

## Environmental Profile and Global Assessment of Trifluoroacetate (TFA).

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### Introduction

Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) were identified as suitable alternatives to CFCs. Among this class of products, a few of them are expected to form trifluoroacetyl halides that will dissolve in the atmosphere to give trifluoroacetate (TFA) salts. Environmental trifluoroacetate can also be produced during the oxidation of others organofluorine compounds released to the atmosphere by human activities such as halothane and isoflurane anaesthetics

As the quantities of fluorocarbons involved at global scale could become relevant a risk assessment process has been undertaken and toxicology, ecotoxicology, environmental fate and potential environmental loads have been studied extensively.

The Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) was formed in 1989 by several chemical companies with the aim to generate the information necessary to evaluate environmental acceptability of a range of fluorocarbons and the studies were co-ordinated with those of government agencies. These activities lead to the preparation of the report AFEAS (1997) "Trifluoroacetic Acid Environmental Risk Assessment" that is the source of information for the present paper and will be soon available in the open literature (1).

### Physico-chemical properties

$\text{CF}_3\text{COOH}$  has a molecular weight of 114, it is a strong organic acid with  $\text{pK}_a$  of 0.23 and it is miscible with water (solubility over 10000 g/l). The vapour pressure is 105.7 hPa at 20°C, the partition coefficient n-octanol/water (log) -0.2.

### Environmental distribution

According to the above reported data, the main compartment at risk is water,  $\text{pK}_a$  shows that the compound is completely dissociated at environmental pH and that TFA behaves as a strong inorganic acid. Small quantities in solution can influence the pH of unbuffered

solutions. Despite its high vapour pressure one cannot expect air to be a compartment at risk due to the extremely high solubility and dissociation constant. However in relatively dry environment volatility and/or presence in air can occur and long range transport could take place. No soil/sediment sorption can be expected, therefore leaching can occur, due to high solubility, anionic form in natural conditions and low K<sub>oc</sub>.

### **Degradation**

Hydrolysis. No degradation was observed under extreme conditions: 95°C, pH 12 for 6 weeks. Photolysis. Under three pH conditions (acidic, neutral, alkaline) no absorption was observed in the UV-Vis area (250-750 nm), therefore TFA cannot be susceptible to photochemical degradation. Reactivity. TFA is resistant to both oxidative and reductive degradation. Biodegradation. The compound is not biodegraded in the prolonged closed bottle test (80 days). Activated sludge tests demonstrate no degradation in a 60 days period. There have been two reports of TFA degradation under anaerobic conditions, however the experimenters and others were unable to reproduce it in subsequent studies.

### **Bioaccumulation in animals and plants**

Potential for bioaccumulation in animals is irrelevant due to the extremely low log K<sub>ow</sub> (-0.2). TFA does not accumulate in lower aquatic-life forms such as bacteria, small invertebrates and some aquatic plants. TFA can accumulate in plants via roots uptake of water. In terrestrial plants some bioaccumulation was seen and the level of concentration is due to transpiration water loss. When transferred to clean hydroponic media, over 80% of the TFA in leaves was found to be water extractable, suggesting no significant metabolism.

### **Ecotoxicology**

Effect of TFA on Activated Sludge. TFA had no discernible effect on the performance of the sludge for the biodegradation of organic carbon. Effect of TFA on metabolism of microbial communities. TFA at concentrations several orders of magnitude higher than those anticipated in the environments did not impact acetate mineralization to carbon dioxide. No effect on growth either on N<sub>2</sub> fixation or with ammonium ion as nitrogen source was noted even at high concentrations. Aquatic toxicity. In acute toxicity tests no effects of NaTFA on Daphnia magna and Brachydanio rerio were found at a concentration of 1200 mg/l. A 7-day study with Lemna gibba revealed a NOEC of 300 mg/l. Based on the results of five toxicity tests with Selenastrum capricornutum a NOEC of 0.12 mg/l was found. However, algal toxicity tests with NaTFA and several others species of algae resulted in EC<sub>50</sub> values which were all higher than 100 mg/l. In a study with mesocosm streams, the long-term exposure to concentration of 31-32 µg/l had no effect on the primary productivity of the diatom dominated algal flora., no alterations of the algal species composition were observed. Terrestrial plants. Application of NaTFA at 1.000 mg/l to seeds of sunflower, cabbage, lettuce, tomato, mungbean, soybean, wheat, corn oats and rice did not affect germination. Foliar application of a solution of 100 mg/l to field grown plants did not affect growth of sunflower, soya, wheat, maize, oilseed rape, rice and

plantain. In hydroponic systems containing NaTFA, no effects were seen on plantain at 32 mg/l, on Triticum and soya at 1 mg/l or on wheat at 10 mg/l.

