

SUPPORTING INFORMATION

Canadian High Arctic Ice Core Records of Organophosphate Flame Retardants and Plasticizers

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Controls and limitations for addressing OPE contamination during field sampling and lab processing. In our experimental design, we took many precautions to avoid contaminating the ice core samples. In the context of OPEs, which are ubiquitous in most commodities, we were particularly concerned with avoiding polymers. The commercially-available ice core drill (Kovacs Mark II coring system, <http://kovacsicedrillingequipment.com/coring-systems/mark-ii/>), does not contain any plastic parts, with the exception of the flight which is on the outside of the barrel and never in contact with the ice core. The inside of the drill barrel, where the ice core enters, is made out of fiberglass. The cutting shoe is made out of aluminum and the cutting teeth are made out of heat treated steel. The drive head is stainless steel and aluminum. More importantly, the entire rind of the core is removed and discarded so that any firm or ice that was touching the inner circumference of the barrel is removed to minimize any contamination.

In addition, we prepared field-exposed blanks consisting of HPLC-grade water in 1 L amber glass bottles that were transported to the field site from Resolute Bay to the Devon Ice Cap and Mt. Oxford icefield and opened in the field during the ice core sampling. These blanks were then shipped back to the lab in Ontario and processed analogously to real samples. The field blanks were compared to “stay” blanks which were the same type of water that had been stored in the lab and never shipped. Our results indicated no contamination arising from the field site activity, however these field blanks have limitations in that they were not handled in a manner identical to the ice core. For example, the field blanks were not in contact with the coring device and were not bagged in the polyethylene tubing for shipment. Probably for this reason, most ice core researchers do not use a field blank as indicated in these ice core studies on pesticides in Austfonna, Svalbard Norway (Hermanson et al. 2005), pesticides in Devon Ice Cap (Zhang et al. 2015), PFAS in Lomonosovfonna, Svalbard (Hartz et al. 2023), pesticides in Lys

glacier, Italy (Villa et al. 2003), lead in Summit, Greenland (McConnell et al. 2002), black carbon in the Tibetan Plateau (Liu et al. 2023), and trace metals in Tupungatito, Chile (Potocki et al., 2022), none of which employ the use of field blanks or any procedural blanks that capture the field sampling and transport processes.

We were not able to eliminate the absolute possibility of polyethylene layflat tubing as a source of OPEs to the ice core, however, based on a weight of evidence, we propose that the plastic tubing was not a major contributor. Polyethylene layflat plastic bags are the standard for transporting ice cores. In our case, 15 to 16 bags were used to ship sections of ice corresponding to 89 to 103 cm lengths per bag. The ice sections were frozen from the time of sampling to shipment and storage. All melting was performed in pre-cleaned 4 L glass bottles. We anticipate the extent of partitioning of OPEs from the plastic bag wrap into the ice core sections to be kinetically and thermodynamically-hindered based on the temperature (-20 to -30 °C) as well as the limited ability of transfer into the solid ice matrix. In addition, results from the Devon Ice Cap ice core indicated exponentially increasing concentrations over the length of the core. We hypothesize that contamination from the plastic wrap into the ice core would have obscured the ability to detect a temporal trend, which is not what we observed. Lastly, the OPE concentrations in the core from the Mt. Oxford icefield were much lower than that observed in the Devon Ice Cap. We used the plastic wrap in both sites for the cores. If the plastic wrap was a significant source of OPEs to the ice, then we'd expect similar results in both locations, which is not what we observed.

The ability to constrain contamination during ice coring is an important area for future study. The challenge is creating a mock ice core sample of the same diameter in an ultra cold environment and then transferring the ice into a layflat plastic tube while remaining in a -20 to -

30 °C environment to mimic that of the actual ice coring location. Future work is warranted to determine contamination, perhaps using simulated field sampling conditions.

UHPLC-MS/MS instrumental analysis of OPE. A reverse phase solvent gradient program was applied to separate OPE using a mobile phase based on water (A) and methanol (B) containing 0.1% formic acid. The initial conditions were 95% A and held for 0.1 min and then ramped to 70%B by 1 min, 80% B by 5 min and 100%B by 7 min, followed by a 2 min hold. The gradient then ramped to 40% B at 10 min, and 5% B at 10.5 min. A constant flow rate of 0.3 ml/min was used and an injection volume of 2 ul. An isolator column comprised of a Luna 5 µm octadecylsilyl column with dimensions, 2.1 x 50 mm (Phenomenex, Sacramento, CA, USA) was inserted downstream of the mixing chamber and preceding the injector. The cone and collision energies applied for multiple reaction monitoring transitions are presented in Tables S1&S2.

Table S1. List of analytes targeted with abbreviation, CAS #, Full name, Mass spectral precursor ion (m/z) and product ion (m/z), optimized cone and collision energy, internal standard used for relative response quantitation, and name of supplier. Analytes are organized in order of chromatographic retention time (RT, min). *DIIPP only measured in Mt. Oxford ice core samples.

name	Full name	CAS	precursor	product	Cone voltage	Collision energy	RT(min)	Internal standard	Supplier
TEP	triethylphosphate	78-40-0	183.1	99.0	30	16	3.22	d15TEP	Aldrich
				127.0		10			
TEEDP	tetraethylenediphosphonate	995-32-4	303.2	173.2	42	26	3.23	d12TCEP	Fluka
				219.3		18			
TCEP	tris(2-chloroethyl)phosphate	115-96-8	285.1	99.2	40	22	3.28	d12TCEP	Aldrich
			287.1			22			
TPPO	triphenylphosphineoxide	791-28-6	279.2	77.2	30	42	3.65	d15TPPO	Sigma
				201.3		26			
TCPP	tris(2-chloroisopropyl) phosphate	13674-84-5	327.1	99.0	24	18	3.86	d18TCPP	Reidel
			329.1			22			
TPrP	tripropylphosphate	513-08-6	225.1	99.0	26	18	3.91	d21TPrP	Aldrich
				141.0		8			
TBPO	tributylphosphineoxide	814-29-9	219.2	91.8	35	28	4.26	d15TPPO	Aldrich
				163.2		25			
TDCPP	tris(1,3-dichloroisopropyl)phosphate	13674-87-8	429.1	99.1	25	22	4.77	d15TDCPP	Reidel
			431.0			24			
TPP	triphenylphosphate	115-86-6	327.1	77.2	54	40	4.88	MTPP	Wellington
				152.3		44			
TDBrPP	tris(2,3-dibromopropyl)phosphate	126-72-7	696.7	99.2	50	24	5.36	d27TnBP	Supelco
			698.7			24			
TiBP	tri-isobutyl-phosphate	126-71-6	267.3	99.2	28	16	5.68	d27TnBP	Sigma
				155.2		8			
TnBP	tri-n-butyl-phosphate	126-73-8	267.3	99.2	28	16	5.85	d27TnBP	Aldrich
				155.2		8			
TBOEP	tris(2-butoxyethyl) phosphate	78-51-3	399.3	199.3	6	14	6.39	M6TBOEP	Aldrich
				299.4		10			
DIIPP*	diphenyl-3-isopropylphenyl phosphate	69515-46-4, 28108-99-8, 64532-94-1	369.1	327.0	12	20	6.89	d21p-TMPP	Chiron
				233.0		26			

