atmosphere

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Supplementary Materials

Investigating the Atmospheric Sources and Sinks of Perfluorooctanoic Acid Using a Global Chemistry Transport Model

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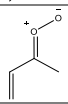
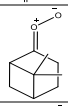
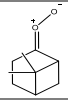
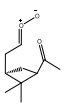
Received: 22 March 2020; Accepted: 17 April 2020; Published: date

Table S1. SCIs added as part of the inclusion of the 'Criegee Field' in the STOCHEM chemical module. Structures and molecular weights are extracted either from the Master Chemical Mechanism [52] or from Chhantyal-Pun et al [28].

Criegee Intermediate	CRI Name	Molecular Weight	Structure
CH_2OO	SCIE	46.03	
syn-CH_3CHOO	SCIPS	60.05	
anti-CH_3CHOO	SCIPA	60.05	
syn-MVKOO	SCIMVS	86.09	
anti-MVKOO	SCIMVA	86.09	
syn-MACROO	SCIMAS	86.09	
anti-MACROO	SCIMAA	86.09	
syn-nopinone oxide	SCIBPS	154.21	
anti-nopinone oxide	SCIBPA	154.21	
syn-pinonaldehyde oxide	SCIPAS	184.24	

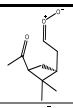
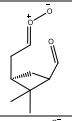
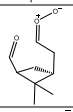
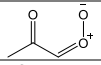
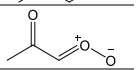
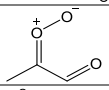
anti-pinonaldehyde oxide	SCIPAA	184.24	
syn-isopinonaldehyde oxide	SCIIPS	184.24	
anti-isopinonaldehyde oxide	SCIIPA	184.24	
syn-$CH_3C(O)CHOO$	SCIMGS	88.06	
anti-$CH_3C(O)CHOO$	SCIMGA	88.06	
syn-$(CH_3)(CHO)COO$	SCIGAS	88.06	
anti-$(CH_3)(CHO)COO$	SCIGAA	88.06	

Table S2. Complete set of the 26 SCI formation reactions included in the STOCHEM chemical module. All rate constants and yields extracted either from the Master Chemical Mechanism [52] or from McGillen et al [53].

SCI Production Route	Rate Constant ($cm^3\ s^{-1}$)	Percentage Yield of SCI
$O_3 + C_3H_6 \rightarrow$ SCIE	$5.51 \times 10^{-15} \times \exp^{(-1878/T)}$	37
O_3 + TBUT2ENE →SCIPA	$6.64 \times 10^{-15} \times \exp^{(-1059/T)}$	10.5
$O_3 + C_5H_8$ →SCIE	$1.03 \times 10^{-14} \times \exp^{(-1995/T)}$	31
APINENE + O_3 →SCIPAA	$8.05 \times 10^{-16} \times \exp^{(-640/T)}$	5
BPINENE + O_3 →SCIBPA	$1.35 \times 10^{-15} \times \exp^{(-1270/T)}$	18
$C_2H_4 + O_3$ →SCIE	$9.14 \times 10^{-15} \times \exp^{(-2580/T)}$	37
$C_3H_6 + O_3$ →SCIPA	$5.51 \times 10^{-15} \times \exp^{(-1878/T)}$	8
$C_3H_6 + O_3$ →SCIPS	$5.51 \times 10^{-15} \times \exp^{(-1878/T)}$	8
TBUT2ENE + O_3 →SCIPS	$6.64 \times 10^{-15} \times \exp^{(-1059/T)}$	10.5
$C_5H_8 + O_3$ →SCIMAA	$1.03 \times 10^{-14} \times \exp^{(-1995/T)}$	4
$C_5H_8 + O_3$ →SCIMAS	$1.03 \times 10^{-14} \times \exp^{(-1995/T)}$	1
$C_5H_8 + O_3$ →SCIMVA	$1.03 \times 10^{-14} \times \exp^{(-1995/T)}$	7
$C_5H_8 + O_3$ →SCIMVS	$1.03 \times 10^{-14} \times \exp^{(-1995/T)}$	14
APINENE + O_3 →SCIPAS	$8.05 \times 10^{-16} \times \exp^{(-640/T)}$	5
APINENE + O_3 →SCIIPA	$8.05 \times 10^{-16} \times \exp^{(-640/T)}$	5
APINENE + O_3 →SCIIPS	$8.05 \times 10^{-16} \times \exp^{(-640/T)}$	5
BPINENE + O_3 →SCIE	$1.35 \times 10^{-15} \times \exp^{(-1270/T)}$	17
BPINENE + O_3 →SCIBPS	$1.35 \times 10^{-15} \times \exp^{(-1270/T)}$	2
MVK + O_3 →SCIMGA	$8.5 \times 10^{-16} \times \exp^{(-1520/T)}$	6
MVK + O_3 →SCIMGS	$8.5 \times 10^{-16} \times \exp^{(-1520/T)}$	6
MVK + O_3 →SCIE	$8.5 \times 10^{-16} \times \exp^{(-1520/T)}$	12
MACR + O_3 →SCIGAA	$1.4 \times 10^{-15} \times \exp^{(-2100/T)}$	1.1
MACR + O_3 →SCIGAS	$1.4 \times 10^{-15} \times \exp^{(-2100/T)}$	1.1
MACR + O_3 →SCIE	$1.4 \times 10^{-15} \times \exp^{(-2100/T)}$	32.5
HC4CCHO + O_3 →SCIGAA	2.4×10^{-17}	2.5
HC4CCHO + O_3 →SCIGAS	2.4×10^{-17}	2.5

