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Mechanism of Perfluorooctanoic acid (PFOA) degradation in aqueous solution under ionization radiation

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PFOA

•Global Widely used as an industrial surfactant in chemical processing and a material feedstock since it was first manufactured in 1940s

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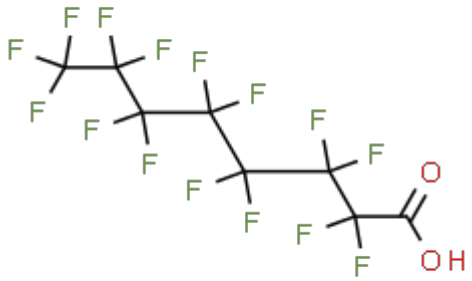
•Extremely persistent in the environment



•Globally detected in soil, water, wild life and humans.

•Carcinogenic and direct adverse effect on human health.

Water radiolysis

G - Value (molecules/100 eV) of water radiolysis:

$H_2O \longrightarrow 2.7e_{aq}^-, 0.6\ H, 2.8OH, 0.45H_2, 0.7\ H_2O_2, 2.7H^+$

Aerated aqueous solution with N_2O at pH 7 : OH

Solution with Ar and t-butanol at pH7 : e_{aq}^-

Solution with Ar and t-butanol at pH2: H atom

PFOA degradation in aqueous

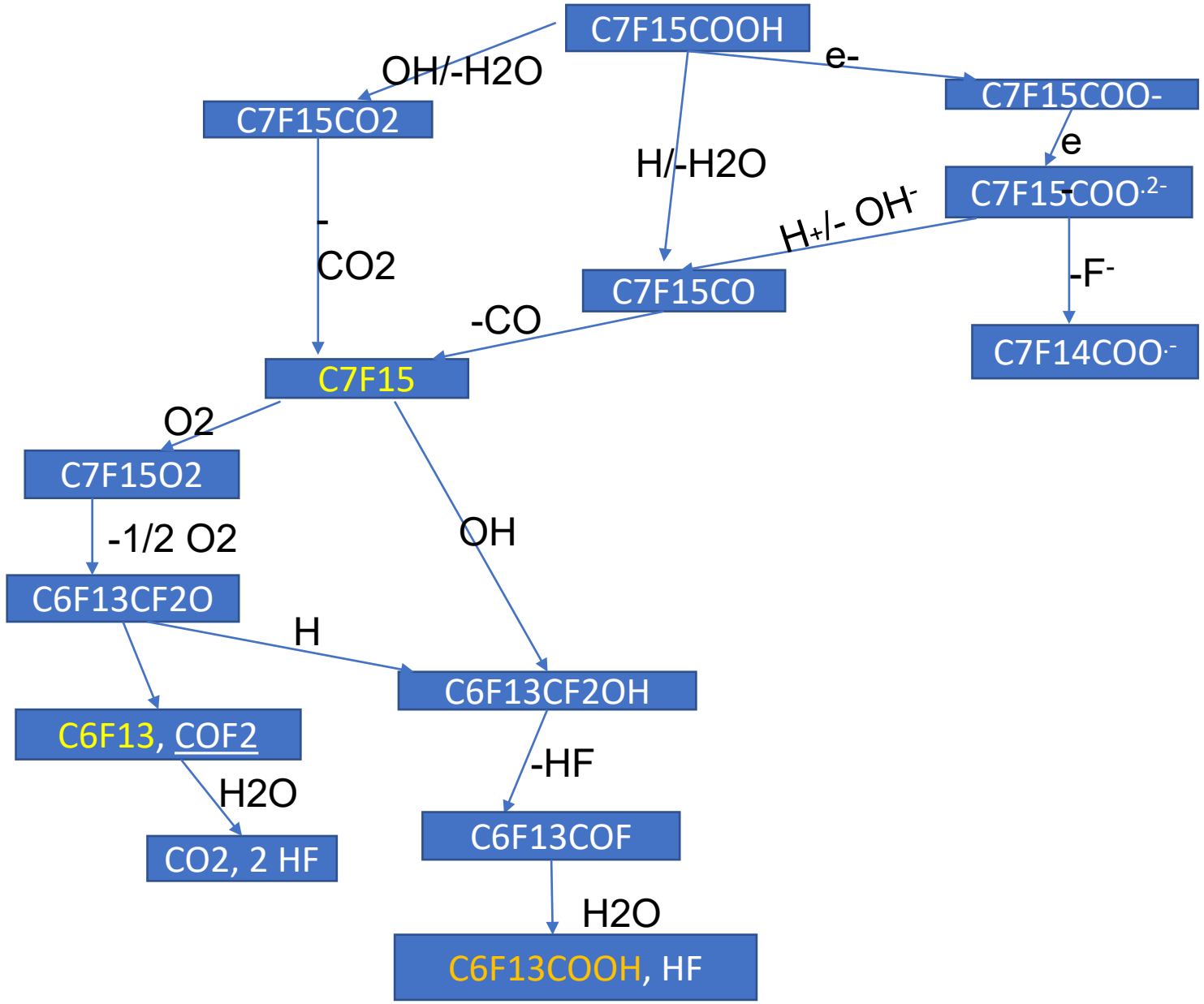
Kinetic programme

75 reactions

35 species

1 atm., RT, aqueous solution

Main degradation products were taken into consideration, F^-



PFOA degradation pathway

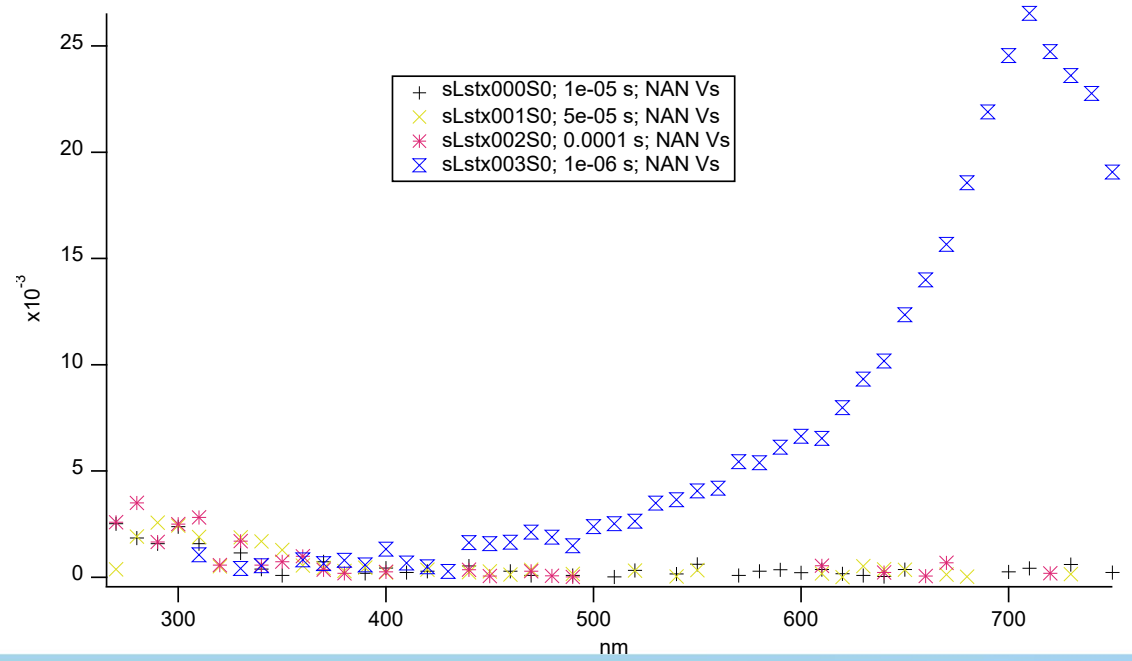
Table 2. Reaction rate constant with PFOA

Radicals	$[M^{-1}S^{-1}]$
OH	$3.0 * 10^7$ $\leq 1.0 * 10^5$ $1.0 * 10^3$
H	$9.0 * 10^7$ $(1.0 * 10^5)$
Hydrated electrons	$(1.3\text{-}5.1) * 10^7$ $1.0 * 10^7$

Anions influence

PFOA reaction with NO_3^- and CO_3^{2-}

PFOA: 0.518mg/l; NO_3^-: 15,2mg/L, Ar bubbling,
hydrated electron decay was observed at 710 nm after 1 µs pulse radiolysis.