name	Full name	CAS	precursor	product	Cone voltage	Collision energy	RT(min)	Internal standard	Supplier
		55864-04-5							
oTOTP	tri-o-tolyl phosphate	78-30-8	369.3	107.2	48	34	6.93	d21p-TMPP	Wellington
mp-TOTP	triclesyl phosphate	563-04-2 78-32-0		166.0	48	30	7.08	d21p-TMPP	Wellington
TBDPP	(tert-butylphenyl)diphenyl phosphate	56803-37-3	383.3	152.2	38	44	7.37	d13 BPDP	Angene
				215.2		36			
EHDPP	ethylhexyl diphenyl phosphate	1241-94-7	363.2	77.0	18	40	7.57	d21p-TMPP	Sigma
				251.2		20			
iDeDPP	isodecyldiphenyl phosphate	29761-21-5	391.4	251.2	16	12	8.15	d21p-TMPP	Accustandard
TXP	trixylyl phosphate	25155-23-1	411.3	179.3	90	44	8.24	d27 TXP	Wellington
				194.3		30			
T2IPP	tris(2-isopropylphenyl) phosphonate	64532-95-2	453.3	327.3	15	30	8.36	d33 p-TIPP	Wellington
				369.4		18			
DTBPP	(ditertbutylphenyl)phenylphosphate	65652-41-7	439.4	327.2	30	28	8.37	d33 p-TIPP	Angene
				383.3		18			
DOPP	dioctylphenyl phosphonate	1754-47-8	383.3	141.2	25	48	8.74	d33 p-TIPP	Aldrich
				159.2		16			
TTBPP	tris(p-tert-Butylphenyl) phosphate	78-33-1	495.4	327.2	92	36	8.92	d33 p-TIPP	Angene
				439.4		22			
TEHP	Tris(2-ethylhexyl)phosphate	78-42-2	435.4	71.1	34	10	9.28	d51TEHP IS	Aldrich
				99.0		10			

Table S2. List of isotopically labeled standards used along with precursor, product ions, cone voltage, collision energy, retention time (min), and supplier.

Acronym	Full name	Precursor (m/z)	Product ion (m/z)	Cone V	Collision energy	Retention time	Supplier
d15TEP	Tri-ethyl phosphate-d15	198.3	102.1 134.0	30	18 12	3.21	Wellington
d12TCEP	Tris(2-chloroethyl) phosphate-d12	297.0 299.3	232.1 67.2	40 40	10 22	3.27	Wellington
d15TPPO	Triphenyl-d15-phosphine oxide	294.2	211.0	26	28	3.61	Aldrich
d18TCPP	tris(2-chloroisopropyl) phosphate d18	347.2	102.1	24	20	3.82	CIL
d21TPrP	Tri-n-propyl phosphate-d21	246.3	102.1	28	20	3.86	CDN
d15TDCPP	Tris(1,3-dichloro-2-propyl) phosphate-d15	446.0	102.1	25	25	4.71	Wellington
MTPP	¹³ C ₁₈ -Triphenylphosphate	345.3	83.2	54	39	4.87	Wellington
d27TnBP	Tri-n-butyl phosphate-d27	294.4	102.2	34	18	5.7	Wellington
M6TBOEP	Tris(2-butoxy-[¹³ C ₂]-ethyl) phosphate	405.3	201.3 303.4	6	14 12	6.4	Wellington
d21pTMPP	Tris-p-tolyl phosphate-d21	390.2	97.9 173.8	48	36 54	7.03	Chiron
d13 BPDP	4-tert-Butylphenyldiphenyl phosphate-d13	396.1	155.1 332.1	38	34 20	7.33	Chiron
d27 TXP	Tris(2,4-dimethylphenyl) phosphate-d27	438.2	189.7 207.5	80	46 32	8.16	Chiron
d33 p-TIPP	Tris(4-isopropylphenyl) phosphate-d33	486.4	342.1 390.2	74	34 26	8.55	Chiron
d51TEHP	Tris(2-ethylhexyl) Phosphate-d51	486.8	102.1	34	10	9.22	Sustainable GR

Table S3. National Federal Production Volume in US according to 2012 and 2020 USEPA CDR Database (<https://www.epa.gov/chemical-data-reporting/access-cdr-data#2020>); As per United States guidelines, data reported in pounds (lbs)[§]; *CBI = confidential business information, data is not released

name	2012 per year chemical production volume in lbs [§]	2020 Per year chemical production volume in lbs [§]	CAS
TEP	1-10 M (i.e. 1,000,000-10,000,000)	1-10 M (i.e. 1,000,000-10,000,000)	78-40-0
TPPO	<1 M	<1 M	791-28-6
TCPP	10 – <50 M	20 – <100 M	13674-84-5
TDCPP	10 – <50 M	1 – <20 M	13674-87-8
TPHP	1 – <10 M	1 – <10 M	115-86-6
TiBP	<1 M	<1 M	126-71-6
TnBP	1– <10 M	1– <10 M	126-73-8
TBOEP	1 – <10 M	1 – <20 M	78-51-3
TBDPP	1 – <20 M	1 – <20 M	56803-37-3
EHDPP	1 – <20 M	1 – <20 M	1241-94-7
iDeDPP	1 – <20 M	1 – <20 M	29761-21-5
TXP	1 – <20 M	1 – <20 M	25155-23-1
DTBPP	1 – <20 M	1 – <20 M	65652-41-7
TTBPP	<1 M	<1 M	78-33-1
TEHP	1 – <20 M	1 – <20 M	78-42-2
TCEP	79,364	CBI*	115-96-8
Tricresyl phosphate	263,591	Not listed	78-32-0
TEEDP	Not listed	Not listed	995-32-4
TPrP	Not listed	Not listed	513-08-6
TBPO	Not listed	Not listed	814-29-9
TDBrPP	Not listed	Not listed	126-72-7
DIPIPP*	Not listed	Not listed	69515-46-4
T2IPP	Not listed	Not listed	64532-95-2
DOPP	Not listed	Not listed	1754-47-8

[§]Conversion to SI units: 1 M lbs is approximately 450 000 kg; 10 M lbs is approximately 4 500 000 kg, 20 M lbs is

approximately 9 100 000 kg, 50 M lbs is approximately 23 000 000 kg, 100 M lbs is approximately 45 000 000 kg, 79 364

lbs is approximately 36 000 kg, 263 591 lbs is approximately 120 000 kg.

Details on QA/QC.

Precision. Twelve samples corresponding to the years 2014, 2013, 2008, 2002, 2000, 1997,

1996, 1993, 1990, 1989, 1988, and 1983, were extracted and analyzed in duplicate to ascertain

precision of the method. The percent difference was generally within 30% (mean \pm standard error $26 \pm 2.4\%$, range 11-35%) Table S4.