Table S3. Complete set of the 26 SCI loss reactions included in the STOCHEM chemical module. The rate constants for the loss processes of SCIs are extracted from Chhantyal-Pun et al [28].

SCI Loss Route	Rate Constant ($cm^3\ s^{-1}$)
SCIE + water dimer	$3.92 \times 10^{-16} \times \exp^{(2930/T)}$
SCIPA + H_2O	1.3×10^{-14}
SCIPA + water dimer	$5.2 \times 10^{-20} \times \exp^{(6124/T)}$
Unimolecular reaction of SCIPS	$2.76 \times 10^{-73} \times T^{27.88} \times \exp^{(3978/T)}$
SCIMAA + H_2O	$2.13 \times 10^{-19} \times (T)^{1.74} \times \exp^{(-929/T)}$
SCIMAA + water dimer	$2.24 \times 10^{-19} \times (T)^{1.73} \times \exp^{(1313/T)}$
Unimolecular reaction of SCIMAA	$5.93 \times 10^{8} \times (T)^{1.46} \times \exp^{(-7832/T)}$
Unimolecular reaction of SCIMAS	$1.59 \times 10^{11} \times (T)^{0.44} \times \exp^{(-6102/T)}$
Unimolecular reaction of SCIMVA	$1.94 \times 10^{12} \times \exp^{(-6150/T)}$
Unimolecular reaction of SCIMVS	$2.46 \times 10^{-76} \times T^{29.09} \times \exp^{(3545/T)}$
SCIPAA + H_2O	1.3×10^{-14}
SCIPAA + water dimer	$5.2 \times 10^{-20} \times \exp^{(6124/T)}$
Unimolecular reaction of SCIPAS	$2.76 \times 10^{-73} \times T^{27.88} \times \exp^{(3978/T)}$
Unimolecular reaction of SCIIPS	$6.95 \times 10^{-66} \times T^{25.7} \times \exp^{(2931/T)}$
Unimolecular reaction of SCIIPA	$2.76 \times 10^{-73} \times T^{27.88} \times \exp^{(3978/T)}$
Unimolecular reaction of SCIBPS	$1.9 \times 10^{9} \times (T)^{1.33} \times \exp^{(-8425/T)}$
SCIBPS + H_2O	$8.46 \times 10^{-23} \times (T)^{2.64} \times \exp^{(121/T)}$
Unimolecular reaction of SCIBPA	$2.76 \times 10^{-73} \times T^{27.88} \times \exp^{(3978/T)}$
SCIMGA + H_2O	1.3×10^{-14}
SCIMGA + water dimer	$5.2 \times 10^{-20} \times \exp^{(6124/T)}$
SCIMGS + H_2O	$2.18 \times 10^{-19} \times (T)^{1.43} \times \exp^{(1268/T)}$
SCIMGS + water dimer	$2.26 \times 10^{-19} \times (T)^{1.43} \times \exp^{(3279/T)}$
Unimolecular reaction of SCIGAS	$2.76 \times 10^{10} \times T^{0.78} \times \exp^{(-5162/T)}$
SCIGAS + H_2O	$7.81 \times 10^{-20} \times T^{1.68} \times \exp^{(575/T)}$
SCIGAS + water dimer	$8.07 \times 10^{-20} \times T^{1.67} \times \exp^{(2828/T)}$
Unimolecular reaction of SCIGAA	$2.76 \times 10^{-73} \times T^{27.88} \times \exp^{(3978/T)}$