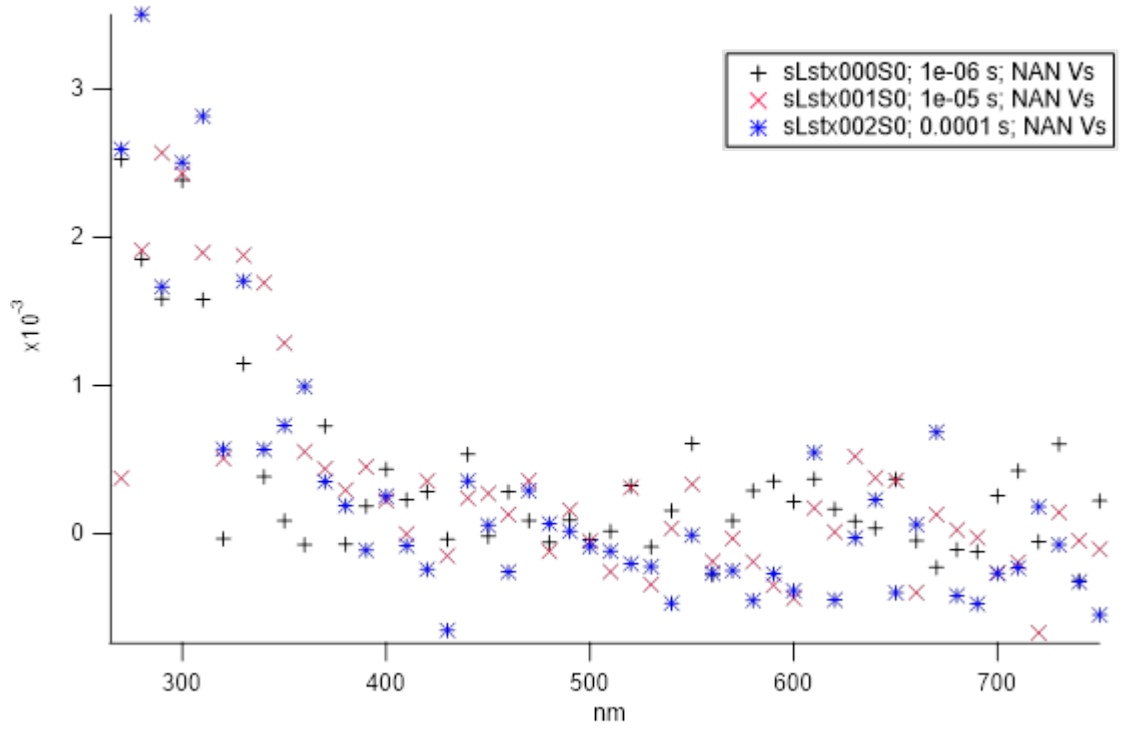
$e_{aq}^- + NO_3^- \rightarrow NO_3^{2-}$, $k_8 = (9.2\text{-}9.9) * 10^9\ M^{-1}.s^{-1}$

e_{aq}^- + PFOA → products, $k_9 = (1.3\text{-}7.0) * 10^7\ M^{-1}.s^{-1}$

PFOA reaction with CO_3^{2-}

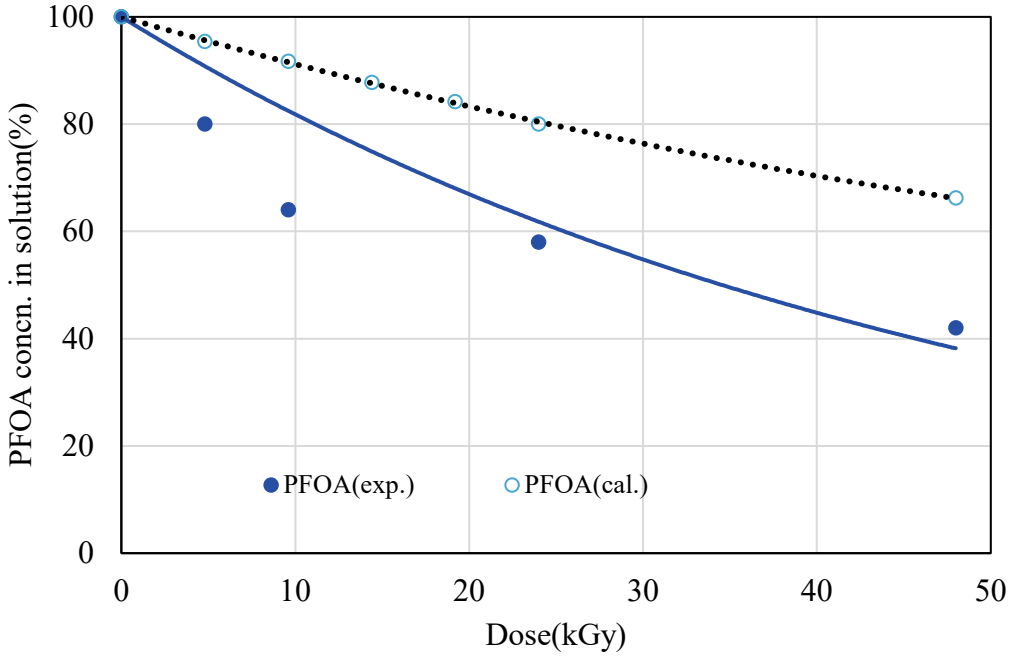
PFOA:0.518mg/l; CO_3^{2-}:0.75mM, N2O bubbling,