Extraction efficiency and recovery. After aliquoting 500 ml (and in some cases duplicate 500 ml) of melted firn for OPE analysis in the Devon Ice Cap samples, the remaining melted sample in the 4 L melt bottle was subsampled and combined. This was deemed a large volume composite melted firn sample that was used for testing recovery and extraction efficiency. The extraction efficiency was evaluated for Devon Ice Cap samples by spiking a cocktail of native and isotopically labeled internal standards into a composite melted ice core sample prior to extraction. The same experiment was conducted with the exception of spiking the native standards post-extraction into the final extract. The ratio of peak areas in the pre-extraction spiked sample and the post-extraction spiked sample corresponds to extraction efficiency (%). The calculated concentration in the pre-extraction spiked sample was compared to the theoretical spike and is expressed as the internal standard-normalized recovery. The spiking level of native standard corresponded to 10 ng/ml in the final extract. For TCPP and TBOEP, the background concentration was much higher than the spiking level and therefore, recovery is best estimated using the extraction efficiency of the native standards, which is a comparison of peak area instead of ng/ml concentration as well as the recovery using the isotopically labeled standards. The results indicate at least 80% extraction efficiency for the majority of the standards supporting the completeness of the extraction method (Table S4). For most analytes, the extraction efficiency was $> 70\%$ but for certain substances the extraction efficiency was 30-60% indicating a diminished affinity for the SPE sorbent. This is a challenge in isolating these analytes from the sample, however, the use of these isotopically labeled standards inherently corrects for recovery issues as demonstrated by the internal standard normalized concentration

recovery. In addition, the area of the isotopically labeled standards in the full suite of samples was compared to the calibration standards and is expressed as an average \pm standard deviation (Table S4). Deviation from 100% for the isotopically labeled standards is a combination of extraction efficiency but also matrix effects.

Table S4. Recovery of native analytes spiked into sample prior to extraction using internal standard normalized concentration (ng/ml recovery %) and extraction efficiency (EE)¹, precision as evaluated using % difference on 11 paired samples², and external recovery of isotopically labeled standards in samples compared to calibration curve

	TEP	TBPO	TPrP	TnBP	TiBP	TDBPP	TPPO	TCEP	TEEDP	TCPP	TDCPP	TPP	
ng/ml recovery (%)	98	89	88	108	74	132	96	71	115	NA	93	96	
EE (%) ¹	29	80	52	88	106	82	85	95	97	87	92	87	
% difference ²	15	NA	NA	11	27	NA	35	15	NA	33	32	33	
± sd	±4.6			±3.1	±4.7		±4.3	±2.9		±8.5	±4.5	±8.5	
	EHDPP	oTOTP	mpTOTP	DOPP	iDeDPP	TBOEP	TXP	TEHP	DTBPP	T2iPPP	TTBPP	TBDPP	DIPI
ng/ml recovery (%)	74	87	98	94	61	NA	111	102	83	72	133	98	102
EE	59	56	58	36	40	94	37	46	41	39	46	50	58
% difference	22	28	27	NA	28	33	NA	NA	33	24	NA	NA	NA
± standard deviation	±5.6	±5.6	±4.4		±5.9	±5.5			±6.3	±5.7			

Recovery of isotopically labeled standards in samples compared to calibration curve (based on peak area):

	d₁₅TEP	d₂₁TPrP	d₂₇TnBP	d₁₅TPPO	d₁₂TCEP	d₁₈TCPP	d₁₅TDCPP	MTPP	M6TBOEP	d₂₇2,4TX P	d₅₁TEHP	d₃₃pTIPP
Average	50	62	70	92	87	82	93	84	84	38	36	38
Standard deviation	±13	±13	±9	±3	±6	±5	±6	±4	±5	±6	±7	±7

$$EE = \frac{\text{peak area}_{\text{native spiked into sample before extraction}}}{\text{peak area}_{\text{native spiked into final extract}}} \times 100\%$$

¹Extraction efficiency (EE) defined as

² There were 11 samples with significant melt volume to allow duplicate extraction of 500 ml subsamples. % difference in concentration was determined for each pair and the average ± standard deviation is reported, n= 11; NA = not available when detection frequency was too low to calculate a % difference between replicates.

Method and instrumental detection limits. All samples were blank corrected using the mean extraction blank. The mean blank levels corresponded to 0.19 ng/ml TEP, 0.13 ng/ml TnBP, 0.067 ng/ml TiBP, 0.38 ng/ml TCEP, 0.47 ng/ml TCPP, 0.39 ng/ml TDCPP, 0.22 ng/ml TPP, 1.8 ng/ml TBOEP, and 0.052 ng/ml iDeDPP. The method detection limit (MDL) was designated as 3 x standard deviation of extraction blanks and corresponded to 0.092 ng/L TEP, 0.081 ng/L TnBP, 0.031 ng/L TiBP, 0.22 ng/L TCEP, 0.49 ng/L TCPP, 0.22 ng/L TDCPP, 0.12 ng/L TPP, 0.36 ng/L isoDeDPP, and 0.58 ng/L TBOEP (Table S5). Several analytes did not have a signal in the method blanks: TBPO, TPrP, TPPO, and TEEDP. For these analytes, the MDL corresponded to the instrument detection limit (IDL). The IDL corresponded to the concentration yielding a signal to noise ratio of 3 (Table S5).

Table S5. Method detection limits using method blanks and instrument detection limits based on signal to noise in instrument response. Units correspond to sample concentration based on a 0.5 ml extract volume and 0.5 L sample volume.

	MDL(ng/L)	IDL(ng/L)		MDL(ng/L)	IDL(ng/L)
TEP	0.092	0.12	TOTP		0.0062
TnBP	0.081	0.013	TXP		0.0010
TiBP	0.031	0.025	TBDPP		0.0430
TCEP	0.22	0.19	DTBPPP		0.0031
TCPP	0.49	0.043	iDeDPP	0.052	0.0271
TDCPP	0.22	0.066	DOPP		0.0072
TPP	0.12	0.022	TTBPP		0.0062
iDeDPP	0.36	0.0044	TEHP	0.0169	0.0026
TBOEP	0.58	0.039	DIPIPP		0.0069
TDBrPP	0.035	0.017			
TBPO		0.023			
TPrP		0.036			
TPPO		0.051			
TEEDP		0.015			
EHDPP		0.027			
T2iPPP		0.0017			

Table S6. Concentrations (ng/L) of OPEs in sectioned Devon Ice Cap ice core with assigned year, depth in centimeters of ice (not water equivalent) and melted volume (continued on next page). Note:2015 concentrations represent 5.5 months of accumulation.

