

## Altitudinal transect of atmospheric fluorinated organic compounds and pesticides in western Canada

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### Introduction

Fluorinated organic compounds constitute a diverse class of compounds used in a variety of consumer and industrial applications<sup>1,2</sup>. They are used as refrigerants, agrochemicals, chemical catalysts/reagents and as surfactants<sup>2</sup>. They also have medicinal applications which include treatment of obesity and clinical depression<sup>2</sup>. Although fluorinated organic compounds have been manufactured for over 50 years, there are no published reports on their total production volumes.

Recent interest has been on the perfluorinated class of surfactants. Perfluorooctanesulfonate (PFOS,  $C_8F_{17}SO_3^-$ ) and perfluorooctanoate (PFOA,  $C_7F_{15}COO^-$ ) are two of the perfluorinated surfactants that have received the most attention. Much of the concern surrounds the ubiquitous presence of both compounds in the environment. PFOS and PFOA have been detected in human serum<sup>3</sup>, freshwater and marine biota<sup>4,5</sup>, surface water<sup>6,7</sup>, and rainwater<sup>8</sup>. The stability that makes fluorinated surfactants so desirable in many applications appears to preclude any degradation or metabolism, and contributes to the global bioaccumulation and persistence of PFOS and PFOA and other perfluorinated carboxylic acids (PFCAs). Based on their physical chemical properties, it is unlikely that PFOS or PFCAs are atmospherically transported in their vapor phase due to low vapor pressures. It has been hypothesized that these chemicals are atmospherically transported to remote areas as volatile precursors and are then deposited<sup>4</sup>.

The objectives of the current research are to measure the atmospheric concentrations of fluorotelomer alcohols (FTOHs) which are volatile precursors of PFCAs, as well as N-ethyl perfluorooctanesulfonamide (N-EtPFOSA) and perfluorooctanesulfonamide (PFOSA), volatile precursors of PFOS in mountains and to test whether altitude has an effect on amount of the chemical in the atmosphere. Air concentrations of endosulfan and hexachlorocyclo-hexanes (HCHs) were examined concurrently.

### Materials and Methods

**Preparation of Passive Air Samplers.** XAD resin was precleaned using a Dionex accelerated solvent extraction system with successive washes of methanol, ethylacetate, and dichloromethane. 60 mL of this cleaned resin in a methanol slurry was added to stainless steel mesh tubes and sandwiched between glass wool plugs. After filling and sealing the ends with crimp style caps the prepared XAD filled tubes were allowed to soak overnight in DCM followed by an overnight soak in methanol. After removal of methanol, the tubes were allowed to dry overnight under UHP nitrogen. Tubes were wrapped in baked aluminum foil and then double packed in sealable plastic bags.

**Deployment of Passive Air Samplers.** Air sampler tubes were deployed in a galvanized steel sampler housing described by Wania et al.<sup>9</sup> on an altitudinal transect from 800 m to 2740 m in the Canadian Rocky and Purcell mountains for a period of five months between late March and late August 2004. Samplers were fastened to wooden posts 2-3 meters above the ground. Retrieved sampler tubes were wrapped in baked aluminum foil and double wrapped in plastic sealable bags, transported to the laboratory and frozen until extraction.

**Extraction of Passive Air Samples.** XAD resin samples were spiked with mass labeled 8:2 and 10:2 FTOH, N-EtPFOSA, endosulfan and  $\alpha$ -HCH and added to a 100 mL stainless steel tube filled with ethylacetate. This was allowed to soak for 15 minutes and then eluted with a further 200 mL of ethylacetate. Samples were dried with hydromatrix and rotovapped using low heat to 1 mL. This was transferred to polypropylene tubes and evaporated to

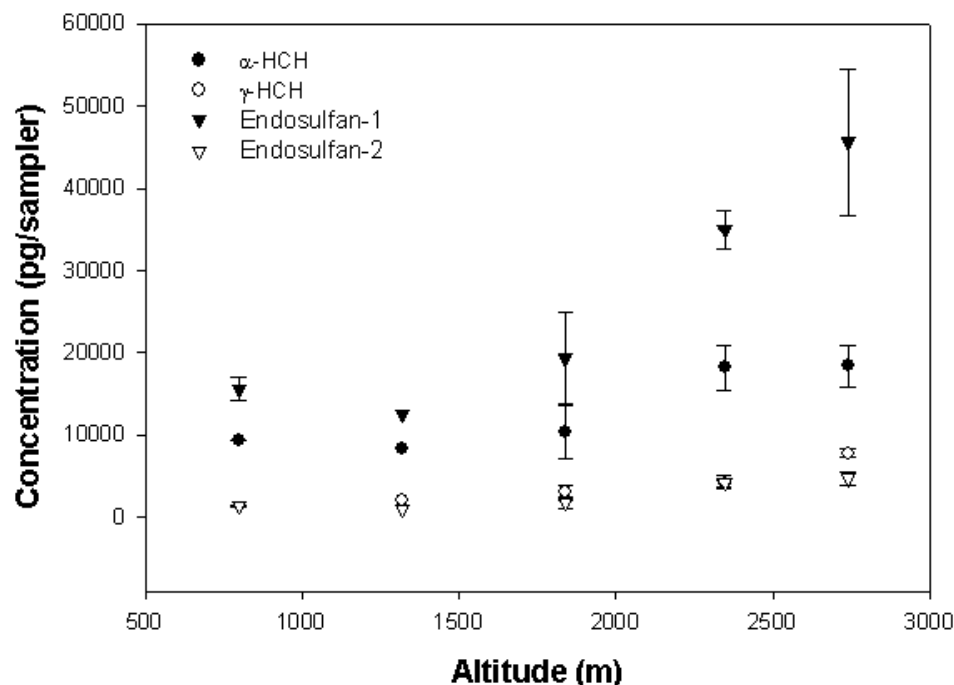
50  $\mu$ L under UHP nitrogen and stored in glass GC vials.

