or metabolism of these compounds have been shown, or are expected, to yield DCA (Stacpoole et al., 1987).

MCA has been observed from chloroacetamide herbicides through what appears to be a photolytically driven N-dealkylation reaction (Wilson and Mabury, 1999).

All three chloroacetic acids exhibit phyotoxicity; the EC50 toxicity toward cellular growth of bean cell suspensions were measured as 200, 600 and 1200 μmol/L for MCA, TCA and DCA, respectively (Frank, 1994). MCA and TCA have been shown to exhibit toxicity toward algae, with EC10s of 0.2 μmol/L and 0.8 μmol/L respectfully (Bringmann and Kuhn, 1978).

To date, the only investigation of the environmental fate of TCA in lake water has been a mathematical modelling exercise, which predicted TCA to persist over a >230 day period (Muller et al., 1996); similar studies with MCA/DCA are lacking. The fate of the chloroacetic acids in river and sea waters was investigated (Hashimoto et al., 1998) with the rate of degradation being greater for MCA, followed by DCA and TCA respectively; approximately one half of the degradation was attributed to microbial action. TFA is considered to be highly persistent under typical environmental conditions. Reaction with hydroxyl radicals in water is slow and a calculated half-life for degradation via this route would be greater than 100 years (Mill, 1994). Microbial degradation may contribute to some removal of TFA but observations of actual transformation

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have proven difficult to repeat (Oremland et al., 1995). The decomposition of each of the CAAs has been investigated in soils (Hirsch et al., 1969, and Jensen et al., 1960). It was shown the relative rate, and order, for degradation of the acids was dependent upon the nature of the microbial strain, although DCA consistently showed the fastest rate of degradation. Under these conditions no degradation of TFA was observed.

There are several different modes by which dehalogenation of HAAs could occur in the environment including oxidative dehalogenation, dehydrohalogenation, dehalogenation by methyl transfer, reductive dehalogenation, and substitutive dehalogenation. Of these possibilities the latter seems to be the most common mechanism for haloacetic acids (Fetzner, 1998). There are several microbial dehalogenases that are available for the dehalogenation of C-2 halogenated alkanoic acids (Slater et al., 1997). Generally these dehalogenases are inducible enzymes with broad substrate specificity, although with low affinity, and do not dehalogenate acids which are substituted in positions other than at the C2 carbon. To date, studies involving these enzymes have focused on halogenated acetic, propionic, and butyric acids (Slater et al., 1997). Currently there are several distinct classes of hydrolytic dehalogenases that have been identified as the enzymes responsible for dehalogenation. In general, microbes containing these enzymes have been shown to have a greater dehalogenating ability for chlorinated than fluorinated acetic acids, which is believed to be directly related to the strength of the carbon-halogen bond. The end result after dehalogenation is the same for all
mechanisms, the replacement of the halogen by a hydroxyl group. If these processes occur in our test systems then we expect the formation of 2-hydroxy-2,2-dichloroacetic acid from TCA. This would rapidly lose HCl to form the acid chloride followed by hydrolysis to produce the first stable product, oxalic acid. DCA would be expected to form glyoxylic acid, through the same reasoning, and MCA would form glycolic acid. Monochloroacetic acid has been shown to undergo microbial degradation to produce glycolic acid as a first formed biodehalogenation product by the action of Methylosinus trichosporium within soils (Castro et al., 1996). In sediment water systems TCA has been shown to undergo degradation through what appears to be a classical microbial mediated process (Bower, 1987) with a slow lag-phase, followed by a rapid phase of decline, but not to completion. Studies have shown that the aqueous hydrolysis of DCA has an activation energy barrier of 155.37 KJ mol\(^{-1}\), indicating that kinetically the rate of hydrolysis would be very small (Zhu et al., 1997). None of the HAA’s absorb light in the actinic portion of the spectrum. It has been suggested that indirect photolysis could play role in the degradation of TFA, if certain criteria were met, such as high concentrations of iron, however experiments are lacking to support this hypothesis (Mill, 1994). Thus, any degradation of the HAAs in field waters would then likely be microbially mediated processes.

There are many methods currently available for the analysis of haloacetic acids in the aqueous environment. For example, extraction and concentration of the acids using ion exchange resins, strong anionic exchange cartridges (SAX),
which are followed by derivatization and analysis by gas chromatography coupled with a suitable detector (Aikawa and Burk, 1997; Benanou et al., 1998; Wujcik et al., 1998). TFA has been measured using SAX extraction and $^{19}\text{F}$ NMR detection (Ellis and Mabury, 2000a; Ellis et al., 2000b; Martin, J.W. et al., 2000). The current work was conducted using a SAX extraction procedure when pre-concentration was required, followed by analysis using ion chromatography (IC).

The purpose of our research was to investigate the fate of four HAAs; trifluoroacetic acid (TFA) and mono, di, trichloroacetic acids (TCA, DCA, and MCA) in field pond waters (microcosms) and using laboratory microcosms. Our objectives were to establish the microbial degradation pathway and residence times in pond water of these HAAs. Studies were conducted over time periods of up to one year. It was our hypothesis that the biodegradation of haloacetic acids in the aqueous environment would be through hydrolytic dehalogenation. Our objectives were to establish the aqueous environmental fate of the four HAA's, and to elucidate the mechanism of degradation through laboratory studies.

4.2 Materials and Methods

4.2.1 Field Study

4.2.1.1 Field Microcosm Design

The University of Guelph Microcosm Facility is located at the Guelph Turfgrass Institute, Ontario, Canada, and consists of 30 artificial ponds (Figure 4.1).
Figure 4.1  Field microcosms used for the fate study of MCA, DCA, TCA, and TFA.

The microcosms are approximately 1.2 m deep with a water depth of 1 m, a diameter of 3.9 m, a surface area of 11.95 m², and have a capacity of approximately 12 m³ of water. The microcosms are below ground with the tops flush with the surface. Galvanised steel panels and support struts provide the basic frame and food grade PVC (Fox Pools Canada) is used to create a closed system relative to the other microcosms. These systems have been used
successfully to examine the fate of anthropogenic compounds in aquatic environments (Bestari et al., 1998a and Bestari et al., 1998b).

To create a more natural system each microcosm bottom was filled with 46 (approximately 52x25x7 cm deep) trays (Plant Product Company, Brampton, Ontario, Canada) containing sediment (Evergreen Sod Company, Waterdown, Ontario) consisting of an amended, even mixture of sand, loam and 20 % organic matter and was hand sifted through a screen with 1/2" mesh. The trays covered approximately 50% of the total surface area (11.95 m²) of the bottom of the microcosms. The water for the microcosm during the pre-treatment period originated from an irrigation pond (62x62x4 m deep) supplied by a well located on-site. The water was circulated among all microcosms for a minimum of two weeks prior to dosing with any HAA, at a rate of about 12 m³ every 24 hours. A 1-m high standpipe allowed for water to drain back into the irrigation pond during this circulation phase. This circulation ensured consistent assemblages of zooplankton and algae in each system as well as water chemistry parameters.

Potted macrophytes (Myriophyllum spicatum), obtained from a nearby pond, were placed in each microcosm in order to provide habitat for juvenile fish and zooplankton. Each microcosm was supplied with a minimum of five such plants. M. spicatum and M. sibiricum were also added as individual plants for in situ toxicity testing. The results of the toxicity study will be reported at a later date.

Cages containing breeding pairs (2 cages, each with 4 pairs) of fathead minnows (Pimephales promelas) were placed in each microcosm. In some studies, pumpkinseed sunfish (Lepomis gibbosus) were added in hanging mesh cages.
The microcosms were open to aerial colonisation by insects and the PVC sides allowed for periphyton growth.

4.2.1.2 Haloacetic Acid Exposure Concentrations and Dosing - Injection System

HAA solutions were injected into the microcosms using a Proven Pony Pump (model 360, Los Angeles, CA), high-volume, low-pressure pump system. A Robusta ABS bilge pump was used to draw water from the microcosm and begin the circulation of the system, which took approximately 5 minutes. Flow from a Pony Pump injected the HAA solution of interest into the flowing stream and microcosm. Each microcosm, including controls, were circulated for 15 minutes after injection.