assigned year	depth (cm)	Melted volume (ml)	TEP	TBPO	TnBP	TIBP	TDBPP	TPPO	TCEP	TEEDP	TCPP	TDCPP	TPP	EHDP	TOTP	DOPP	iDeDPP	TBOEP	TXP	TEHP	DTBPPP	T2IPPP	TTBPP	TBDPP
2015	37	735	19	<LOD	44	1.4	<LOD	0.83	31	0.23	158	12	29	1.15	0.31	<LOD	2.3	24	<LOD	0.11	0.15	0.13	<LOD	0.42
2014	81	1659	26	<LOD	31	1.3	<LOD	0.93	23	0.23	159	9.0	36	0.70	0.30	2.6	2.2	17	0.023	0.033	0.046	0.46	<LOD	0.14
2013	128	999	18	<LOD	30	1.4	<LOD	0.78	17	0.49	150	6.1	517	0.57	0.42	<LOD	0.99	9.0	0.036	0.044	0.55	7.7	2.5	3.5
2012	162	809	15	<LOD	22	0.75	<LOD	1.3	13	<LOD	67	8.5	24	0.48	0.12	<LOD	1.7	11	<LOD	<LOD	0.048	0.58	<LOD	<LOD
2011	183	505	8.4	<LOD	21	1.0	<LOD	2.2	10	0.095	573	4.5	48	0.43	0.25	<LOD	0.98	23	0.004	<LOD	0.14	0.72	<LOD	0.30
2010	221	1005	13	<LOD	24	0.86	<LOD	1.4	11	0.13	58	6.0	37	0.39	1.1	4.4	0.65	12	<LOD	<LOD	<LOD	0.32	<LOD	<LOD
2009	256	1012	13	<LOD	12	0.65	<LOD	1.2	7.2	<LOD	16	4.6	5.5	0.42	0.17	<LOD	0.58	6.6	0.007	0.015	0.038	0.04	<LOD	0.096
2008	293	1518	12	<LOD	28	1.0	<LOD	1.8	18	0.053	42	4.2	15	0.71	0.19	<LOD	1.6	11	0.007	0.051	0.051	0.14	<LOD	0.071
2007	336	794	9.3	<LOD	18	0.58	<LOD	1.6	9.8	<LOD	79	2.2	18	1.9	0.13	<LOD	2.3	5.4	0.008	0.004	0.061	0.26	<LOD	<LOD
2006	357	504	14	<LOD	13	0.86	<LOD	1.7	9.9	<LOD	25	4.3	4.2	0.38	0.12	<LOD	0.84	46	0.063	<LOD	0.040	<LOD	<LOD	<LOD
2005	393	1220	12	<LOD	10	0.89	<LOD	0.30	4.3	<LOD	13	2.8	17	0.31	0.064	5.6	0.47	13	0.026	0.008	<LOD	0.20	<LOD	<LOD
2004	420	1161	4.9	0.15	13	0.62	<LOD	0.30	8.8	0.18	56	6.9	55	0.54	0.14	5.5	0.79	11	<LOD	0.072	0.021	0.64	<LOD	<LOD
2003	448	1185	9.9	<LOD	7.0	0.80	<LOD	0.59	4.2	<LOD	13	1.7	6.9	0.16	0.040	<LOD	0.30	5.7	0.031	<LOD	0.025	0.099	<LOD	<LOD
2002	505	1483	12	0.27	17	0.79	<LOD	0.16	8.3	0.047	32	4.3	4.9	0.36	0.14	<LOD	0.30	15	0.021	0.009	0.051	<LOD	<LOD	0.17
2001	553	1470	6.8	0.21	13	0.61	<LOD	0.42	7.2	0.36	10	5.1	3.8	0.20	0.070	<LOD	0.077	24	0.010	0.013	<LOD	<LOD	<LOD	0.055
2000	600	1292	8.2	0.49	14	0.90	<LOD	0.34	5.9	0.38	579	7.0	45	0.16	0.10	<LOD	0.23	11	0.011	0.009	0.043	0.56	0.14	0.074
1999	620	884	5.2	<LOD	13	0.68	<LOD	0.60	8.6	0.12	12	6.1	4.8	0.48	0.11	<LOD	0.53	17	0.109	<LOD	0.12	0.025	<LOD	<LOD
1998	669	625	4.7	<LOD	14	0.76	<LOD	0.34	8.8	<LOD	9	5.6	6.6	0.37	0.089	<LOD	0.51	13	0.008	<LOD	0.098	0.006	<LOD	<LOD
1997	711	1422	5.5	<LOD	12	0.77	<LOD	0.74	5.8	0.18	28	4.7	7.2	0.30	0.076	<LOD	0.31	6.3	0.030	<LOD	0.079	0.069	<LOD	<LOD
1996	755	1199	4.0	<LOD	13	0.61	<LOD	0.49	9.1	<LOD	24	3.0	20	0.29	0.086	<LOD	0.31	5.8	0.032	<LOD	0.096	0.27	<LOD	<LOD
1995	789	972	2.6	<LOD	8.2	0.29	<LOD	0.070	4.1	<LOD	13	1.7	3.9	0.16	0.094	<LOD	0.16	7.8	0.029	<LOD	0.028	0.013	<LOD	<LOD
1993	878	1316	2.8	<LOD	6.2	0.29	<LOD	0.063	3.3	0.071	15	1.4	17	0.10	0.047	<LOD	0.16	5.0	0.027	<LOD	0.029	0.28	<LOD	<LOD
1992	934	1940	9.7	0.20	11	0.47	<LOD	0.086	5.0	<LOD	18	1.9	13	0.33	0.062	4.2	0.11	9.5	<LOD	<LOD	<LOD	0.095	<LOD	<LOD
1991	974	1012	5.0	0.14	6.4	0.38	<LOD	0.11	3.5	0.057	6.7	1.9	8.7	0.26	0.057	<LOD	0.25	7.6	0.007	0.021	0.019	0.055	0.023	0.17