#### **Mammalian toxicity**

TFA is not metabolised in mammalian systems to any great extent. The half-life of TFA in humans is 16 hours. In one study, 2 of 5 mice died from a dose of 150 mg/kg of HTFA, no deaths were seen when mice were given an oral dose of 5.000 g/Kg of NaTFA. In an acute inhalation toxicity study the LC 50 for mice was 13.5 mg/l (2,90 ppm) and for rats it was 10 mg/l (2,14 ppm). This would classify TFA as having low inhalation toxicity. The irritation threshold for humans was 54 ppm. It is a severe irritant to the skin. Concentrations as low as 2% were moderate skin irritants. Repeat administration of aqueous solutions have shown that TFA can cause increased liver weight and induction of peroxisomes. Relative to the doses (0.5% in diet or 150 mg/kg/day by gavage) the effects are mild. In a series of Ames assays, TFA was reported to be non-mutagenetic. Although TFA was shown to accumulate in amniotic fluid following exposure of pregnant animals to high levels of halothane (1,200 ppm), no foetal effects were seen.

#### **Global detection and environmental loads**

The potential flux of TFA from all known actual sources has been estimated to be currently 2800 t/y worldwide, which would be equivalent to less than 2 ng/l in the rainfall of central Germany. Surprisingly, TFA has been found there and in the rest of the world at far higher concentrations. Rainwater in Europe contains up to 100 ng/l, the River Rhine contains up to nearly 600 ng/l, while 40,000 ng/l has been found in lake water in the United States and 200-250 ng/l in Pacific and Atlantic seawater. Similar concentrations have been observed in contemporary water and air samples from Nevada, USA, Canada, Australia and South Africa, suggesting that there is one or more large unknown sources of environmental trifluoroacetate

#### **Modelling future emissions**

The decomposition mechanisms of CFCs depend on physical and chemical properties and processes that are relatively well understood so that it is possible to calculate accurately the future atmospheric concentrations of precursors to trifluoroacetate, given a particular set of scenarios for emissions. In addition these models take account of the geographical distributions of the concentration of hydroxyl radicals with which the parent compounds react, of the emissions of the parent compounds and of the rainfall that scavenges trifluoroacetic acid from the atmosphere. Starting from a given scenario it has been calculated that the tropical concentration would be up to 2  $\mu\text{mol/m}^3$  and that this would be equivalent to 100 ng/l of rainwater. Over Europe the deposition rate in 2020 would be about 0.5  $\mu\text{mol/m}^3$  and, over the USA, levels would be up to double this. These values are of the same order of magnitude as those calculated by other authors, on the basis of a scenario from the USEPA, and the latitudinal variation (up to a factor of 40) and longitudinal variation (a factor of 3) are also similar. In the year 2020, the modelled decomposition flux of HFC-134a was calculated to be 115 kT/yr, with a further 20 kT/yr

each of HCFCs 123 and 124 and the implied global deposition of trifluoroacetic acid then would be 155 kT/yr. This quantity, and the rainwater concentrations derived from it, are used as standards for the risk assessment, the predicted environmental concentration has been set at 0.1 µg/l

### Risk assessment

The environmental risk from TFA as degradation product of CFCs substitutes can be deduced from the value of the ratio of exposure to effect or of Predicted environmental Concentrations to Predicted No Effect Concentrations (PEC/PNEC).

In rain water it has been calculated an average concentration of 0.1 µg/l as global PEC by year 2020. An important question remains concerning the origin of the large present levels of TFA which have been measured and which cannot be explained by the known sources. These levels, in the range of 0.1 µg/l for water and 20 ng/l for air, are roughly 60 times what would come from known sources today and more or less equal to what is anticipated in 25 years from now.

Given the high thermodynamical stability of the CF<sub>3</sub> group, no abiotic mineralisation process neither biodegradation has been observed or is forecast. The physico-chemical properties of TFA allow to predict an absence of bioaccumulation in animals. In terrestrial plants accumulation can take place but is transient and effects on vegetation can be observed only in experiments using non environmentally relevant concentrations.

TFA has shown to be non effective on several types of metabolism related to basic biogeochemical cycles. Acute tests on fish, daphnia and algae show no effects at large concentrations (up to 1 g/l TFA). This is reinforced by toxicological data on mammals. The NOEC for the standard algal species Selenastrum capricornutum is around 0.10 mg/l (as TFA). To see if this sensitivity was general among algae, 10 other species belonging to 4 different classes have been tested resulting in NOEC > 100 mg/l. It is proposed to use as a PNEC<sub>aqua</sub> (the NOEC for Selenastrum) as a worst case, without any further safety factor, PNEC<sub>aqua</sub> = 0.1 mg/l.

Research on effects on higher plants, as they could be exposed to TFA in rain water through leaves and TFA in pore water through roots, gave threshold for effects on wheat and soya around 5 mg/l with a NOEC = 1 mg/l. Other studies show that nitrogen fixation is not affected up to 1 mg/kg soil. Therefore, a conservative figure could be PNEC<sub>soil</sub> = 0.1 mg/l

In conclusion, no noticeable risk can be anticipated from TFA produced by atmospheric degradation of HCFCs and HFCs, as there is a 1000-fold difference between PNEC and expected PECs from present and future production of these chemicals.

### References

AFEAS, (*Report*) Trifluoroacetic Acid Environmental Risk Assessment. The Alternative Fluorocarbons Environmental Acceptability Study (AFEAS). Washington D.C. USA, 1997, 61pp.