For each of the studies outlined, the compound was weighed out the day of the actual exposure and suspended in redistilled deionized water. The pH of each solution was then adjusted to 8.5 using \( \text{NaOH}_{\text{aq}} \).

4.2.1.3 Haloacetic Acid Exposure Concentrations and Dosing - TFA, TCA, DCA, and MCA Dosing

For the 1997 TFA (Caledon, Georgetown, ON.) study the concentrations were 10 and 100 \( \mu \text{g/L} \) (four microcosms each) and 300 and 1000 \( \mu \text{g/L} \) (two microcosms). In addition to these there were also three controls ponds. For the 1998 study, the TFA concentrations were 100, 1000, 3000, and 10000 \( \mu \text{g/L} \), which were applied in a similar fashion to three microcosms each. The
concentrations used in the studies (1998) with TCA (Aldrich, Milwaukee, WI),
DCA and MCA (1999) (Acros, Unionville, ON) were as follows; TCA 50, 500,
3000, and 10000 µg/L; DCA and MCA concentrations were 3000, 10000, 30000
and 100000 µg/L. For each acid there were also three control ponds included.
Microcosm assignments were randomly made.

4.2.1.4 Field Sampling Regime

Water samples for HAA analysis and routine water chemistry
determinations were taken at day -1, at one hour, 1, 2, 4, and 7 days, and on a
weekly or biweekly basis until completion of each study. A metal integrated
water column sampler was used to collect the water residue samples (Solomon
et al., 1982). Integrated sub-samples from a minimum of four randomly selected
locations in the microcosm were collected and stored as composite 1 L, 500 mL
or 250 mL samples in an amber bottle. These samples were stored at 4°C until
analysis by IC. All sample containers were prepared by soaking overnight in a
10 % (v/v) HCl solution, cleansing with a hot detergent solution, rinsing with hot
tap water, distilled tap water, and then drying in a drying oven at 150°C
overnight.

4.2.1.5 Field Water Chemistry

Water chemistry was monitored on a regular basis throughout each study.
Maximum and minimum temperatures and dissolved oxygen (DO)
measurements (YSI model 57 DO meter) were taken daily during the course of
the study. On selected sampling days, specific water parameters were measured (water hardness, alkalinity, dissolved organic carbon (DOC), total nitrogen and phosphates as well as pH).

4.2.2 Laboratory Study

4.2.2.1 Laboratory Microcosm Design

Wet sediment used in the field studies and obtained from the Guelph Microcosm Facility, and was oven dried at 100°C for 3 hrs. Dry sediment (5g) was added to clear 120 mL narrow mouth screw capped Boston round bottles (VWR Canlab Mississauga, ON). Experimental solutions (20 μg/mL sample, plus control and blank) were gently poured onto the sediment taking care not to cloud the water, then loosely capped and placed on a north facing windowsill. The approximate exposure to the sun each day for the solutions during the months of June and July ’99 was 12-14 hrs. Aliquots (5 mL) were taken at appropriate time intervals from each solution and analysed by ion chromatography (IC). Samples were taken at appropriate time intervals based upon the analyte of interest. The analysis times (hrs) for each of the acids were in the following range; MCA 0 – 360, DCA 0 – 194, TCA 0 – 724, TFA 0 – 2880, Oxalic acid 0 – 50.

4.2.2.2 Preparation of Experimental Solutions for Laboratory Microcosm Studies

TCA, DCA, MCA, and TFA were separately monitored in pond waters by setting up individual experimental solutions containing 20 μg/mL of each
chemical (n = 2). These solutions were prepared using the following procedure. A stock solution for each of the analytes at a concentration of 2000 µg/mL was prepared in pond water. A 1 mL aliquot from this stock solution was further diluted in 100 mL of pond water to give a final concentration of 20 µg/mL; a total of 10 sample solutions were prepared. This procedure was also followed in the preparation of the control solutions, with the only difference being the addition of 10 µg/mL of HgCl₂ (Aldrich, Milwaukee, WI) in the 20 µg/mL solution. The control solutions were also prepared in duplicate. Control pond water with no analyte added, was used as a blank. All solutions were stored in the refrigerator before commencement of the experiment. At the allotted time interval, aliquots were drawn using a syringe (Henke – Sass Wolf GMBH, Tuttlingen/Germany) and injected directly into a Dionex LC25 Chromatography Oven.

4.2.3 Analytical Methods

4.2.3.1 Extraction, Derivatization and Detection of Oxalic Acid, Glycolic and Glyoxylic Acid from Laboratory Solutions

Blank pond water and experimental solutions, which contained either TCA, DCA, or MCA, were obtained at a time point in which the parent compound had degraded through one half-life. A 20 µg/mL stock standard of oxalic, glycolic and glyoxylic acids (BDH, Toronto, ON. And Aldrich, Milwaukee, WI respectively) were used as control solutions. A 10 mL aliquot of each was acidified to pH 1 using concentrated HClₐq. Sodium chloride was added to each while stirring until saturation. This was extracted using four 25 mL portions of ethyl acetate,
the layers were combined, dried (anh. MgSO₄) and filtered before concentrating to 1 mL under reduced pressure. The solutions which contained TCA, MCA, oxalic and glycolic acids were transferred to 1.8 mL borosilicate glass ROBO vials and 100 μL of N-methyl-[(t-butyl-dimethylsilyl)]-trifluoroacetamide (MTBSTFA) with 1% t-butyl-dimethyl chlorosilane (1% t-BDMS) (Caledon, Georgetown, ON.) was added to each. The vials were covered with screw caps and placed in the oven for 30 mins at 60°C. To the solutions which contained DCA and glyoxylic acid, 1 ml of an etheral solution of diazomethane was added. The solutions were then analysed by GC-MS.

4.2.3.2 Gas Chromatography – Mass spectrometry

When appropriate, derivitized samples were run on a Perkin-Elmer GC Auto System XL equipped with a Turbomass quadrupole mass spectrometer, run in EI mode, with a 30 m, 0.25 mm Simplicity 5 column (Supelco, Oakville, ON). The carrier gas was helium at a flow rate of 0.5 mL/min. The oven temperature programme was 50°C for 1 min, followed by a temperature ramp of 10°C/min to a final temperature of 200°C. The mass spectrometer was set to full scan mode (30-600 mass units).

4.2.3.3 Ion Chromatography

TFA in the field studies was analysed using a Perkin Elmer Series 200 IC pump equipped with a Dionex Ionpac AS14 column, and an Alltech 1000 HP conductivity suppresser and conductivity detector were used. The mobile phase
was 3.5 mmol NaHCO$_3$/0.5 mmol Na$_2$CO$_3$ at a flow rate of 1.0 mL/min isocratically.

For the analysis of all HAAs in the laboratory studies and for the CAAs in the field studies, a Dionex – DX 500 Chromatography System equipped with an AS-11-2 mm column was used which was in turn attached to an AG-11-2 mm guard column, a CD20 Conductivity Detector, a GP50 Gradient Pump, and an E0 1 Eluent Organiser were used. A direct inject valve with a 25 µl loop was used along with an AS40 Automated Sampler for longer runs.

Separation of all the analytes was obtained using the following gradient program: Samples were initially injected at an eluent concentration of 90% DI water and 10% 0.005M NaOH for 5 min. Between 5 and 6.5 mins the eluent was changed to 99.9% DI water and 0.1 M NaOH. This was immediately followed by an eluent gradient between 6.5 and 18 mins to give a final eluent concentration of 82% DI water and 18% 0.1M NaOH. Between 18 and 22 mins, the eluent was changed to 100% 0.1M NaOH for 14 min.

4.2.3.4 ICP-AES measurement of metal trends

The measurement of metals was carried out using a Perkin Elmer Optima 3000DV inductively coupled plasma spectrometer. The parameters associated with the measurement of each metal are as follows; Plasma - Auxiliary, Nebulizer = 15, 0.5, 0.8 L/min, Power - 1300 W, view height = 15 mm, Pump - Sample 1.0 mL/min; flush rate, time = 4.0 mL/min, 10s; read delay = 60s, Wavelength of
Analysis (nm) - Ni = 232.003, Cr = 205.56, K = 766.443, Sr = 407.771, Na = 330.237, Ca = 317.933.