assigned year	depth (cm)	Melted volume (ml)	TEP	TBPO	TnBP	TiBP	TDBPP	TPPO	TCEP	TEEDP	TCPP	TDCPP	TPP	EHDP	TOTP	DOPP	iDeDPP	TBOEP	TXP	TEHP	DTBPPP	T2iPPP	TTBPP	TBDPP
1990	1016	1352	11	0.13	7.7	0.63	<LOD	0.53	4.8	0.056	15	1.8	6.9	0.33	0.10	<LOD	0.17	8.1	0.002	0.022	0.048	0.036	<LOD	<LOD
1989	1176	1473	6.2	0.39	7.4	0.57	<LOD	1.7	5.6	0.038	16	3.0	9.4	0.35	0.089	1.9	0.17	13	0.028	<LOD	0.025	0.089	<LOD	<LOD
1988	1096	1013	5.1	0.26	5.4	0.40	<LOD	1.6	3.7	0.093	18	2.4	15	0.50	0.065	2.1	0.17	7.6	0.007	0.008	0.003	0.007	0.003	<LOD
1987	1136	1525	4.1	0.29	7.5	0.24	<LOD	1.6	4.5	0.086	43	3.1	22	0.45	0.085	4.4	0.10	6.7	0.025	<LOD	<LOD	0.30	<LOD	<LOD
1986	1169	1004	3.0	<LOD	6.3	0.67	<LOD	0.17	3.6	1.1	3.8	1.6	1.8	0.23	0.042	<LOD	0.20	8.3	0.012	0.028	0.027	<LOD	<LOD	<LOD
1985	1208	1226	2.9	<LOD	5.6	0.33	<LOD	1.2	4.5	0.14	12	2.6	14	0.82	0.053	<LOD	0.18	6.7	0.026	<LOD	0.057	0.16	<LOD	<LOD
1984	1235	829	14	<LOD	6.7	0.54	<LOD	0.33	6.3	<LOD	43	2.0	28	0.45	0.11	<LOD	0.37	14	0.037	<LOD	0.14	0.55	<LOD	<LOD
1983	1285	996	8.4	<LOD	5.7	0.40	<LOD	0.16	4.0	0.23	37	3.4	8.5	0.38	0.10	<LOD	0.18	18	0.008	0.018	0.11	0.22	0.011	0.11
1982	1328	1367	5.0	<LOD	8.8	0.59	<LOD	0.26	4.3	0.24	7.1	2.8	7.2	0.41	0.15	<LOD	0.24	6.2	0.029	0.039	0.10	0.15	0.086	0.33
1981	1359	1004	3.8	<LOD	5.3	0.28	<LOD	0.18	3.0	0.057	5.0	4.4	4.0	0.20	0.10	<LOD	0.16	7.1	0.023	<LOD	0.11	0.22	<LOD	<LOD
1980	1387	1010	9.4	0.26	8.5	0.65	<LOD	1.0	5.3	0.078	11	3.1	16	0.26	0.076	5.5	0.11	14	0.061	<LOD	<LOD	0.19	<LOD	<LOD
1979	1397	1015	2.9	<LOD	8.4	0.90	<LOD	6.7	6.0	0.052	22	2.5	6.2	1.2	0.080	<LOD	0.21	6.2	<LOD	<LOD	0.13	<LOD	<LOD	<LOD

Table S7. Concentrations (ng/L) of OPEs in sectioned Mt. Oxford ice core with assigned year, depth in centimeters of ice (not water equivalent) and melted volume (continued on next page). Note: Concentration in 2017 only includes 5.5 months of accumulation.

assigned year	depth (cm)	melt volume (ml)	TEP	TBPO	TnBP	TiBP	TDBPP	TPPO	TCEP	TEEDP	TCPP	TDCPP	TPP	EHDP	O-TOTP	M,P-TOTP	DOPP	IDEDP	TBOEP	T35DMPP	TEHP	DTBPP	T2iPPP	TTBPP	TBDPP	DIPIP
2017	8	144	10	<LOD	15	14	<LOD	<LOD	20	0.11	96	9.6	5.2	3.6	<LOD	2.8	<LOD	1.8	75	<LOD	2.2	1.3	0.25	0.24	1.4	0.085
2016	41	600	6.3	<LOD	6.8	26	<LOD	0.35	3.0	<LOD	52	6.9	6.8	5.3	<LOD	12	<LOD	2.2	55	<LOD	1.9	1.2	0.12	0.36	2.0	0.14
2015	64	564	4.6	<LOD	4.3	19	<LOD	0.25	7.4	0.038	38	5.4	5.3	2.9	<LOD	1.0	<LOD	0.82	34	<LOD	0.81	0.47	0.050	0.12	0.85	0.081
2014	89	445	7.2	<LOD	4.1	9.2	<LOD	0.19	8.4	0.084	39	4.6	4.0	2.2	<LOD	0.76	<LOD	1.0	41	<LOD	0.79	0.21	0.047	0.076	0.50	0.052
2013	133	1215	4.1	<LOD	2.2	10	<LOD	0.12	5.8	<LOD	60	3.6	2.6	2.4	0.61	0.69	<LOD	1.2	34	<0.24	1.1	0.36	0.059	0.083	1.2	0.042
2012	163	835	3.6	<LOD	3.1	14	<LOD	0.12	7.1	0.030	38	3.9	2.5	2.2	<LOD	<LOD	<LOD	1.4	24	<LOD	0.86	0.15	0.072	0.043	0.41	0.048
2011	196	1186	3.4	<LOD	2.3	6.3	<LOD	0.39	5.1	<LOD	34	3.0	1.3	1.7	<LOD	<LOD	<LOD	0.45	17	<LOD	0.55	0.10	<LOD	<LOD	0.28	0.020
2010	227	699	1.5	<LOD	3.1	15	<LOD	0.23	5.2	<LOD	106	3.8	1.6	1.8	<LOD	<LOD	<LOD	0.52	30	<LOD	0.77	0.13	0.055	0.050	0.31	0.025
2009	282	1099	2.3	<LOD	2.2	15	<LOD	0.11	4.0	<LOD	44	17	1.9	2.9	<LOD	0.40	<LOD	0.90	27	<LOD	0.54	0.12	0.053	0.036	0.41	0.057
2008	324	1062	<LOD	<LOD	2.2	14	<LOD	0.15	<LOD	<LOD	25	1.9	1.5	1.7	<LOD	<LOD	<LOD	0.52	23	<LOD	0.41	0.11	0.039	<LOD	0.30	0.019
2007	353	682	0.72	<LOD	2.1	3.7	<LOD	0.18	3.3	<LOD	182	2.5	1.7	1.4	<LOD	0.34	<LOD	0.79	14	<LOD	0.64	0.13	0.65	<LOD	0.24	0.025
2006	387	791	2.5	<LOD	1.8	9.1	<LOD	0.15	1.9	<LOD	39	2.1	1.7	1.9	<LOD	<LOD	<LOD	0.59	20	<LOD	0.52	0.11	0.049	<LOD	0.32	0.028
2005/06	413	709	0.58	<LOD	3.2	0.77	<LOD	0.11	0.53	<LOD	7.4	0.96	0.76	0.59	<LOD	<LOD	<LOD	0.24	3.9	<LOD	0.37	0.090	<LOD	<LOD	<LOD	0.009
2004	447	742	2.4	<LOD	3.3	8.7	<LOD	0.68	5.5	<LOD	43	8.3	3.0	2.4	<LOD	<LOD	<LOD	0.91	25	<LOD	0.36	0.13	0.37	0.040	0.45	0.040
2003	492	1299	3.4	<LOD	1.7	5.0	<LOD	0.24	3.7	0.020	21	3.0	1.7	1.5	<LOD	<LOD	<LOD	0.53	12	<LOD	0.34	0.083	0.044	<LOD	0.33	0.041
2002	519	788	8.8	<LOD	3.1	8.7	<LOD	0.27	3.7	<LOD	55	4.2	2.8	2.9	<LOD	0.83	<LOD	2.3	26	<LOD	0.72	0.16	0.049	<LOD	0.51	0.048
2001	545	835	5.5	<LOD	3.3	15	<LOD	1.0	5.1	<LOD	47	4.2	1.5	3.6	<LOD	<LOD	<LOD	0.96	41	<LOD	0.77	0.40	0.039	0.039	0.52	0.029
2000	589	1287	3.1	<LOD	1.9	6.5	<LOD	0.25	3.5	<LOD	27	4.1	1.1	1.6	<LOD	<LOD	<LOD	0.65	15	<LOD	0.42	0.13	0.048	<LOD	0.22	0.009
1999	619	845	3.9	<LOD	3.3	5.8	<LOD	0.36	4.8	0.13	27	3.1	2.0	1.7	<LOD	<LOD	<LOD	0.98	16	<LOD	0.48	0.14	<LOD	<LOD	0.29	0.025
1998	661	1305	4.4	0.26	1.7	7.4	<LOD	0.10	3.2	<LOD	34	2.6	1.1	1.1	2.6	0.48	<LOD	0.59	24	<0.24	0.71	0.10	<LOD	0.004	0.27	0.023
1997	687	790	<3.7	<LOD	3.5	7.8	<LOD	0.073	0.77	0.023	18	3.0	1.1	1.5	<LOD	<LOD	<LOD	0.47	20	<LOD	0.34	0.17	0.077	0.043	0.42	0.024
1996	731	1456	3.9	<LOD	2.5	4.2	<LOD	0.098	2.6	<LOD	38	2.9	0.99	1.1	5.7	0.69	<LOD	0.39	19	<0.24	0.29	0.060	<LOD	<0.030	0.35	0.016
1995	774	1321	4.3	<LOD	2.8	5.1	<LOD	<LOD	2.6	<LOD	25	2.1	5.2	1.3	5.2	0.70	<LOD	1.1	21	<0.24	0.33	0.093	<LOD	<0.030	0.37	0.027
1994	804	955	0.61	<LOD	3.8	3.8	<LOD	0.071	0.75	<LOD	5.7	1.4	0.88	1.2	<LOD	<LOD	<LOD	0.24	11	<LOD	0.21	0.078	<LOD	<LOD	<LOD	0.007