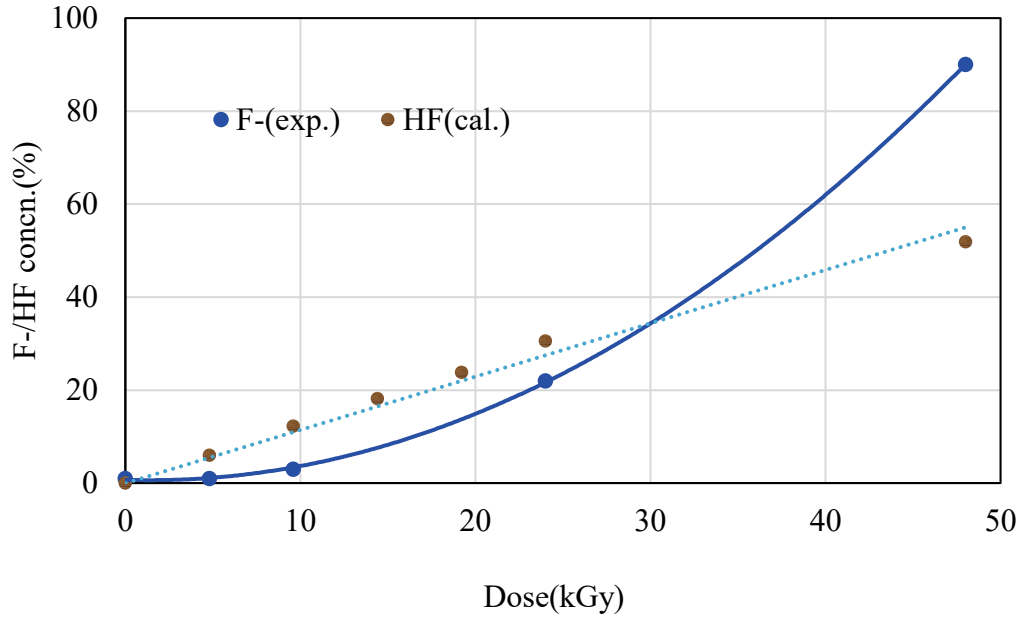
$CO_3^{\cdot-}$ radical formation was observed at 600 nm after pulse radiolysis



$OH + CO_3^{2-} \rightarrow CO_3^{\cdot-} + OH^-$, $k_4 = 4.0 * 10^8$ $M^{-1}.s^{-1}$