4.2.3.5 SAX extraction of TFA

For the analysis of aqueous environmental samples with low concentrations of the acids (<100 µg/L), a preconcentration step was employed (Ellis and Mabury, 1999). Aqueous samples (50 mL) were filtered using 0.45 µm filter paper (Sigma-Aldrich, Oakville, ON). They were then passed sequentially through an IC-Ba cartridge (Alltech, Guelph, ON) and two 500 mg SAX columns (Varian, Mississauga, ON). The cartridges were then eluted using 2 M NaOH(aq), and the eluent analysed for TFA using ion chromatography. Standards were prepared by passing control pond water through the SAX system, followed by the addition of a known amount of TFA.

4.3 Results and Discussion

4.3.1 The environmental fate of TCA, DCA, and MCA in field waters and under laboratory conditions

In the field studies, an initial induction period was seen for the CAAs before degradation of the parent compound was observed (Figure 4.2(a-d)). The induction period was dependent upon the substrate. After the induction period, rapid degradation of each of the CAAs was observed (Table 4.1). The half-lives were calculated by assuming pseudo first order kinetics. DCA had the shortest half-life at 28 hours, MCA 157 hours, and TCA 345 hours (Table 4.1).
The average rate of degradation of TCA, DCA and MCA is shown through the combination of three different pond dosing concentrations. An initial induction period of approximately 48 hours for TCA, 24 hours for DCA, and 48 hours for MCA are indicated. Degradation half-lives (n=3) of 345 hours (TCA), 28 hours (DCA), and 157 hours (MCA) are noted.

A comparison of the fate of TCA, DCA, and MCA in pond water, with the results expressed as the percentage remaining as a function of time. Data is the combination of the results obtained at different pond concentrations for each of the acids. Initial concentrations were as follows; TCA 1(3), 3(3), and 10(3) mg/L, DCA 10(2), 30(2), and 100(2) mg/L, MCA 3(4), 6(4), and 12(4) mg/L. The number of ponds used at each concentration is indicated in parentheses. Each pond was analysed twice. A linear combination of the errors associated with individual results was used to calculate the absolute standard deviation.
Table 4.1. The induction periods associated with HAAs used in the field studies and in mechanistic laboratory studies. Pseudo first order degradation rates are given, calculated subsequent to the induction period.

<table>
<thead>
<tr>
<th>Haloacetic Acid</th>
<th>Induction Period (Field)</th>
<th>Induction Period (Lab)</th>
<th>Field Half-life ($T_{1/2}$)</th>
<th>Lab Half-life ($T_{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCA</td>
<td>48</td>
<td>120</td>
<td>345</td>
<td>379</td>
</tr>
<tr>
<td>DCA</td>
<td>24</td>
<td>23</td>
<td>28</td>
<td>20</td>
</tr>
<tr>
<td>MCA</td>
<td>48</td>
<td>143</td>
<td>157</td>
<td>113</td>
</tr>
<tr>
<td>TFA</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

1 Induction periods are given in hours. They are reported as the hour of the sample analysed, prior to the observation of degradation within a sample.

2 Half lives are reported in hours.

An induction period suggests the subsequent degradation occurred as a result of microbial activity (Jensen et al., 1960). If the degradation had occurred through an abiotic process such as hydrolysis or photolysis, it would be expected to initiate at time $> 0$. The time for induction was dependent upon the number of chlorine atoms which the acid contained. The induction time was estimated as the final sampling time in which little or no degradation was seen. The induction period and rate of degradation of the CAAs were effectively independent of the applied concentration (Figure 4.3(a-c)).
Figure 4.3 (a-c) A comparative concentration dependent rate study in Guelph Microcosms for the degradation of TCA, DCA and MCA is shown. The concentration levels are: 1, 3 and 10 mg/L for TCA, 10, 30 and 100 mg/L for DCA, and 3, 6 and 12 mg/L for MCA. Results are presented as log concentration versus log time.
This indicates the order of the reaction is pseudo zeroth order with respect to the acid, and the rate of reaction was dependent upon the concentration of microbes present. TCA and MCA had approximately the same induction time of 48 hours (Table 4.1) while DCA had the shortest induction time of approximately 24 hours. These results suggest the identity of the microbial population responsible for degradation was different for DCA than TCA or MCA, or that their bioavailability and susceptibility degradation differed. The order of degradation of the acids is identical to that which was observed using soil microbes (Hirsch and Alexander, 1969). These researchers also observed the presence of an initial induction period.

Field results were compared with those obtained for the laboratory microcosms, which were prepared in a manner so as to mimic the ponds. The induction period was typically longer for MCA and TCA in laboratory experiments (Table 4.1). This enhanced induction period can be accounted for in the experimental preparative methodology used. In order to obtain accurate masses of sediment, the sediment was dried prior to use. This may have resulted in a reduction in microbial biomass, and hence the subsequent increase in the induction period. DCA was observed to have the same induction period in both the field and laboratory settings. This is consistent with the hypothesis that DCA degradation occurs through an alternate microbial pathway, when compared with either TCA or MCA. Further evidence for this is presented by the fact that when the solution containing DCA, which had completely degraded was spiked with MCA, degradation of the MCA was not immediately observed, and a further
induction period was required before degradation occurred (data not shown). No degradation was seen for any of the HAAs if the sediment was absent from the laboratory microcosm. The rates of decay for TCA were similar in both field and laboratory systems (Figure 4.4).

![Graph comparing rates of degradation for TCA in field water and laboratory conducted experiments.](image)

**Figure 4.4** The comparison of rates of degradation for TCA in field water and in laboratory conducted experiments toward the mechanism of degradation within field water. The half-life of TCA is indicated in both media. Half-lives were calculated subsequent to the induction period, with pseudo first order kinetics imposed.

From Table 4.1 it can be seen that the magnitude and relative order of the degradation rates are similar for all three CAAs for both systems. Furthermore, in the laboratory experiments the half life of TCA is approximately three times that of MCA, suggesting the replacement of the chloride is the rate limiting step in
the reaction. If microbial degradation of the CAA leads to cleavage of a carbon-chlorine bond, then the half life of the parent molecule should decrease as the number of chlorines increase. The fact that DCA had the shortest half life, despite having two chlorine atoms, suggests the microbial action occurring is unique to this CAA. The difference in half lives of MCA and TCA can be accounted for through the inclusion of two more chlorine atoms.

Key products were identified and monitored in order to elucidate the pathway responsible for microbial degradation. For each of the three CAAs, the concentration of chloride was monitored as a function of time. A linear increase was observed for each acid, with loss of the parent compound.

After TCA had degraded through one half life, the reaction system was acidified and extracted with ethyl acetate. The volume was then reduced under pressure and the residue derivitized with MTBSTFA. The presence of oxalic acid was confirmed by GC-MS based upon the retention time and molecular ion of the derivitized extract (molecular ion = 306 (1.2%), corresponding to the di-t-butyldimethylsilyl ester, base peak 108 (M-C$_{14}$H$_{30}$, 2 x Bu')). Oxalic acid was also confirmed by retention time comparison with an authentic standard using IC. The systems in which TCA had degraded were also spiked with oxalic acid, which was observed to have a shorter half life than TCA. Oxalic acid was never seen to significantly accumulate as degradation proceeded. A similar extraction procedure was used in the identification of glycolic acid produced through the degradation of MCA (molecular ion = 292 (2.1 %), corresponding to the silyl ester, base peak 94 (M-C$_{14}$H$_{30}$)). For DCA, the reaction mixture and a standard
solution containing glyoxylic acid were extracted, as in the case of TCA and MCA, and derivitization was carried out using an ethereal solution of diazomethane in place of MTBSTFA. Glyoxylic acid was identified as a degradation product (molecular ion = 88, corresponding to the methylated acid, base peak 87 (M-1)). The degradation mechanisms outlined in Figure 4.5 were proposed based upon results from this investigation and literature evidence for similar systems (Slater et al., 1997).
Figure 4.5 The proposed degradation pathways and products for TCA, DCA, and MCA in field waters based upon laboratory experiments. Reagents that were monitored and observed products are indicated in bold, and those, which are inferred, are bracketed.
These results are similar to those obtained by Hashimoto et al., 1998. Their findings show that TCA is the most stable of the three CAAs in the aquatic systems investigated. However, the overall half lives of all CAAs were uniformly longer in their study. This may be attributed to river and seawaters being used in their case, while pond waters and sediments were used in the current studies, or that, in the waters used in their investigations, an alternate microbial strain was responsible for the degradation which took place.