assigned year	depth (cm)	melt volume (ml)	TEP	TBPO	TnBP	TiBP	TDBPP	TPPO	TCEP	TEEDP	TCPP	TDCPP	TPP	EHDP	O-TOTP	M,P-TOTP	DOPP	IDEDP	TBOEP	T35DMP	TEHP	DTBPP	T2iPPP	TTBPP	TBDPP	DIPIP
1993	837	1025	1.3	<LOD	1.8	8.5	<LOD	0.29	0.45	<LOD	12	3.8	0.89	1.5	<LOD	<LOD	<LOD	0.28	21	<LOD	0.31	0.094	0.32	<LOD	0.26	0.017
1992	877	1215	1.8	<LOD	2.6	14	<LOD	0.19	1.8	<LOD	44	2.3	1.4	3.2	<LOD	0.27	<LOD	0.78	30	<LOD	0.45	0.15	0.039	0.024	0.41	0.018
1991	927	1648	2.3	0.094	4.2	7.4	<LOD	0.072	3.0	<LOD	38	2.4	1.8	1.4	8.1	0.91	<LOD	1.00	19	0.30	0.34	0.27	<LOD	0.12	0.51	0.020
1990	957	933	2.7	<LOD	3.1	5.8	<LOD	0.11	3.3	<LOD	13	2.1	1.0	1.1	<LOD	<LOD	<LOD	0.29	13	<LOD	0.22	0.11	<LOD	<LOD	0.18	0.005
1989	987	927	3.3	<LOD	3.2	5.2	<LOD	<LOD	2.9	<LOD	30	2.4	1.0	1.1	<LOD	<LOD	<LOD	0.31	3.7	<LOD	0.19	0.11	<LOD	<LOD	0.27	<LOD
1988	1011	947	4.3	<LOD	2.4	4.6	<LOD	0.14	3.3	<LOD	29	7.3	1.3	1.2	<LOD	<LOD	<LOD	0.28	6.3	<LOD	0.22	0.14	<LOD	<LOD	<LOD	0.010
1987	1057	1542	2.6	<LOD	1.6	3.9	<LOD	<LOD	2.2	<LOD	35	1.9	0.83	1.4	4.3	0.32	<LOD	0.58	22	<0.24	0.41	0.10	0.016	0.044	0.36	0.024
1986	1081	928	3.1	<LOD	3.4	9.1	<LOD	0.26	3.6	<LOD	24	3.0	1.4	1.9	<LOD	<LOD	<LOD	0.61	27	<LOD	0.23	0.14	<LOD	<LOD	0.31	0.023
1985	1103	671	4.6	<LOD	3.3	3.5	<LOD	0.19	2.5	<LOD	12	2.4	1.1	0.90	<LOD	0.34	<LOD	0.36	11	<LOD	0.20	0.11	0.024	0.024	0.18	0.024
1984	1137	1175	4.2	<LOD	2.9	3.7	<LOD	0.20	2.5	<LOD	11	2.4	1.1	1.4	<LOD	<LOD	<LOD	0.36	16	<LOD	0.24	0.100	0.025	0.025	0.25	0.019
1983	1168	1116	3.2	<LOD	2.7	6.6	<LOD	0.24	2.6	<LOD	19	2.3	0.94	1.6	<LOD	<LOD	<LOD	0.32	29	<LOD	0.32	0.15	<LOD	<LOD	0.28	0.029
1982	1197	1032	3.0	<LOD	3.0	6.3	<LOD	0.080	3.0	<LOD	25	1.6	0.91	1.2	<LOD	<LOD	<LOD	0.31	15	<LOD	0.19	0.11	<LOD	<LOD	0.23	0.009
1981	1235	1302	4.5	<LOD	1.8	6.4	<LOD	<LOD	1.9	<LOD	30	1.8	1.0	1.1	<LOD	0.14	<LOD	0.41	12	<LOD	0.28	0.079	<LOD	<LOD	0.23	0.015
1980	1276	1507	3.6	0.17	2.0	7.1	<LOD	<LOD	3.5	<LOD	83	2.1	1.2	2.0	<LOD	0.23	<LOD	0.70	16	<LOD	0.34	0.087	<LOD	<LOD	0.25	0.019
1979	1300	804	4.8	<LOD	2.5	8.4	<LOD	0.13	2.6	<LOD	16	2.7	1.2	1.6	<LOD	<LOD	<LOD	<LOD	21	<LOD	0.27	0.27	<LOD	<LOD	0.27	0.009
1978	1316	543	1.6	<LOD	3.2	1.3	<LOD	<LOD	1.3	<LOD	9.8	1.2	0.55	0.43	<LOD	<LOD	<LOD	0.14	4.4	<LOD	0.14	0.072	<LOD	<LOD	<LOD	0.004
1977	1338	791	1.7	<LOD	1.8	0.65	<LOD	<LOD	2.4	<LOD	5.8	1.4	0.86	0.54	<LOD	<LOD	<LOD	0.23	4.1	<LOD	0.15	0.070	<LOD	<LOD	<LOD	0.010
1976	1361	852	3.2	<LOD	4.9	15	<LOD	0.19	4.0	<LOD	38	2.1	2.2	3.4	<LOD	0.80	<LOD	0.59	33	<LOD	0.47	0.18	<LOD	<LOD	0.34	0.036
1975	1385	941	2.8	<LOD	3.0	12	<LOD	0.13	3.0	0.087	54	1.8	1.0	2.2	<LOD	0.33	<LOD	0.56	28	<LOD	0.22	0.37	<LOD	<LOD	0.62	0.019