Table S4. The reactions depicting the potential chemical degradation routes of HPE in the atmosphere. Rate Constants and yields are extracted from Taatjes et al [23].

Reaction	Rate Constant ($cm^3\ s^{-1}$)	Yield
PFOA + SCI → HPE	4.9×10^{-10}	100
HPE + OH → CO_2 + HF	4.8×10^{-12}	20
HPE + OH → PFOA + HCOOH	4.8×10^{-12}	80

Table S5. The deposition parameters included for HPE in the STOCHEM−HPE-values assumed to be the same as those for organic hydroperoxides [57].

Deposition Type	Deposition Parameter(s)	Value(s)	Unit
Dry deposition	Land/Sea Deposition Velocity	5.0/5.0	$mm\ s^{-1}$
Wet deposition	Dynamic/ Convective Scavenging Coefficient	2.0/4.0	cm^{-1}

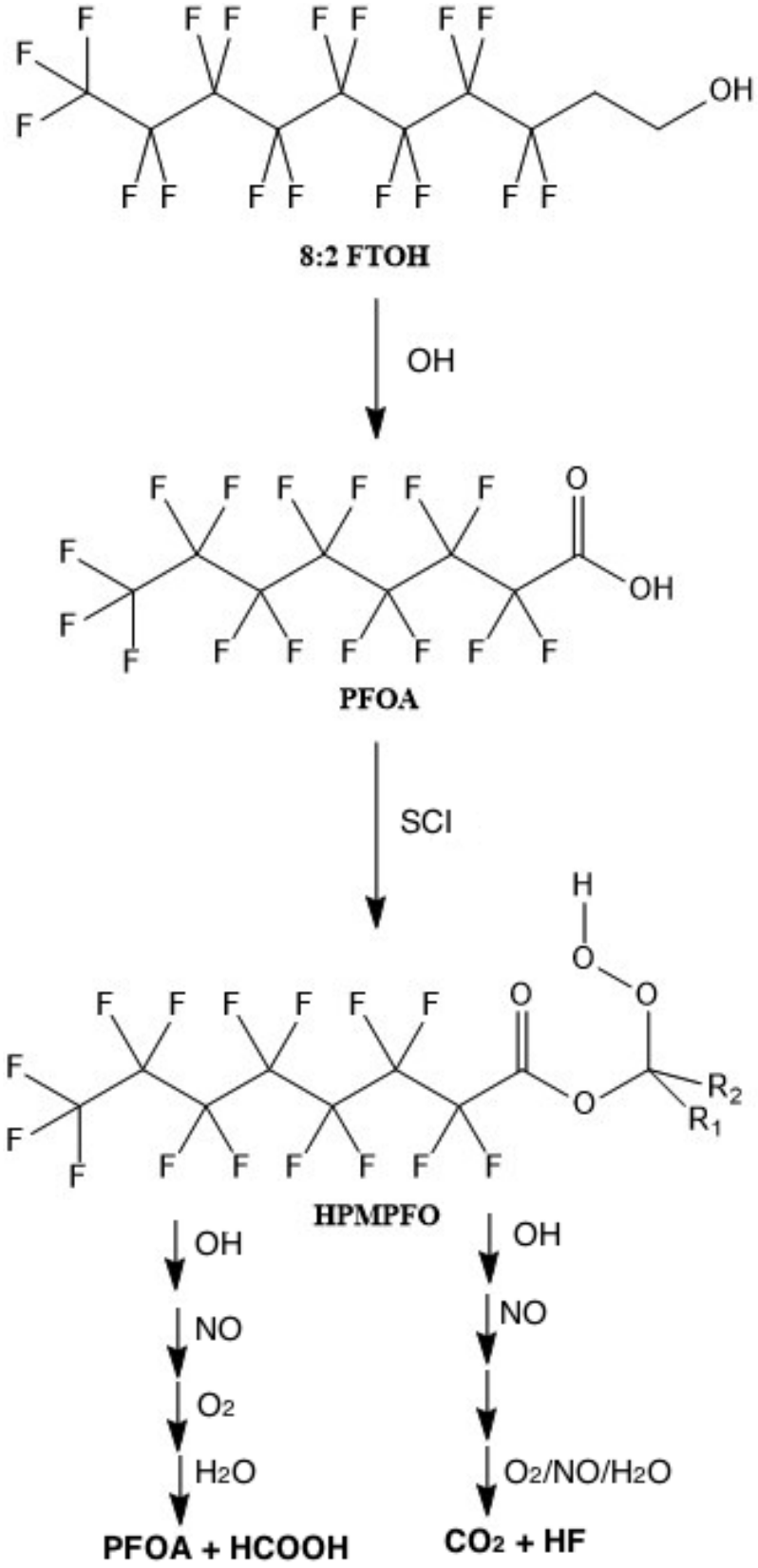


Figure S1. Schematic diagram of the formation and loss reactions of PFOA.

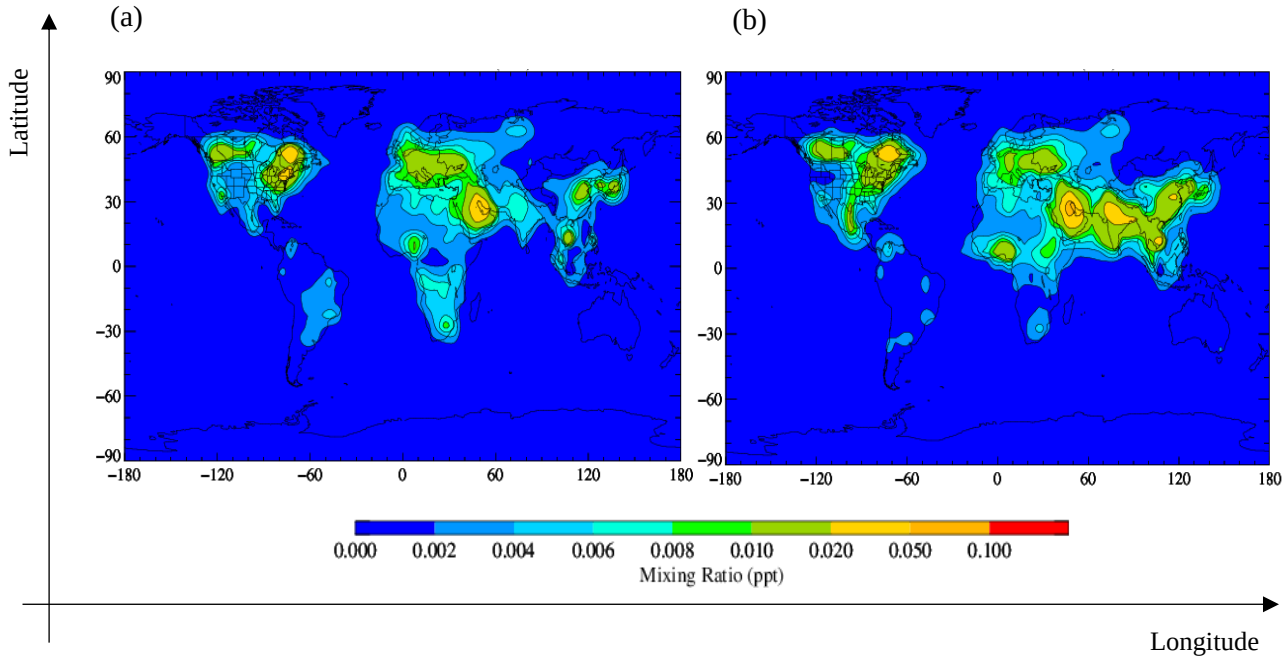


Figure S2. The surface distribution plot depicting the surface level mixing ratios of PFOA for (**a**) the northern hemispheric summer months (June–July–August) and (**b**) the northern hemispheric winter months (December–January–February).