Over the period in which the CAAs were observed to degrade no significant change in water chemistry parameters was observed (±=RSD); alkalinity 172.2±2.2 mg/L CaCO₃, hardness 300.6±5.1 mg/L CaCO₃, pH 7.9±0.1, temperature 24.8±0.3°C (max) and 20.2±0.1°C (min), and dissolved oxygen 7.9±0.3 mg/L.

4.3.2 The environmental fate of TFA in field waters and under laboratory conditions

Field studies with TFA were conducted over two separate years (1997-98 and 1998-99). No degradation of TFA was observed in the time scale of the field experiments (up to one year, Figure 4.6). There was no change in the TFA concentration over the period June – October (Figure 4.6a), but following this, a reduction of up to 35 % TFA was observed for the months November – January. For the period of February-March, the concentration of TFA subsequently returned to initial concentration levels.
Figure 4.6(a) The fate of TFA at three pond concentrations in 1997. No degradation of TFA are observed in the experimental time scale. A reduction in the concentration of TFA is seen over the winter months. Levels are viewed to rise again toward spring.

(b) The fate of TFA at three pond concentrations in 1998. No reduction or degradation is observed within the experimental time scale over the winter months.
It is hypothesised that the decrease and subsequent increase in TFA over the winter/spring months can be accounted for by an enforced partition of the TFA into an as yet unidentified phase. The formation of ice within the pond would be expected to lead to the enhancement of TFA concentrations in the aqueous phase, due to thermodynamic exclusion from the ice. Indeed, when a solution containing TFA, sediment, phytoplankton, and pond water was placed in a freezer at -20°C and ice allowed to form, the measured aqueous TFA concentration increased (Figure 4.7).

Figure 4.7  TFA concentration dependence in laboratory minicosms as a function of temperature and the formation of ice.
The aqueous TFA field samples for the November – December period were also analysed for nickel, chromium, potassium, strontium, sodium, and calcium using inductively coupled plasma spectroscopy with atomic emission detection (ICP-AES), and also for sulphate and chloride using ion chromatography (IC). A comparison of the results obtained for these analytes with those obtained for TFA were made (Figure 4.8). As can be seen, as TFA decreases no similar trend was observed for the other ions. This suggests the results obtained for TFA can not be accounted for through sampling or analytical error.
Figure 4.8 (a) A comparison of the relative concentrations of six metals, chloride and sulphate with TFA in pond water samples obtained in the winter months.

(b) A decrease in the concentration of TFA (1997) is observed over days 78 – 238.

No such decrease in TFA was observed for the subsequent year (Figure 4.6). It is hypothesized in the period between subsequent years the biotic and/or suspended particulate matter concentrations were different and one of these may be the phase into which TFA was partitioning.

The laboratory microcosm experiments were also extended to the study of TFA. As shown in Table 4.1, no degradation of TFA was observed. Furthermore,
when TFA was spiked into a solution in which TCA had degraded, no degradation was observed; this suggested the microbes responsible for TCA degradation were not capable of transforming TFA.

4.4 Conclusions

Evidence from this study suggests chloroacetic acids are rapidly dechlorinated to nonpersistent products, primarily via microbially mediated hydrolysis, under the conditions investigated. It is suggested that the microbial population responsible for the degradation of TCA and MCA are the same, while those responsible for DCA degradation are different. This conclusion is based on the similarity of induction periods and the fact that rates of decay of TCA are approximately three times that for MCA. The initial step in the degradation of each CAA is proposed displacement of the chloride through enzymatic action. This enzymatic hydrolysis results in the production of oxalic, glyoxalic and glycolic acids form TCA, DCA and MCA respectively. The resultant acids in turn, degraded more rapidly than the parent compound from which they were produced. The persistence of these acids in the environment is proposed to follow the order TCA>MCA>DCA.

TFA was not observed to degrade appreciably in the aqueous environment over the time scale of the field experiments conducted (1 year). It is suggested the partitioning of TFA into an as yet undetermined phase can be enhanced at low temperature. Further studies toward this phenomenon are required.
Chloroacetic acids have a much shorter persistence in the pond waters compared with trifluoroacetic acid (Figure 4.9). Further, our data confirms other studies which suggest that TFA should have a long residence time in the environment, and therefore will likely accumulate over time.

Figure 4.9 Comparison of the relative rates of TFA, TCA, DCA and MCA degradation in field waters over a six month period (June – November). The fate of TFA was averaged over two consecutive one year studies.
4.5 References


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Chapter Five

The Thermolysis of Fluoro- and Chlorofluoropolymers: a Possible New Source of Haloacetic and Perhaloalkanoic Acids to the Environment

Article Submitted to be published in Nature 2000
5.1 Introduction

The replacement CFC gases, HCFC-123, 124, and HFC-134a, are known to degrade in the troposphere, through reaction with hydroxyl radicals, to TFA (Franklin, 1993). TFA is expected to be a long-lived environmental species and currently has no known significant loss mechanism (Boutonnet et al., 1999). Studies have suggested that at higher concentrations, such as those observed in surface waters with seasonal evapo-concentration cycles (Berends et al., 1999), TFA will exhibit mild phytotoxicity (Tromp et al., 1995). Environmental modeling calculations conducted for TFA predict a concentration of 0.1-0.12 μg/L in rainwaters between the years 2010 and 2020 (Boutonnet et al., 1999; Kotamarthi et al., 1998); based upon the assumption that TFA originates from the CFC replacement gases. Environmental measurements (Jordan and Frank, 1999; Berg et al., 2000; Wujcik et al., 1999) 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 0.12 μg/L (Jordan and Frank, 1999); and no major alternative source has been identified to explain these observations. Although there is some controversy within the literature, it would appear that the TFA observed in precipitation is largely a result of urban activities. For example concentrations of <0.002 – 0.092 μg/L for remote sites compared with 0.050 – 1.100 μg/L for industrialized urban sites (Von Sydow, et al., 2000). The unidentified source of TFA is likely to be anthropogenic in origin, as there are no known naturally occurring trifluoromethylated compounds (Peters and Hall, 1960). A second long-lived fluorinated acetic acid, CDFA, has recently
been identified in rainwaters (Martin et al., 2000). Direct evidence of a source responsible for its production has yet to be established, although CFC-113 may contribute.

Agrochemicals, anaesthetics and fluoropolymers are the three major, distinct, categories into which environmental emissions of fluorine containing anthropogenic organic compounds can be subdivided. Both agrochemicals (Ellis and Mabury, 2000) and anaesthetics (Jordan and Frank, 1999) have been shown to produce TFA, however, they can be eliminated as major contributors due to the quantities that are currently being emitted into the atmosphere (Jordan and Frank, 1999). Fluoropolymers, such as polytetrafluoroethylene (PTFE or Teflon®), are potential sources, due to their heavy usage in urban and industrial areas. Additionally, the amount of perfluorinated organic materials used is rapidly increasing. In 1988 the average annual global consumption of fluorinated polymers was 40 000 t (Feiring, 1994) and by 1997 this figure had risen by almost 220% based upon sales (Holloway, 2000). It is projected that this trend will continue at an annual increase of at least 7% pa.

In order to produce the CF₃- or CF₂Cl- unit required for haloacetic acid formation, the polymer would have to undergo decomposition and subsequent rearrangement. The two main modes by which this could occur are through thermal or photolytic processes; however the latter can be ruled out because actinic radiation is not energetic enough to evoke these reactions. Fluoropolymers are being designed and modified specifically for employment in areas of high thermal stress, such as in 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 employed in areas of elevated temperature, a grouping composed primarily of fluoropolymers (Johns and Stead, 2000). The subcategory of plastics known as engineering plastics, in particular fluoropolymers, operate at the extreme of the polymers temperature performance (Johns and Stead, 2000). PTFE, for instance, will endure 260°C for ~2.3 years (Imbalzano, 1991) until failure due to degradation (Simon and Kaminsky, 1998). Fluoropolymers are, largely, either recycled or degrade in situ (Simon and Kaminsky, 1998) resulting in research concerning the toxicity of the decomposition materials (Arito and Soda, 1977). It is well established that the onset of thermal degradation of fluoropolymers initiates cleavage of the backbone and subsequent rearrangement to produce significant amounts of trifluoromethylated species (Jollie and Harrison, 1997). The incineration, or combustion, of fluoropolymers has previously been proposed as a source of TFA (Jordan and Frank, 1999) and CDFA (Martin et al., 2000). These processes differ from thermolysis in that a source of fuel is used in order to purposefully evoke complete decomposition. Furthermore, it is unlikely to yield environmentally significant levels of TFA, or TFA precursors, due to the high temperatures and oxidizing conditions employed, which results in the cleavage of most carbon fluorine bonds (Jollie and Harrison, 1997). Polychlorinated dioxins and furans are produced in the low temperature burning of domestic wastes, and analogously this may be also be an important source of fluoroacids (Lemieux et al., 2000).
The objective of this study was to show the possibility of the direct and indirect production of haloacetic acids (HAAs) through the thermolysis of fluorinated polymers and to investigate the production of other perhalogenated compounds that may be of environmental significance.