$OH + PFOA \rightarrow$ products, $k_5 \leq 3.7 * 10^7$ $M^{-1}.s^{-1}$

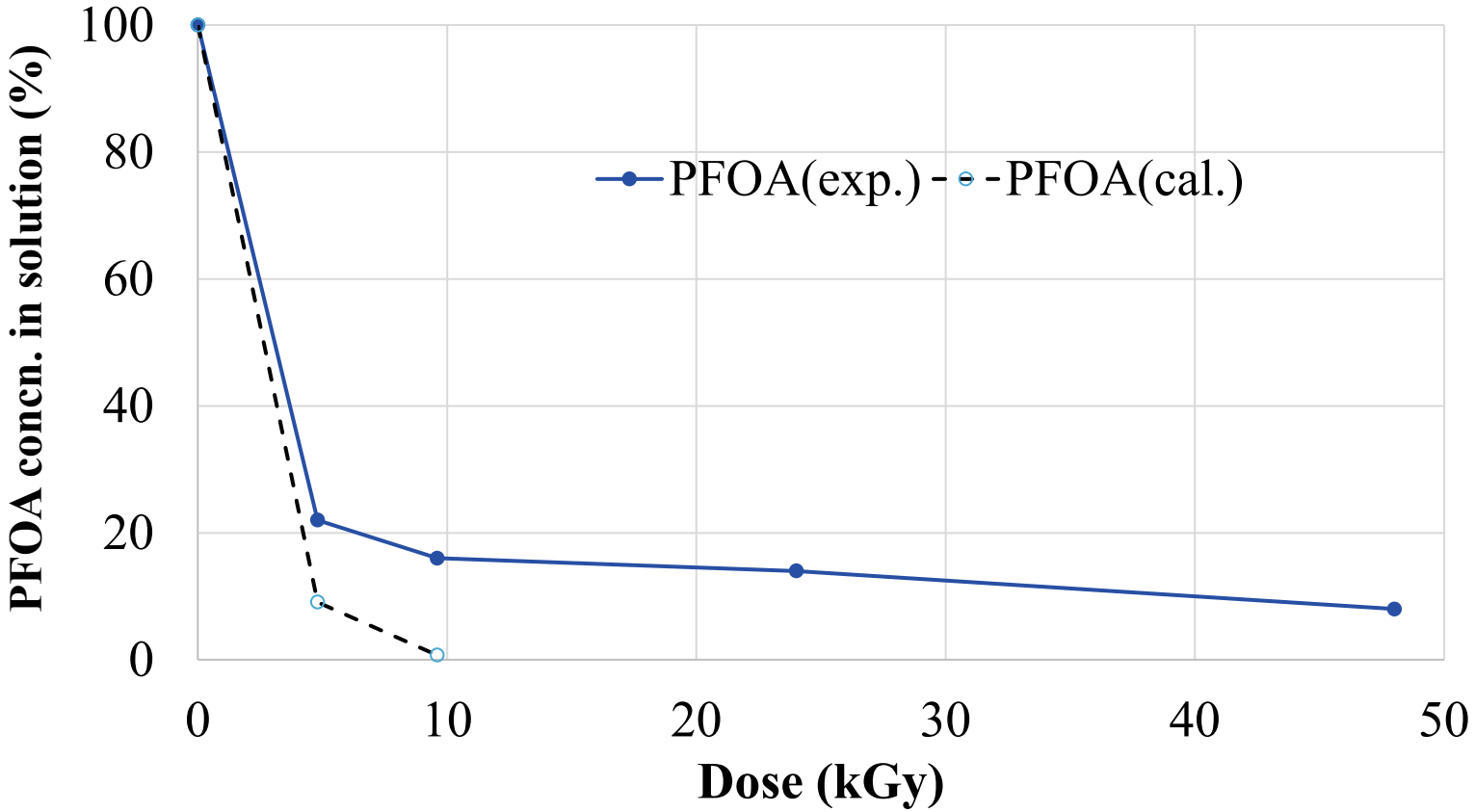




PFOA decomposition and F-/HF formation in aerated solution of pH 7.0 under gamma-ray irradiation (init. concn. = 1 mg/L)