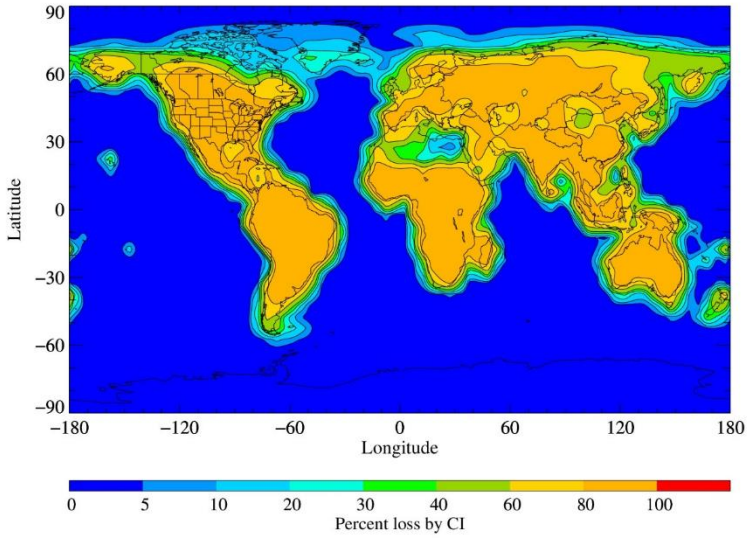


Figure S3. The surface distribution plot depicting the surface level percentage of PFOA removed as a result of its reaction with SCIs using dated kinetic data from McGillen et. al. [53] and Chhantyal–Pun et. al [34].

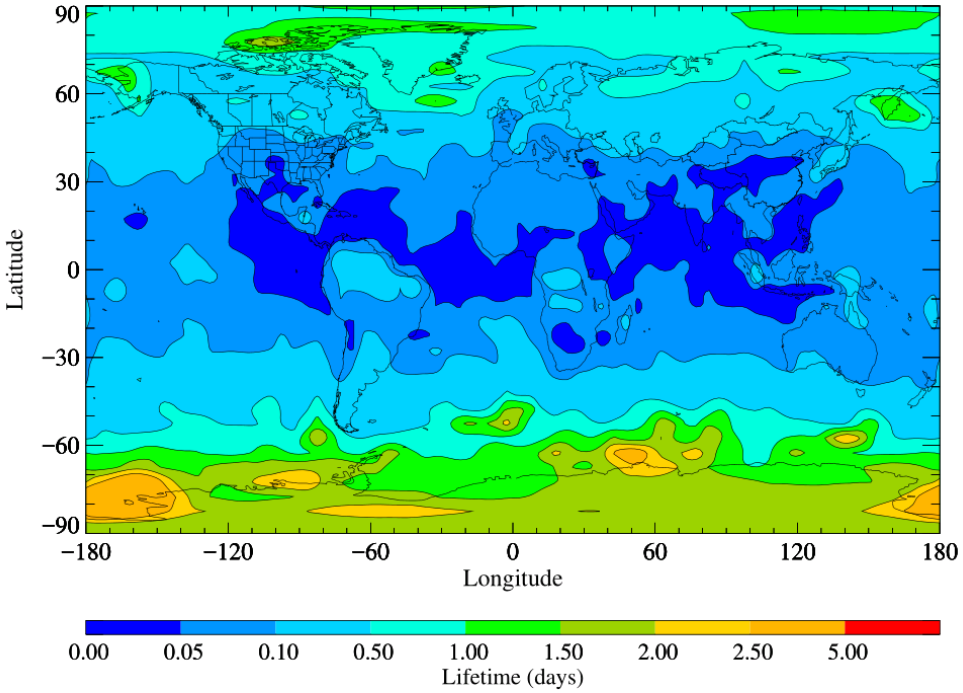


Figure S4. The surface distribution plot depicting the average lifetime of PFOA with respect to reaction with OH in days.