Table S8. Correlation matrix for OPE concentrations in Devon Ice Cap core. Significant ($p < 0.05$) correlations are in red. When Spearman correlation coefficient (R_s) > 0.70 , cell is shaded and $R_s > 0.80$ is in bold and outlined. Excluded are substances with detection frequencies $< 50\%$: TBPO, TDBPP, DOPP, TEHP, TTBP, TBDPP.

		TEP 36	TnBP 36	TiBP 36	TPPO 36	TCEP 36	TEEDP 25	TCPP 36	TDCPP 36	TPP 36	EHDP 36	TOTP 36	iDeDPP 36	TBOEP 36	TXP 30	DTBPPP 30	T2iPPP 31
TEP	Rs	1.00	0.60	0.61	0.28	0.61	0.12	0.54	0.43	0.34	0.31	0.57	0.59	0.50	0.01	0.20	0.25
	p-value	--	1.E-04	9.E-05	0.10	7.E-05	0.58	8.E-04	9.E-03	0.04	0.07	3.E-04	2.E-04	2.E-03	0.98	0.30	0.18
TnBP	RS	0.60	1.00	0.75	0.34	0.91	0.25	0.61	0.70	0.40	0.41	0.73	0.74	0.41	-0.01	0.33	0.31
	p-value	1.E-04	--	1.E-07	0.04	7.E-15	0.23	8.E-05	2.E-06	0.02	0.01	5.E-07	3.E-07	0.01	0.97	0.07	0.09
TiBP	RS	0.61	0.75	1.00	0.38	0.69	0.26	0.46	0.54	0.27	0.28	0.49	0.68	0.40	0.03	0.32	0.23
	p-value	9.E-05	1.E-07	--	0.02	3.E-06	0.22	5.E-03	6.E-04	0.11	0.09	2.E-03	6.E-06	0.01	0.87	0.09	0.21
TPPO	RS	0.28	0.34	0.38	1.00	0.53	-0.23	0.40	0.29	0.25	0.60	0.32	0.37	0.07	-0.04	0.15	0.12
	p-value	0.10	0.04	0.02	--	1.E-03	0.27	0.02	0.08	0.14	1.E-04	0.06	0.03	0.67	0.84	0.42	0.53
TCEP	RS	0.61	0.91	0.69	0.53	1.00	0.16	0.67	0.69	0.45	0.59	0.75	0.78	0.42	0.07	0.39	0.37
	p-value	7.E-05	7.E-15	3.E-06	1.E-03	--	0.45	7.E-06	3.E-06	0.01	1.E-04	2.E-07	2.E-08	0.01	0.70	0.03	0.04
TEEDP	RS	0.12	0.25	0.26	-0.23	0.16	1.00	0.17	0.43	0.18	-0.01	0.13	0.22	0.20	0.17	0.18	0.46
	p-value	0.58	0.23	0.22	0.27	0.45	--	0.41	0.03	0.38	0.95	0.53	0.30	0.34	0.45	0.42	0.04
TCPP	RS	0.54	0.61	0.46	0.40	0.67	0.17	1.00	0.49	0.74	0.50	0.63	0.56	0.24	-0.09	0.27	0.64
	p-value	8.E-04	8.E-05	5.E-03	0.02	7.E-06	0.41	--	3.E-03	3.E-07	2.E-03	3.E-05	4.E-04	0.16	0.64	0.14	1.E-04
TDCPP	RS	0.43	0.70	0.54	0.29	0.69	0.43	0.49	1.00	0.35	0.35	0.66	0.53	0.52	0.03	0.33	0.36
	p-value	9.E-03	2.E-06	6.E-04	0.08	3.E-06	0.03	3.E-03	--	0.04	0.04	1.E-05	8.E-04	1.E-03	0.90	0.07	0.05
TPP	RS	0.34	0.40	0.27	0.25	0.45	0.18	0.74	0.35	1.00	0.39	0.38	0.42	0.07	0.00	0.16	0.83
	p-value	0.04	0.02	0.11	0.14	6.E-03	0.38	3.E-07	0.04	--	0.02	0.02	0.01	0.68	0.98	0.40	9.E-09
EHDP	RS	0.31	0.41	0.28	0.60	0.59	-0.01	0.50	0.35	0.39	1.00	0.54	0.57	0.12	-0.11	0.40	0.21
	p-value	0.07	0.01	0.09	1.E-04	1.E-04	0.95	2.E-03	0.04	0.02	--	7.E-04	3.E-04	0.47	0.56	0.03	0.27
TOTP	RS	0.57	0.73	0.49	0.32	0.75	0.13	0.63	0.66	0.38	0.54	1.00	0.69	0.36	-0.06	0.42	0.39
	p-value	3.E-04	5.E-07	2.E-03	0.06	2.E-07	0.53	3.E-05	1.E-05	0.02	7.E-04	--	3.E-06	0.03	0.74	0.02	0.03
iDeDPP	RS	0.59	0.74	0.68	0.37	0.78	0.22	0.56	0.53	0.42	0.57	0.69	1.00	0.23	0.00	0.32	0.31
	p-value	2.E-04	3.E-07	6.E-06	0.03	2.E-08	0.30	4.E-04	8.E-04	0.01	3.E-04	3.E-06	--	0.17	1.00	0.08	0.09
TBOEP	RS	0.50	0.41	0.40	0.07	0.42	0.20	0.24	0.52	0.07	0.12	0.36	0.23	1.00	-0.02	0.23	0.15
	p-value	2.E-03	0.01	0.01	0.67	0.01	0.34	0.16	1.E-03	0.68	0.47	0.03	0.17	--	0.93	0.22	0.43
TXP	RS	0.01	-0.01	0.03	-0.04	0.07	0.17	-0.09	0.03	0.00	-0.11	-0.06	0.00	-0.02	1.00	0.24	0.14
	p-value	0.98	0.97	0.87	0.84	0.70	0.45	0.64	0.90	0.98	0.56	0.74	1.00	0.93	--	0.24	0.49
DTBPPP	RS	0.20	0.33	0.32	0.15	0.39	0.18	0.27	0.33	0.16	0.40	0.42	0.32	0.23	0.24	1.00	0.28
	p-value	0.30	0.07	0.09	0.42	0.03	0.42	0.14	0.07	0.40	0.03	0.02	0.08	0.22	0.24	--	0.17
T2iPPP	RS	0.25	0.31	0.23	0.12	0.37	0.46	0.64	0.36	0.83	0.21	0.39	0.31	0.15	0.14	0.28	1.00
	p-value	0.18	0.09	0.21	0.53	0.04	0.04	1.E-04	0.05	9.E-09	0.27	0.03	0.09	0.43	0.49	0.17	--

Table S9 Correlation matrix for OPE concentrations in Mt. Oxford core. Significant ($p < 0.05$) correlations are in red. When Spearman correlation coefficient (R_s) > 0.70 , cell is shaded and $R_s > 0.80$ is in bold and outlined. Excluded are substances with detection frequencies $< 50\%$: TEEDP, TOTP, TXP.