Species contribution to PFOA decomposition

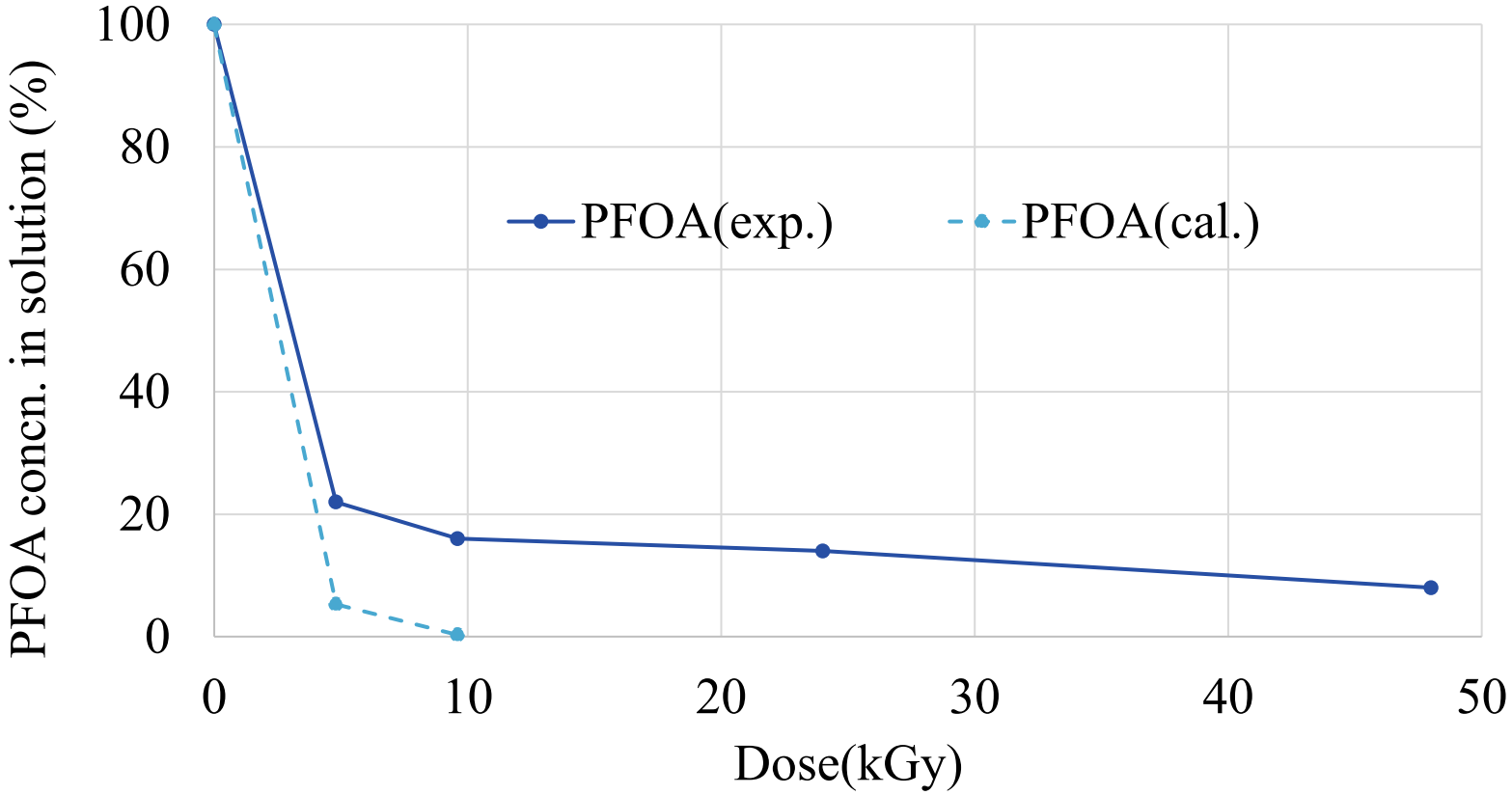
OH: 78.5%; e-: 21.4%; H: 0.1%



1 mg/L PFOA decomposition in Ar saturated solution of pH 2 with 20 mg/L of t-butanol under gamma irradiation.

