Kopinke, F.-D., **Frenzel, L.-M.** (2021):
Comment on “Thermal stability and decomposition of perfluoroalkyl substances on spent granular activated carbon”
Environ. Sci. Technol. Lett. **8** (4), 362 - 363

http://doi.org/10.1021/acs.estlett.0c00742

Comment on the article „Thermal stability and decomposition of perfluoroalkyl substances on spent granular activated carbon“ published by Xiao et al. in Environmental Science & Technology Letters (2020)

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The study of Xiao et al. [1] deals with thermal stability of perfluoroalkyl substances (PFAS), in particular with the decomposition pathways of PFAS during thermal reactivation of spent granular activated carbon (GAC). The study gives valuable insights into the behavior of perfluorinated carboxylic acids (PFCAs) and sulfonic acids (PFSAs). They show clearly that – contradictory to the common belief – PFCAs start to be decomposed at low temperatures such as 200°C, whereas PFSAs are much more stable (decomposition at ≥400°C). It is worth mentioning that this rank in thermal stability does not correlate with the strength (as bond dissociation energy at 298 K, BDE) of the weakest bonds in the two substrate groups. The carbon-carbon bond in perfluorooctanoic acid (PFOA) is significantly stronger than the carbon-sulfur bond in perfluorooctane sulfonic acid: $\mathrm{BDE}_{\mathrm{C7F15\text{-}COOH}}$ = 88.0 kcal/mol vs. $\mathrm{BDE}_{\mathrm{C8F17\text{-}SO3H}}$ = 62.3 kcal/mol [2]. In contrast to the highly relevant concern of this study, we see some significant deficits and misinterpretations which need clarification.

The uncertainties start with the *speciation* of the investigated substrates. Speciation, i.e. the explicit description of the chemical species under investigation, is an essential point when comparing stability of compounds. The authors specify their substrates as acids throughout the entire article. This may hold for the carboxylic acids in the pure state. However, loading of PFCAs on GAC from pH neutral water will hardly end up in protonated species. PFCAs and even more the PFSAs are strong acids (e.g. $\mathrm{p}K_\mathrm{A}$ = 0-1 and -3.3 for PFOA and PFOS, respectively [3-6]) which do exist in aqueous solution as well as in the adsorbed state as anions. One can expect that protonated species and salts behave differently, with respect to volatility and thermal stability. Looking more deeply in the SI part of the article [1], the reader learns that all PFCAs were provided as (protonated) acids whereas all PFSAs were provided as potassium salts (Table S1). Does it mean that the various thermal treatment experiments were conducted with different initial speciation of the two compound classes, PFCAs and PFSAs? This would mean that the thermal stability of acids has been compared with that of salts - a feature that should not be denied to the reader. In our opinion, it would be more adequate to compare the thermal behavior of similar species, i.e. of PFAS salts. In addition, the question arises why investigating *free acids* when they do not appear in any environmental compartment or adsorption system?

Furthermore, it is very likely that thermodesorption behavior of adsorbates depends on their initial loading. This is an essential information. Such data are missing for all experiments with PFAS on GAC.

Reliable analytical determination of the target compounds is a basic requirement for any quantitative study. Figure 1 presents recoveries of 11 PFAS obtained by extraction of pre-spiked GAC samples with methanol under various extraction conditions. The extraction with MeOH + 100 mM NaOH yields recoveries of 132% to 261% for all PFCAs. The narrow scattering ranges of about ±5% point to well reproducible results. These ‚over-recoveries‘ were not discussed nor explained in the article. If there is no reasonable explanation, the reader can hardly accept all the other recoveries <100%. PFAS recoveries, however, are among the key information for most of the presented experiments.

It is a general shortcoming of this study that thermal treatments of PFAS samples are a superposition of volatilization and decomposition, in many cases. This overlap is denoted by the authors with the term ‚destabilization‘. It is clear that the nature of the two processes – a physical and a chemical one - is quite different. Nevertheless, the authors describe the result of this overlap by means of first-order kinetics (no data shown) resulting in first-order rate constants k. These rate constants were than correlated with temperature T over the range 100°C to 150°C for PFOA ‚destabilization‘ in terms of an Eyering-like plot, i.e. $\ln(k/T)$ vs. $1/T$ (Figure 2e). It is clear that these data reflect volatilization rates. Should volatilization be described by a transition-state based theory resulting in the Eyering equation? – definitely not. Surprisingly, a nitrogen flow ‚destabilizes‘ PFOA significantly more than O_2 or CO_2. In this point, Figures 2e and 2d are contradictory. It must be mentioned that the ordinates in Figures 2e and 2f are mathematically incorrect.

The authors state that „PFAS exhibited the following order of thermal stability: PFSAs >> ... PFOA > PFBA ...“ (p. 346 in [1]). However, there are no data which prove that

PFOA is thermally more stable than PFBA. Rather, the authors mix thermal stability with volatility.

The authors applied a thermal desorption-pyrolysis system (CDS Analytical) connected to a CG-MS device for identification of PFOA decomposition products. In this technique, the sample was heated up with a so-called pyroprobe heater to 200°C or 300°C for 30 s. Then the released products were collected at the GC column entrance and analyzed. The interface between the pyroprobe heater and the GC injector was held at 300 or 350°C, respectively (p. S5 in [1]). It is important to know, what the interface is. It is a heated chamber wherein the pyroprobe heater is introduced before controlled heating of the sample is started. This means, the sample (and the released products) may be heated or come into contact with surfaces having higher temperatures than the nominal treatment temperature, e.g. 300°C instead of 200°C or 350°C instead of 300°C. This makes it difficult to assign the result of pyrolysis to a defined temperature. As an example, how can one trust a statement that the thermal decomposition of PFOA does start at a temperature as low as 200°C, if the (evaporating) substance passed a zone with about 300°C?

The chemical evaluation of the results is summarized in Figure 4, which presents thermal decomposition pathways of PFOA in an inert atmosphere, based on the TD-Pyr-GC-MS product data. In the corresponding paragraph (p. 347 in [1]) it is stated: „The single sharp peak (m/z = 395.1) observed at 200°C and a GC retention time of 5.172 min corresponds to the radical of 2H polyfluorocarboxylic acid (2HPFOA) ... „. Do the authors actually interpreat GC-detected products in terms of radicals? It is very clear that radicals cannot be detected by GC analysis. A careful inspection of the presented chromatograms and related mass spectra makes it likely that the first (and only) product peak refers to perfluoroheptene (C_7F_{14}) and the second peak refers to the substrate PFOA. The presented mass spectra fit very well to library spectra of these substances. The broadness of the first peak at about 2 min retention time may be due to the incomplete focussing of the highly volatile compound at the entrance of the GC column. Perfluoroheptene is a plausible primary and volatile decomposition product of PFOA. However, it does not appear in the proposed reaction scheme (Figure 4).

A closer inspection of Figure 4 reveals, that radicals, diradicals and carbenes (CF_2) play major roles in the proposed reaction scheme. Only CO_2 and C_2F_4 are detectable closed-shell products. The reader gets the impression that the authors interpreat the fragmentation pattern in the observed mass spectra rather than the thermal decomposition products. This impression is supported by the coincidence of given *m/z* values in the mass spectra (Figure 3) and in the reaction scheme (Figure 4c). However, the fragmentation pattern is caused by electron-impact ionization rather than by thermal activation. Briely, the reaction scheme in Figure 4 appears to us highly misleading.

Finally, it would be nice to compare the thermal stabilities of PFAS in the pure state and as adsorbates on GAC. Unfortunately, the study does not present such a comparison.

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