5.2 Materials and Methods

5.2.1 Chemicals

Sodium monofluoroacetate (MFA), difluoroacetic acid (DFA), chlorodifluoroacetic acid (CDFA), hexafluoropropene (HFP), 4’-(trifluoromethoxy)acetanalide (TFMAA), PTFE, chloro(polytrifluoroethylene (CPTFE), poly(tetrafluoroethylene-co-tetrafluoroethylene perfluoropropylether) (ECTFE), PFPE, and all fluorinated acids were purchased from Aldrich Chemical Company (Mississauga, Canada). Trifluoroacetic acid (TFA) was purchased from Caledon (Georgetown, Canada), methyl-d₄ alcohol from Isotech Inc. (Miamisburg, OH). Slick 50® from Petro-Lon (Mississauga, Canada). The frying pan from Cornerstone (Hong Kong) coated with Dupont Teflon and Kel-F® from Supelco (Bellefonte, PA).

5.2.2 NMR Spectrometer Parameters

All spectra were obtained at 25°C on a Varian Unity 500, 3 channel spectrometer operating at 470.297 MHz and equipped with a 5-mm Nalorac ¹⁹F proton decoupling probe. Free induction decays (FID) were zero filled by making the fourier number equal to twice the number of data points. Chemical shifts...
were recorded relative to CFCI₃ (0.000 ppm). The ¹⁹F 1D nmr spectra were recorded between −40 and −200 ppm using a spectral window digitized to 128,000 points. We used the same spectral window for the 2D COSY spectra. 1024 time increments were collected and zero filled 4096 points with sine bell weighting along both dimensions. 16 scans were collected per increment and the recycling delay was 1 s.

5.2.3 Gas Chromatography – Mass Spectroscopy Parameters

For identification and quantification using GC/MS, aqueous samples were added to ethyl acetate containing 2,4-difluoroaniline and dicyclohexylcarbodiimide to produce the acid analide in a method similar to that of Scott and Alaee (1998). Analysis was performed on a gas chromatograph (HP Model 5890 Series II) interfaced to a quadrupole mass selective detector (HP Model 5971A) operating in single ion mode, and equipped with a 70 eV electron ionization source. GC separation was performed on a fused silica capillary column coated with cross linked 5 % phenyl methyl siloxane (HP-5MS, 30m x 0.25mm, film thickness 0.25 μm), using helium as a carrier gas. The injector temperature was 220°C and the initial oven temperature was 50°C for 2 minutes, increasing at a rate of 5°C min⁻¹ to 250°C. A procedural blank was run with each sample set.

Gas samples were analyzed by direct injection to a Perkin-Elmer GC Auto System XL equipped with a Turbomass quadrupole mass spectrometer, run in EI mode, with a 60 m, 0.32 mm GasPro column (J & W, Oakville, ON). The carrier gas was helium at a flow rate of 0.5 mL/min. The oven temperature programme
was 50°C for 1 min, followed by a temperature ramp of 10°C/min to a final
temperature of 200°C. The mass spectrometer was set to full scan mode (30-
600 mass units)

5.2.4 Thermolysis Procedure

The polymer, or commercial material, of interest (2g) was placed in a
quartz boat that was then inserted into a quartz tube (60cm), and placed in an
oven. Air was continually passed over the sample (≈2L/min). The oven
temperature was then ramped to 560°C (11°C/min). The evolved thermolysis
materials were collected in a manner befitting their physical nature and the
method of analysis used (Section 5.2.5).

5.2.5 Collection Procedures

For 19F nmr analysis of the volatile organics, the products were collected
in a round-bottomed flask at -78°C. The flask was then cooled to -196°C and
transferred to a vacuum line (≈16 Torr) upon which it to was evacuated. An nmr
tube containing 700μL of CD3CN cooled to -196°C was connected in series with
the flask. The flask was then allowed to warm to room temperature and the
products transferred to the nmr tube. After 1-hour period the nmr tube was
sealed and allowed to warm to room temperature and an nmr spectrum collected
immediately.

For the analysis of perhalo-acids, the polymer decomposition off-gases
were bubbled through an aqueous Na2CO3 solution (pH 10.2). For 19F nmr
quantification, 500μL of this solution was added to an nmr tube containing 500μL of CD$_3$CN spiked with a known concentration of the internal standard, trifluoromethoxyacetanalide. Quantification was conducted by comparison to an external calibration using a method similar to that of Ellis et al. (2000)

For the quantification of volatile gases produced in the polymer decomposition, the off-gases were collected in a glass vessel of known volume at -78°C. After decomposition was complete the vessel was sealed and allowed to warm to room temperature. Aliquots were removed using a gas tight syringe and directly analyzed using GC-MS. Quantification was performed by comparison to an external calibration.

Blanks consisting of all reagents were run to ensure that products observed were produced as a direct result of polymer decomposition.

5.2.6 Environmental Modeling

A two-box model was developed to predict the concentration of TFA observed in Toronto rainwater. This type of modeling system was developed by the Dutch and has been validated by the European EPA. It is used to eliminate compartmental boundary problems. In order to create a model of this nature to estimate rainfall concentrations of TFA in metro Toronto, several assumptions and approximations had to be made. These assumptions and the justification in making them are as follows:
1. The total amount of fluoropolymer available in year 2000 within N. America, which could undergo thermolytic degradation, is not known. However, we have used a figure that grossly underestimates the true value. As a result of this the predicted TFA concentration in rainwater will also be underestimated. A figure of 191,281 tons, the total amount produced in N. America in the last five years (Holloway, 2000) was arrived at on the following basis; most fluoropolymers have a life expectancy of up to 20 years (Jordan and Frank, 1999). It is reasonable to assume that the total amount of these polymers, which were produced in the last five years, would be a low base figure to use as the total amount present on the continent.

2. The annual amount of fluoropolymers which were thermally degraded was 0.1% of the total amount present. This percent value is used is conservative as it is known that a large fraction of fluoropolymers are designed for, and used in, areas of high thermal stress and as a result degrade thermally (Johns and Stead, 2000).

3. North America is considered to be a box in which there is no input to the system of TFA due to fluoropolymer degradation outside this area. This is a good approximation, as TFA is known to have a short residence time in the gas phase before rain out (Tromp et al., 1995).

4. Atmospheric gaseous TFA is only deposited through rain and dry gaseous deposition to all types of surfaces. Given a $K_{ow}$ value of $4.75 \times 10^6$ for TFA (Bowden et al., 1996), it is reasonable to assume that the dry deposition velocity of TFA was estimated using the equation $-111.92 \text{ s/m} + 67 \text{ s/m} + 105$
s/m x K_H (van Pul et al., 1998). TFA is not known or expected to adhere to aerosols to an important extent.

5. The system is at steady state. I.e. there is no net change in the rates of the processes taking place.

6. There is no atmospheric degradation of TFA on the time scale of the model. No degradation processes of TFA in the environment are known (Ellis et al., 2000).

7. The mass of fluoropolymer thermally degraded is proportional to population density. Fluoropolymers are used largely for industrial processes and therefore would be extensively used in urban areas. The input of TFA through non-industrial uses, such as in cookware would also be proportional to population density.

8. The average production of TFA from fluoropolymers is 7.8 % based upon our results for PTFE.

The two box model employed is shown diagrammatically in Figure 5.1.
Figure 5.1 The box model employed.