Species contribution to PFOA decomposition

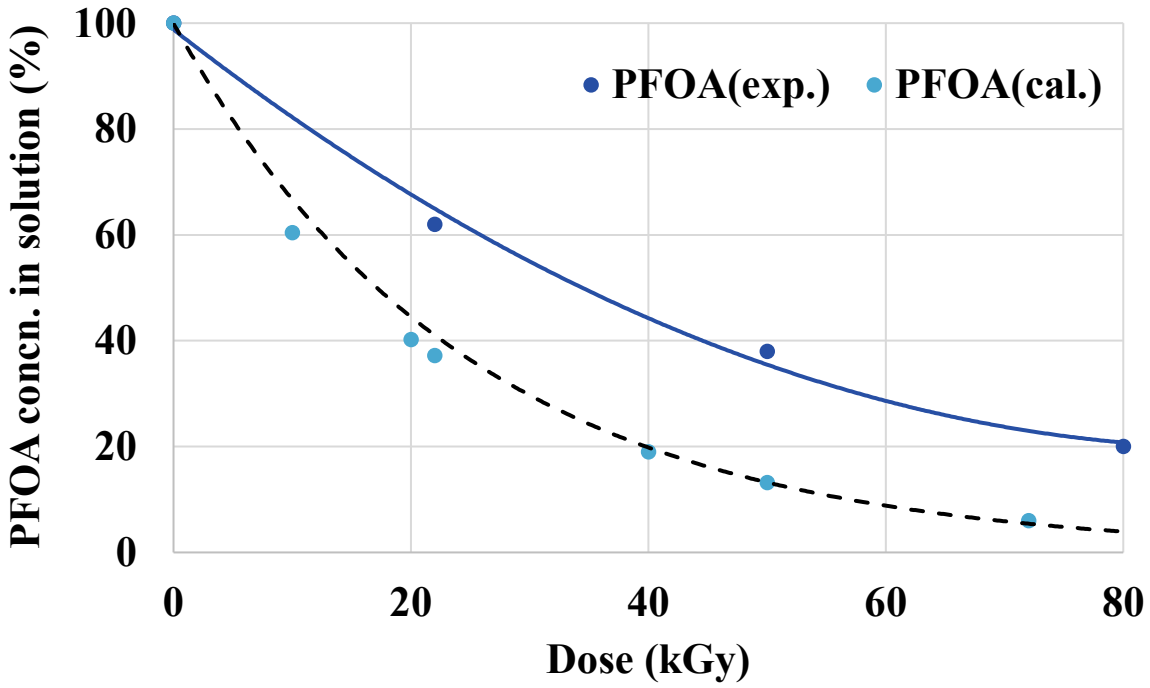
OH: 1.19%; e-: 0.01%; H: 98.8%

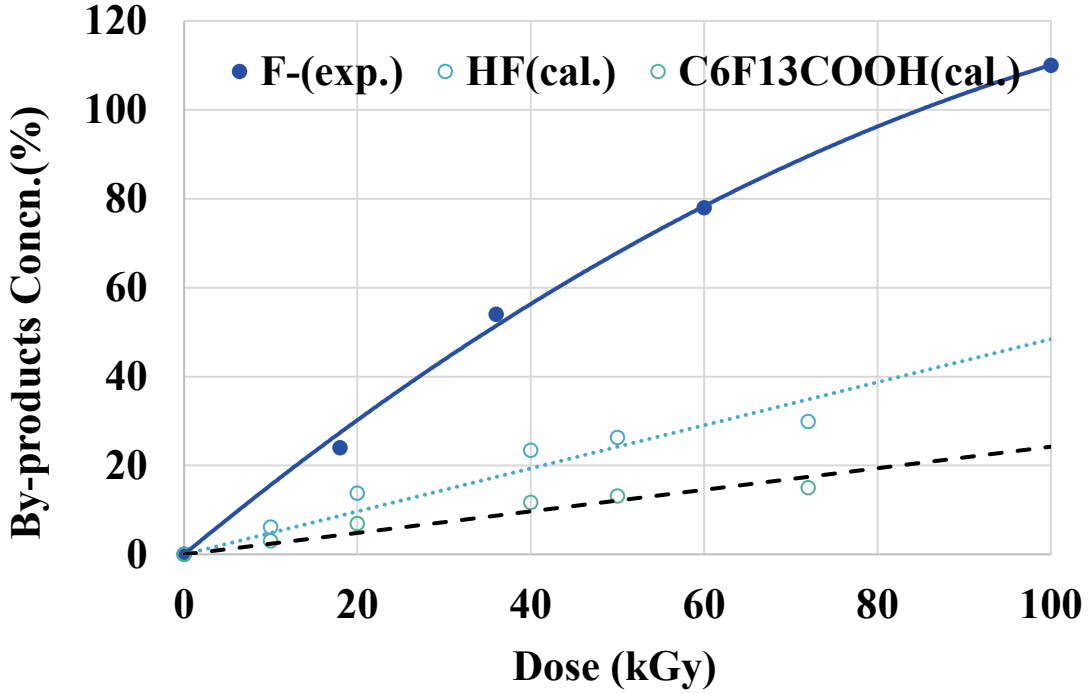


1 mg/L PFOA decomposition and F- formation in Ar saturated solution of pH 7 with 20 mg/L of t-butanol under gamma irradiation.