**GC/MS Analysis of Air Samples.** 2  $\mu$ L of sample was injected on a Hewlett Packard GC/MS equipped with a J&W 60 m DB-5 column. Positive chemical ionization was used for analysis of fluorinated compounds while negative chemical ionization was used for pesticide analysis. Ions used for quantitation and confirmation (when available) were: 8:2 FTOH ( $m/z$  427, 465); mass labeled 8:2 FTOH ( $m/z$  431, 469); 10:2 FTOC ( $m/z$  527, 565); mass labeled 10:2 FTOH ( $m/z$  531, 565); N-EtPFOSA ( $m/z$  528); mass labeled N-EtPFOSA ( $m/z$  533); PFOSA ( $m/z$  500);  $\alpha$ -HCH ( $m/z$  253, 259); d- $\alpha$ -HCH ( $m/z$  255, 261);  $\gamma$ -HCH ( $m/z$  253, 259); endosulfan ( $m/z$  404, 406) and d-endosulfan ( $m/z$  408, 410).

**Quality Assurance.** All compounds were normalized to the corresponding mass labeled surrogate compound responses. PFOSA was normalized to deuterated NetPFOSA and  $\gamma$ HCH normalized to deuterated  $\alpha$ -HCH responses but not blank subtracted. Method detection limits (MDLs, pg/sampler) were: 8:2 FTOH (653); 10:2 FTOH (64); N-EtPFOSA (16); PFOSA (13); endosulfan 1 and 2 (5403 and 342). Neither  $\alpha$ - nor  $\gamma$ -HCH were detected in blanks.

## Results and Discussion

**Pesticides in Air.** Pesticides were quantified in the air samples in order to test the performance of our method. HCHs and endosulfan have been monitored in mountain environments in the past<sup>10</sup>. Our results agree with those found in previous studies, specifically we also observed an increase in the air concentrations of certain volatile pesticides with altitude (see Figure 1). This is attributed to their spring time release into the atmosphere from the melting snowpack. As snowpack depth is strongly correlated with altitude in this region, a larger deposition, and therefore also higher re-volatilisation, of pesticides per unit area is expected at higher altitude.



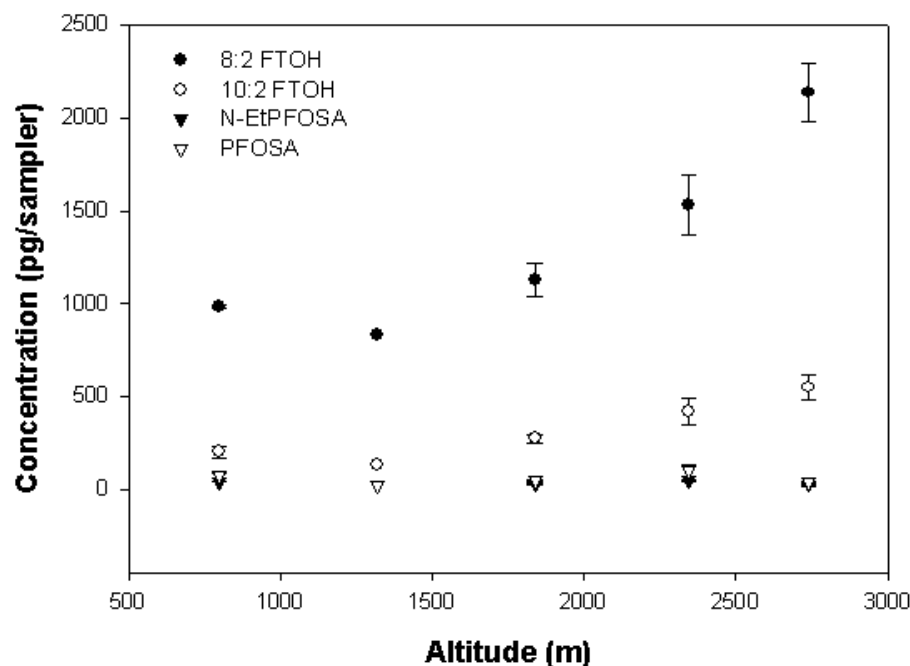
**Figure 1:** Concentrations of Pesticides in Mountain Air as a Function of Altitude

**Fluorinated Organic Compounds in Air.** FTOHs are characterized by relatively high volatility (254 Pa for 8:2 FTOH and 144 Pa for 10:2 FTOH)<sup>11</sup>. It was previously unclear whether these compounds would be deposited in the snowpack, considering their relatively high vapor pressures as compared with pesticides monitored in this experiment. Our results show that there is an increase in the amount of FTOHs in air with increasing altitude likely indicating snow deposition (see Figure 2). Further studies are required to further investigate whether this observation is truly the

result of snow deposition and release from the melting snowpack, or the result of the chemicals reaching equilibrium in the sampler due to their relatively high volatility.

A similar trend was observed for PFOSA and N-EtPFOSA except for the highest elevation where amounts are reduced. We are not aware of any study reporting detection of PFOSA in air. As such we are not certain whether it is present in the air or if it is degraded N-EtPFOSA. We are also not certain whether the decrease in amount at the highest elevation is due to lower vapor pressures for these compounds or if it is a locational difference as samplers at 800-2345m were on one mountain while the sampler at 2740 m was in a different range further east. This should be

further investigated. How these trends will be correlated with PFCA and PFOS concentrations in air and biota is currently unknown.



**Figure 2:** Concentration of FOCs in Mountain Air as a function of Altitude.

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