N_{cg} and N_{gc} – amount of material moving between the continent and the globe and vise versa.

N_{cm} and N_{mc} – amount of material moving between the continent and the metro Toronto area and vice versa.

E_c and E_m – emissions of TFA in the gas phase to the atmosphere through the thermal degradation of fluorinated polymers.

N_{dm} and N_{dc} – rain deposition of TFA to metro Toronto and the to the continent.

N_{am} and N_{ac} – dry deposition of TFA on to water bodies within metro Toronto and the continent.
Each process ($N$) is defined as a flux of material (Eqn 1). This is the rate of movement as a function of the concentration of the material in the defined medium.

$$N = G \text{ (m}^3\text{/h}) \times C \text{ (kg/m}^3\text{)}$$

where $G = h.A/\tau$. $h$ is the mixing height (6 km for the continent and 1 km for metro Toronto), $A$ is the area and $\tau$ is the residence time (6 hours for metro and 5 days for the continent).

The rate of change of material, which is a function of net processes causing input minus net processes causing an output, in the continent and in Metro Toronto can now be expressed at steady state as:

**Metro Toronto**

$$\frac{dM}{dt} = E_m + N_{cm} - N_{mc} - N_{dm} - N_{am} = 0$$

$$= E_m + G_{cm}.C_{ac} - C_{am}(G_{mc} + G_{m}.1/K_{aw} + \nu_{am}.A_m) = 0$$

**Equation 2.**

- $G_{cm}.C_{ac}$ = continent metro flux x concentration in continental air.
- $C_{am}$ = concentration in metro air.
- $G_{mc}$ = metro continent flux.
- $G_{m}.1/K_{aw}$ = rain flux for metro x reciprocal of the air water partition coefficient.
- $\nu_{am}.A_m$ = dry deposition velocity from metro air x area of metro.
- $E_m$ = Fraction of population in Metro compared with North America = 0.811%. Thus, 191, 281 x 0.811 % = 1551.28 tons of fluoropolymer
consumed per year. 1551.28 at a thermolysis rate of 0.1%, of
which 7.8% is converted to TFA.

\[ G_{cm} = 1.053 \times 10^{11} \text{ m}^3/\text{h} \]
\[ G_{mc} = 1.053 \times 10^{11} \text{ m}^3/\text{h} \]
\[ C_{am} = \text{Unknown variable} \]
\[ C_{ac} = \text{Unknown variable} \]
\[ G_{rm} = \text{rain flux. Average yearly precipitation of } 689.3 \text{ mm (0.6893 m)} \]
\[ (\text{Environment Canada). Volume of rain } 0.6893 \text{ m} \times 6.32 \times 10^8 \text{ m}^2 = \]
\[ 4.3564 \times 10^8 \text{ m}^3. \]
\[ = 4.973 \times 10^4 \text{ m}^3/\text{h}. \]
\[ K_{aw} = 4.75 \times 10^{-6}. \]
\[ u_{am}.A_m = 1/(192 \text{ s/m} + 67 \text{ s/m} + 105 \text{ s/m} \times K_{aw}) \times 6.32 \times 10^8 \text{ m}^2. \]
\[ = 8.7686 \times 10^8 \text{ m}^3/\text{h}. \]

Substituting these variables into Eqn 2.

\[ 0 = 1.381 \times 10^{-2} \text{ kg/h} + (1.053 \times 10^{11} \text{ m}^3/\text{h} \times C_{ac}) - C_{am} \times 1.2454 \times 10^{11} \text{ m}^3/\text{h}. \]

**North America**

\[ dM/dt = E_c + N_{gc} + N_{mc} - N_{cg} - N_{cm} - N_{dc} - N_{ac} = 0 \quad \text{Eqn 3.} \]
\[ = E_c + G_{gc}C_{sg} + G_{mc}C_{am} - C_{ac}(G_{cg} + G_{cm} + G_{rc}1/K_{aw} - u_{ac}.A_c) = 0 \]
\( G_{cg}.C_{ag} \) = global continent flux \( \times \) concentration in air for globe.

\( G_{mc}.C_{am} \) = metro flux \( \times \) concentration in air for metro.

\( G_{cg}.C_{ac} \) = continent global flux \( \times \) concentration in continent air.

\( G_{rc}.C_{ac}.1/K_{aw} \) = continental rain flux \( \times \) concentration in continent air \( \times \) reciprocal of the air water partition coefficient.

\( \nu_{ac}.A_{c} \) = dry deposition velocity from continental air \( \times \) area of the continent

\( E_{c} \) = 191, 281 tons of fluoropolymer present, at a thermal degradation rate of 0.1 \%, of which 7.8 \% is converted to TFA.

\( = 1.703 \text{ kg/h} \)

\( G_{gc} \) = 6 km \( \times \) 19,348,750 km\(^2\)/5 days

\( = 9.6744 \times 10^{14} \text{ m}^3/\text{h} \)

\( C_{ag} \) = 0 (considering only fluoropolymer emissions)

\( G_{mc} \) = 1 km \( \times \) 632 km\(^2\)/6 hours

\( = 1.053 \times 10^{11} \text{ m}^3/\text{h} \)

\( C_{am} \) = Unknown variable

\( C_{ac} \) = Unknown variable

\( G_{cg} \) = 9.6744 \( \times \) 10\(^{14}\) m\(^3\)/h

\( G_{cm} \) = 1.053 \( \times \) 10\(^{11}\) m\(^3\)/h

\( \bar{G}_{rc} \) = Average yearly precipitation of 876 mm (0.876 m). Volume of rain 0.876 m \( \times \) 1.9348 \( \times \) 10\(^{13}\) m\(^2\) = 1.695 \( \times \) 10\(^{13}\) m\(^3\).

\( = 1.935 \times 10^9 \text{ m}^3/\text{h} \).

\( K_{aw} \) = 4.75 \( \times \) 10\(^{-6}\).

\( \nu_{ac}.A_{c} \) = \( 1/(192 \text{ s/m} + 67 \text{ s/m} + 105 \text{ s/m} \times K_{H}) \times 1.9349 \times 10^{13} \text{ m}^2. \)
Substituting these variables into eqn 3.

\[ 0 = 1.703 \text{ kg/h} + (1.053 \times 10^{11} \text{ m}^3/\text{h} \times C_{am}) - C_{ac} \times 1.6394 \times 10^{15} \text{ m}^3/\text{h} \]

Using Eqn 2 and Eqn 3 were then used in conjunction to obtain:

\[ C_{am} = 1.118 \times 10^{-13} \text{ g/L} \]

Thus, if the air TFA concentration is primarily lost due to rain out

\[ C_{water} = C_{am}/K_{aw} \]

\[ = 1.118 \times 10^{-13} \text{ g/L} / 4.75 \times 10^{-6} \]

Therefore the calculated concentration is 23.53 ng/L in rainwater for Metro Toronto.

5.3 Results and Discussion

5.3.1 The Thermolysis of Neat Fluorinated Polymers

Tetrafluoroethylene (TFE), hexafluoropropene (HFP) and cyclooctafluorobutane (c-OFB) were the major gaseous materials produced upon thermolysis of the neat fluorinated polymers and commercially available products tested (Table 5.1). Chlorofluoropolymers, e.g. CPTFE, analogously yielded
chlorotrifluoroethene (CTFE), chloropentafluoropropene (CPFP) and 1,2-dichlorohexafluorocyclobutane (DCHB).
Table 5.1  Positively identified species produced in the thermal decomposition of fluoropolymers and commercial fluoropolymer products

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Thermal Product Identified</th>
<th>Percent Produced</th>
<th>Commercial Polymer</th>
<th>Thermal Product Identified</th>
<th>Percent Produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE</td>
<td>TFE (1,2)</td>
<td>-</td>
<td>Teflon® Frying Pan</td>
<td>TFA (1)</td>
<td>1.2x10^3 (4)</td>
</tr>
<tr>
<td></td>
<td>HFP (1,2)</td>
<td>10.8 (4)</td>
<td></td>
<td>CDFA (2)</td>
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(1) Identified by NMR, (2) identified by MS, (3) quantified by NMR, (4) quantified by MS. A dash indicated that the analyte was positively identified but not quantified. The percentage produced is calculated from the ratio of the mass of product relative to the mass of material thermally decomposed. 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, 1,3-DCTFP, 1,3-dichlorotetrafluoropropene, 1,1,3-TCTFP, 1,1,3-trichlorotetrafluoropropene, PFPE, polytetrafluoroethylene-co-tetrafluoroethylene perfluoropropylether. For the long-chain acids, n=1-14, m=1-7, x=0-2, y=1-3, z=1-2, p=9-13.
HFP has the potential to react with OH radicals in the troposphere to produce TFA (100% conversion) (Mashino et al., 2000). The reaction kinetics of CPFP with OH are expected to be similar to that of HFP based upon its reaction with other radicals (Paleta et al., 1997) and the behavior of similar molecules (Mashino, M. et al, 2000) producing CDFA in the troposphere.