Species contribution to PFOA decomposition

OH: 1.1 %; e-: 11.7%; H: 87.2%

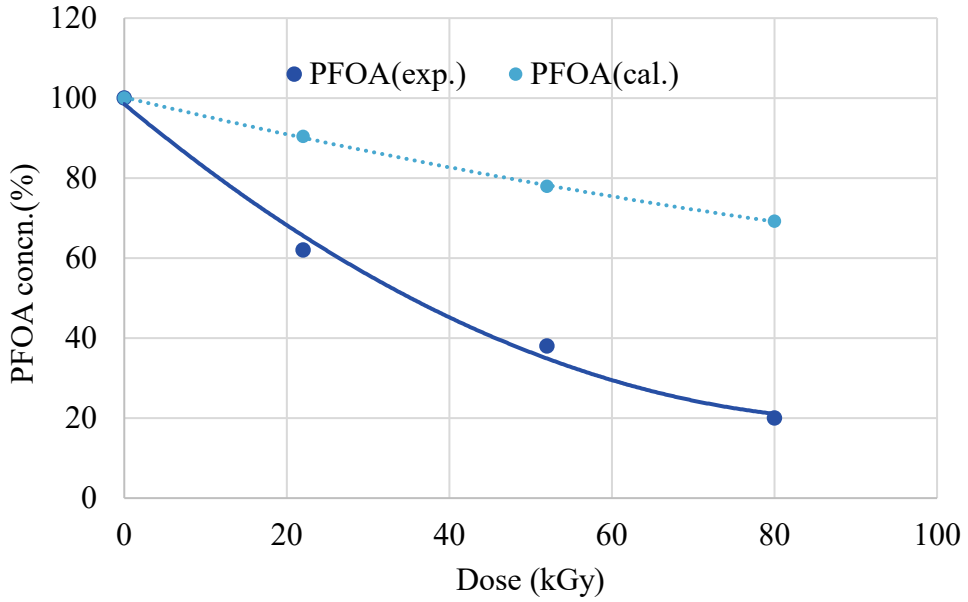


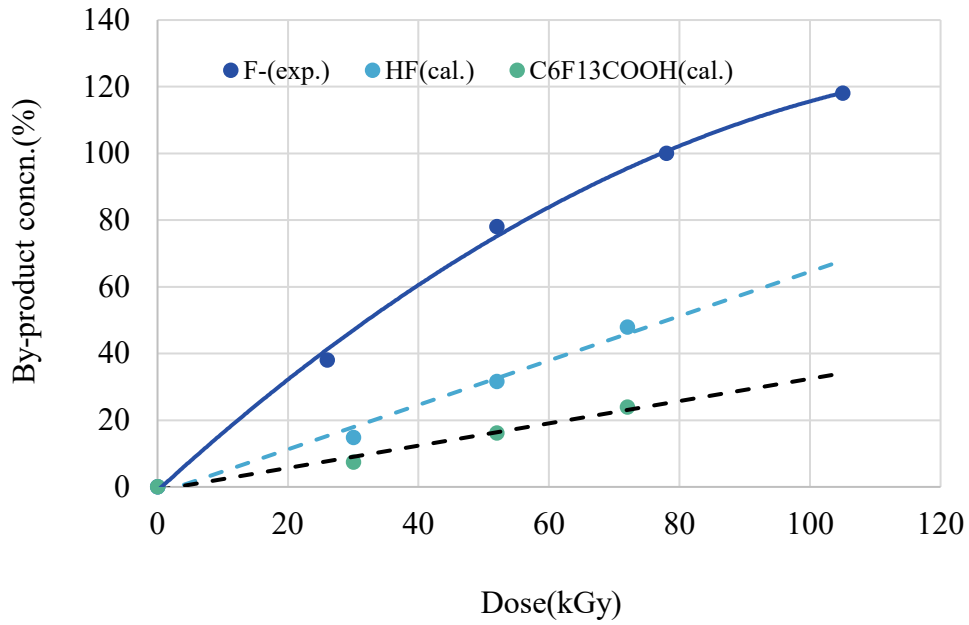


1 mg/L PFOA decomposition and F^- formation in Ar saturated solution of pH 7 with 20 mg/L of t-butanol under EB irradiation.

Species contribution to PFOA decomposition

OH: %; e-: 2.2%; H: 97.8%





1 mg/L PFOA decomposition and F- formation in Ar saturated solution of pH 2 with 20 mg/L of t-butanol under EB irradiation.

Species contribution to PFOA decomposition

OH: 4.0 %; e-: -; H: 96.0%

Table 3 Main species contributing to PFOA decomposition

Condition	OH	e^-	H	Dose (kGy)
Gamma-ray, aerated , pH=7	78.5%	21.4%	0.1%	48
Gamma-ray, Ar with t-butanol, pH=2	1.19%	0.01%	98.8%	9.6
Gamma-ray, Ar with t-butanol, pH=7	1.1%	11.7%	87.2%	9.6
EB, Ar with t-butanol, pH=7	~	2.2%	97.8%	0.036
EB, Ar with t-butanol, pH=2	4.0%	~	96.0%	72

Conclusions

•Based on the modeling calculation results of PFOA, PFOA might be degradated under EB or gamma-ray irradiation.

•HF, PFHeptaneA($C_6F_{13}COOH$) were predicted as by-products, CO_2, CO were also predicted.

• In aerated solution, OH and e^- play important role for PFOA degradation; with t-butanol presence, H play dominant role.

Conclusions (Cont.)

- Reaction rate of H with PFOA is set being $1.0*10^5$, which is two orders lower than experimental result.

- Due to lack of enough literatrue data, expecially the rate constants of the intermediate species and some chemical reactions sensitive to pH of the solution, it makes the calculation more difficult.(challenge)

Thank you

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