A large, previously unidentified, class of thermolysis compounds, perhalogenated acids (PHAs), is also shown in Table 5.1. These acids can be subdivided into those with straight polyhalogenated linear alkyl chains and those which contain an ether linkage at the chain terminus. A variety of acids were produced, with chain lengths reaching 24 carbon atoms. The yield of the acid was observed to decrease with increasing carbon number (Figure 5.2).

![Figure 5.2](image-url)  
**Figure 5.2** Representative TIC trace showing the perfluorocarboxylic acids (PFCs) produced in the thermal decomposition of PTFE.
TFA and CDFA were the major acids to be observed in the thermolysis of the fluoro- and chlorofluoropolymers (Figure 5.3), while other longer chained perhalogenated acids that were also identified in lower yield; which were presumably overlooked in previous investigations due to analytical limitations.
Figure 5.3  NMR results for CPTFE thermolysis. A. $^{19}$F nmr spectrum of the main volatile fluorinated compounds produced. B. Expansion of spectrum to emphasize selected signals of interest CPFP, CDFA, and TFA.
The positive identification of CPFP made by the use of $^{19}\text{F} - ^{19}\text{F}$ NMR correlation spectroscopy (Figure 5.4). The resultant signals produced from the four fluorine atoms are correlated to one another, indicating that the atoms are in the same spin system, i.e. attached to the same molecule. This taken with the splitting pattern observed, shown in Figure 5.2, univocally proves, that this compound is indeed produced through the thermal decomposition of the CPTFE.

Figure 5.4 $^{19}\text{F} - ^{19}\text{F}$ correlation NMR for CPFP produced in the thermal degradation of CPTFE.
A mechanism, primarily involving the reaction of a CF$_2$ carbene unit, is proposed for the production of the major compounds observed (Figure 5.5).

**Figure 5.5** Proposed significant pathways in the thermal decomposition of fluoropolymers.

This mechanism is supported by key products observed by several other researchers (Jollie and Harrison, 1997; Atkinson and Atkinson, 1957; Ignateva, et al., 1995; Arito and Soda, 1977; Miesowicz, 1987; Buravtsev and Kolbanovsky, 1999) and the additional products observed in this investigation. As indicated by the bold arrow, the most significant step in the thermal decomposition is the formation of carbene radicals. Longer chain diradicals are also formed which can undergo fluorine abstraction or reaction with carbonyl fluoride to produce radical
fluorinated alkanes (p=0-4) or ethers. These radicals then react with the air present to form perfluorinated acids (n=0-13, m=1-7), the yield being inversely proportional to the number of carbons in the chain. The product yield distribution is temperature and atmosphere dependant. As TFA is thermally labile at the temperatures used to evoke thermal breakdown of the fluoropolymer (Jollie and Harrison, 1997), it must be formed due to the reaction of fluorocarbon radicals with the stream of air flowing over the polymer as it exits the reaction chamber. CPTFE and other polyfluorinated polymers have not been studied in nearly the same depth. We hypothesize the mechanism for degradation is similar based upon the distribution of related products observed in this investigation.

5.3.2 The Thermolysis of Commercial Materials Containing Fluoropolymers

The incorporation of fluoropolymers into commercial products that are used in high temperature applications, (ie. the teflonized engine additive Slick 50®), also results in thermal decomposition under an oxygenated environment to produce TFA and/or CDFA along with numerous other PHAs (Table 5.1). Although the significance from a single source may be small, the incorporation of fluorinated polymers into commercial materials continues to increase, and could result in the accumulation of these compounds in the environment.
5.3.3 The Environmental Impact

These results may explain the high TFA concentrations currently observed in precipitation (especially in urban areas), and the presence of other chlorofluoroacids, such as CDFA. They may also help to account for the seemingly contradictory reports that, in some instances, urban areas have higher concentrations of TFA in comparison with remote locations, while others have reported that the concentrations are similar in both regions. These observations can be attributed to HAAs being produced directly through thermolysis of the polymer which undergo short-range transport and also indirectly from the reaction of OH with propenes, which may allow for longer-range transport (HFPs tropospheric life-time 9 days based upon its reaction kinetics with OH (Mashino, et al., 2000)). It has been suggested that if HFP is produced from fluoropolymers, even to a small degree, that this would be a significant environmental burden of TFA (Mashino et al., 2000). To further support this hypothesis a two box environmental model was applied in order to equate the concentration of TFA observed rainfall with the amount of fluoropolymer consumed per annum for the city of Toronto relative to North America (See Materials and Methods for a full description of the model). Estimations were made by considering the flux of TFA to the gas phase, and in turn the flux in and out of Toronto with respect to North America. After consideration of all other major fluxs (e.g. dry deposition) the average rainfall concentrations were estimated. The major uncertainty used for this calculation is the percentage of fluoropolymers which ultimately undergo thermolytic degradation. We have used
a value of 0.1 % per year of the lowest estimated amount of fluoropolymer present in North America. Our estimates of the thermal degradation rate and total fluoropolymer mass are considered to be conservative because the degree to which these polymers are used in thermal applications is far higher and indirect production from HFP was not included (Mashino, M. et al, 2000). The model shows that there is the potential for a TFA concentration of ~25 ng/L in Toronto rainwater as a direct result of fluoropolymer thermolysis. These results are in accordance with those which have been experimentally observed (Eliis et al., 2000), further they are close to the level of urban enrichment observed by independent researchers (Cahill and Seiber, 2000).

These results may also help explain the presence of TFA in waters that are dated older than when the CFC replacement gases first came into use (Von Sydow, et al., 2000), cf. PTFE was first discovered in 1938 and used with increasing extensity since the 1940s.

From an environmental fate perspective, thermal degradation of the polymers produces monomeric units that will degrade in the troposphere to CO₂ (Atkinson and Atkinson, 1957), or halogenated propenes (Rizvi et al., 1995, Taves, 1968) (Figure 5.6), that degrade to produce long-lived HAAs (Mashino et al, 2000). Reaction processes are either proposed from this study, or are based upon those observed in the available literature (Mashino et al, 2000; Simon and Kaminsky, 1998; Mashino et al., 2000b; Rivzi et al., 1995; Arito and Soda, 1977; Hynes et al., 1999; Dubey et al., 1996; Teruel et al., 1999; Atkinson, 2000).
Figure 5.6  Proposed environmental reaction pathways for the thermal
degradation of fluoro- and chlorofluoro- polymers. Square boxes
represent environmentally transient species ($t_{1/2}<1$ year) and
curved boxes represent compounds with significant lifetimes
($t_{1/2}>10$ years) and important environmental impacts.

Both polymers primarily produce their corresponding monomers,
perhalopropenes, and cyclic perhalobutenes upon heating. In the presence of air
a smaller, although significant, concentration of perhaloacids ($x=0-2$, $y=1-3$, $z=1-2$, $n=1-13$, $m=1-7$) are produced, of which TFA and CDFA are the most
significant (1-10% w/w). Tropospheric oxidation of the perhalopropenes also
predominantly leads to, or is expected to lead to, the formation of TFA and CDFA. The thermal decomposition of the chlorofluoropolymers leads to the production of saturated chlorofluorocarbons (CFCs), which, upon migration to the stratosphere are known to cause the depletion of the ozone layer. HAAs and PHAs produced directly from the polymer are expected to be terrestrially deposited through wet and dry deposition (Tromp et al., 1995). Several PHAs, such as perfluorooctanoic acid (PFOA), have been observed in human blood samples since the 1960s (Taves, 1968). PFOA and Perfluorodecanoic acid (PFDA) have been shown to act as peroxisome proliferators and as inhibitors of gap junctional intercellular communication (Upham et al., 1998; Vanden Heuvel, 1996). PFOA uses are being phased out by the manufacturer due to environmental persistence and pervasiveness (Brown and Mayer, 2000). CFCs were produced through the decomposition of CPFTEs and may migrate to the stratosphere causing an impact on the ozone layer. The short chain perfluorinated alkanes and cycloalkanes produced have an estimated tropospheric half-life of greater than 2000 years and have been linked with causing effects on the global climate by acting as greenhouse gases (Ravishankara et al., 1993).
5.4 Conclusions

Thermal degradation is expected to be a primary mode of destruction for highly stable fluoropolymers. The thermolysis of Teflon® and Kel-F® resulted in the production of trifluoroacetate and chlorodifluoroacetate (7.7 and 9.5% w/w respectfully) which is proposed to contribute to the atmospheric burden of both haloacetic acids. Environmental modeling suggests that this may be a significant source of TFA in Toronto rainwater (~25 ng/L). Their thermal degradation also leads to the production of species that are known, or are suspected, to degrade to these acetates in the troposphere; both acetates are persistent environmental pollutants with no known degradation pathways. 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 and environmental impacts and are themselves being phased out of the U.S. market. The production of known greenhouse gases (fluorocarbons) and stratospheric ozone depleters (chlorofluorocarbons) have also been measured.
5.5 References


*Environ. Tox. Chem.* 18, 1053.


Environment Canada, 900 Bay St., Toronto, M7A 1N3.


   *Science.* 259, 194.


Chapter Six

Further Directions
6.1 Introduction

It is now widely accepted that the breakdown of certain HCFCs and HFCs in the troposphere lead to the production of TFA (Kanakidou, et al., 1995; Edney and Driscoll, 1992; Edney et al., 1991). The gas phase TFA is then predominately terrestrially deposited through rainfall events. However, the rainwater concentrations of TFA that are predicted from these sources are exceeded when compared to those that are currently being measured (Jordan and Frank, 1999). Chapter 3 of this thesis sheds partial light on possible production of TFA originating from trifluoromethylated pesticides. Although these studies have concentrated upon the production of TFA from such pesticides in surface waters, it is not difficult to envisage the possibility of extrapolating these results to photolysis of volatile trifluoromethyl analogues in the gas phase. In Chapter 5 results were presented which suggest that significant amounts of TFA could be produced either directly, or indirectly, through industrial and domestic use of fluorinated polymers in high temperature applications. Taken together these results may help explain the excess TFA observed in rainwater.

What is perhaps also interesting is the recent work conducted which suggests a pre-industrial source of TFA (Von Sydow et al., 2000). In this study 20-m firns were collected in East Antarctica. The firns were subdivided into dates covering the last century and subsequently analyzed for TFA. The results presented suggest TFA concentrations in the range 3 – 56 ng/L. As yet no source for the observed TFA has been put forward. In similar field studies, deep ocean measurements of TFA have been made (Christoph and Frank, 2000). As
in the case of ice cores, depth profiles within water can often be used to date water samples and hence the production of analytes. Samples in this study were taken at a depth of 4000m. Results indicate concentrations of TFA in the range of 180 – 200 ng/L. Harnisch et al. (2000), have recently recognized the presence of small fluorinated organic and inorganic compounds in igneous and metamorphic rocks (e.g. CF₄, CF₃Cl, CF₂Cl₂, CFCI₃, CHF₃, SF₆ and NF₃). Although TFA was never detected, it was suggested that the process responsible for the production of these compounds might also be linked to a geological source of TFA, hence explaining the deep ocean levels of TFA. However, it is noted that the compound SF₆ which extremely persistent in the environment, similar to TFA, is not observed in ocean deep waters and its origin is assumed to be almost solely anthropogenic (Ravishankara et al., 2000). If this is indeed the case, then it is difficult to see such geological processes being a major source of TFA in the oceans. Furthermore, the ocean measurements have yet to be repeated, and until so, must be viewed with some skepticism.

6.2 Hypothesis for Future Work

If TFA is indeed produced by pre-industrial processes, it is reasonable to eliminate the possibility of a major biological source on the bases that of the tens of millions of isolated organic compounds none have contained a trifluoromethyl group, and only a small handful bear one fluorine atom (Gribble, 1992). This would then lead to the postulation that the process is geological. However, studies of possible geological sources, such as that described in section 6.1,
and the production of fluorinated compounds through volcanic activity, have not yielded TFA, nor have they yielded a significant alternate precursor to TFA. There is yet another possibility, a pre-industrial anthropogenic source. In predicting this source several key factors must be taken into consideration. For example, in the unknown process there must be a reasonably large source of fluoride and elevated temperatures and/or pressures must be present in order to invoke C – F bond formation. There must be a large source of organic carbon present, and finally the anthropogenic practice would have to have been widely spread in order to obtain environmentally significant levels of TFA.

The burning of fossil fuels, e.g. coal, is one such activity that embodies all of these prerequisites. For example:

(a) Coal often has a high fluoride concentration, 20 – 500 ppm (Martinez-Tarazona et al., 1994).

(b) When burned domestically temperatures range from 300 to 500°C (Oztas and Yurum, 2000).

(c) It has a high organic carbon content which when burned has been shown to yield a variety of organic compounds such as small carboxylic acids (e.g. oxalic acid) (Bou-Radd et al., 2000; Lu et al., 2000).

(d) These organic compounds have not only been shown to be produced in the pyrolysis process but have also been shown to survive it.
It is postulated that the action of burning coal may produce significant levels of TFA. In order to test this hypothesis two distinct areas of experimentation could be conducted. The first is the direct measurement of the gases produced in the burning of coal by $^{19}$F nmr. This would allow the identification of any fluorinated species, including TFA, produced. Secondly, if TFA is indeed produced from coal burning then one might expect the spatial distribution of TFA in older waters to closely correlate with areas in which large coal burning activities were carried out. Evidence for such a correlation was made with sulphur dioxide emissions in Europe for the period 1880 – 1991, on the basis of present sulphur concentrations and depositions within soils (Mylona, 1996).

6.3 Thesis Conclusions

$^{19}$F nmr has been shown to be a viable technique for the study of fluorinated acids at environmentally significant concentrations within aqueous rain water samples. Particular emphasis was placed upon the TFA and CDFA as analytes, as these have been shown to be increasing in rainwaters. Key parameters for the method of analysis were fully investigated and optimized. For a given analyte it was shown that in order to obtain maximum sensitivity the choice of solvent was of importance, and that the choice of this solvent was analyte specific. The method was applied to rain water for TFA and the results were compared well with those obtained by an excepted GC-MS method.
The total source of the TFA levels which are being observed in rain and surface waters are currently unknown. It has been shown herein that a potentially large source of TFA to the surface waters surrounding the Great Lakes is through the photochemical degradation of the Lampricide, TFM. A clear mechanistic understanding of this transformation was established. Key to the production of the TFA is a trifluoromethylquinone. It is hypothesized that an inhibitory of a trifluoromethylated aromatic pesticide to form such a quinone will result in the ultimate fate of the fluorine being as fluoride, conversely if the quinone is formed then TFA will also be produced.

Fluorinated polymers are used with increasing commonality, both in the workplace and domestically. One of the main applications for such polymers is in areas of high thermal stress. The research which has been conducted herein (Chapter 5) has shown that upon thermal degradation many yield fluoro- acids, including TFA, and in the presence of chlorine a sweep of chlorofluoro- acids are formed. Furthermore, molecules that are known to degrade to haloacetic acids in the troposphere are also produced. This allows for the long-range transport of TFA to rural and remote areas.

Taken together, the photodegradation of trifluoromethyl pesticides and the thermolysis of fluoropolymers helps to explain the high levels of TFA which are seen in Canadian rain and surface waters.

The microbial degradation of the chloroacetic acids within pond waters has been investigated. Results indicate that trichloroacetic acid is the most persistent of these acids and is therefore likely to be the most pervasive of the
three. TFA also applied to the same pond degradation studies. No degradation was observed for a period of one year. This indicated that TFA is an extremely long-lived environmental pollutant. As there are no known degradation processes continued production of TFA is expected to cause an accumulation of the compound within bodies of water leading to levels which may show toxic effects.
6.4 References