		TEP	TnBP	TIBP	TPPO	TCEP	TCPP	TDCPP	TPP	EHDP	IDEDPP	TBOEP	TEHP	DTBPPP	T2iPPP	TBDPP	DIPI
	# Detects	41	43	43	35	42	43	43	43	43	42	43	43	43	22	38	42
TEP	RS	1.00	0.20	0.27	0.14	0.30	0.21	0.44	0.48	0.32	0.49	0.35	0.34	0.41	-0.25	0.24	0.45
	p-value	--	0.21	0.09	0.38	0.09	0.18	4.E-03	1.E-03	0.04	1.E-03	0.02	0.03	0.01	0.29	0.17	4.E-03
TnBP	RS	0.20	1.00	0.26	0.09	0.07	0.04	0.23	0.33	0.28	0.23	0.29	0.11	0.53	0.22	0.44	0.26
	p-value	0.21	--	0.09	0.56	0.70	0.80	0.13	0.03	0.06	0.14	0.06	0.49	3.E-04	0.33	0.01	0.09
TIBP	RS	0.27	0.26	1.00	0.33	0.24	0.61	0.52	0.63	0.86	0.61	0.86	0.65	0.71	0.20	0.63	0.60
	p-value	0.09	0.09	--	0.03	0.17	1.E-05	3.E-04	6.E-06	1.E-13	2.E-05	2.E-13	2.E-06	1.E-07	0.37	2.E-05	2.E-05
TPPO	RS	0.14	0.09	0.33	1.00	1.00	0.13	0.49	0.34	0.46	0.23	0.35	0.35	0.32	0.03	0.07	0.33
	p-value	0.38	0.56	0.03	--	--	0.42	7.E-04	0.03	2.E-03	0.15	0.02	0.02	0.03	0.88	0.66	0.03
TCEP	RS	0.30	0.07	0.24	1.00	1.00	0.20	0.48	0.38	0.49	0.31	0.33	0.33	0.20	0.02	0.08	0.41
	p-value	0.09	0.70	0.17	--	--	0.26	3.E-03	0.02	3.E-03	0.07	0.05	0.05	0.25	0.95	0.68	0.02
TCPP	RS	0.21	0.04	0.61	0.13	0.20	1.00	0.46	0.63	0.69	0.73	0.62	0.70	0.52	0.45	0.58	0.60
	p-value	0.18	0.80	1.E-05	0.42	0.26	--	2.E-03	6.E-06	3.E-07	3.E-08	9.E-06	2.E-07	4.E-04	0.03	1.E-04	3.E-05
TDCPP	RS	0.44	0.23	0.52	0.49	0.48	0.46	1.00	0.65	0.57	0.58	0.52	0.59	0.56	0.53	0.47	0.63
	p-value	4.E-03	0.13	3.E-04	7.E-04	3.E-03	2.E-03	--	3.E-06	7.E-05	5.E-05	4.E-04	4.E-05	9.E-05	1.E-02	3.E-03	7.E-06
TPP	RS	0.48	0.33	0.63	0.34	0.38	0.63	0.65	1.00	0.73	0.87	0.62	0.72	0.61	0.41	0.64	0.83
	p-value	1.E-03	0.03	6.E-06	0.03	0.02	6.E-06	3.E-06	--	3.E-08	1.E-13	1.E-05	4.E-08	2.E-05	0.06	1.E-05	2.E-11
EHDP	RS	0.32	0.28	0.86	0.46	0.49	0.69	0.57	0.73	1.00	0.76	0.85	0.73	0.74	0.22	0.72	0.72
	p-value	0.04	0.06	1.E-13	2.E-03	3.E-03	3.E-07	7.E-05	3.E-08	--	6.E-09	6.E-13	3.E-08	2.E-08	3.E-01	4.E-07	9.E-08
IDEDPP	RS	0.49	0.23	0.61	0.23	0.31	0.73	0.58	0.87	0.76	1.00	0.68	0.77	0.64	0.33	0.70	0.78
	p-value	1.E-03	0.14	2.E-05	0.15	0.07	3.E-08	5.E-05	1.E-13	6.E-09	--	8.E-07	2.E-09	4.E-06	0.13	1.E-06	2.E-09
TBOEP	RS	0.35	0.29	0.86	0.35	0.33	0.62	0.52	0.62	0.85	0.68	1.00	0.70	0.72	0.22	0.76	0.70
	p-value	0.02	0.06	2.E-13	0.02	0.05	9.E-06	4.E-04	1.E-05	6.E-13	8.E-07	--	2.E-07	5.E-08	0.32	4.E-08	3.E-07
TEHP	RS	0.34	0.11	0.65	0.35	0.33	0.70	0.59	0.72	0.73	0.77	0.70	1.00	0.53	0.37	0.59	0.76
	p-value	0.03	0.49	2.E-06	0.02	0.05	2.E-07	4.E-05	4.E-08	3.E-08	2.E-09	2.E-07	--	2.E-04	0.09	9.E-05	4.E-09
DTBPPP	RS	0.41	0.53	0.71	0.32	0.20	0.52	0.56	0.61	0.74	0.64	0.72	0.53	1.00	0.31	0.65	0.55
	p-value	0.01	3.E-04	1.E-07	0.03	0.25	4.E-04	9.E-05	2.E-05	2.E-08	4.E-06	5.E-08	2.E-04	--	0.16	1.E-05	2.E-04
T2iPPP	RS	-0.25	0.22	0.20	0.03	0.02	0.45	0.53	0.41	0.22	0.33	0.22	0.37	0.31	1.00	0.29	0.38
	p-value	0.29	0.33	0.37	0.88	0.95	0.03	0.01	0.06	0.33	0.13	0.32	0.09	0.16	--	0.19	0.08
TBDPP	RS	0.24	0.44	0.63	0.07	0.08	0.58	0.47	0.64	0.72	0.70	0.76	0.59	0.65	0.29	1.00	0.68
	p-value	0.17	0.01	2.E-05	0.66	0.68	1.E-04	3.E-03	1.E-05	4.E-07	1.E-06	4.E-08	9.E-05	1.E-05	0.19	--	3.E-06
DIPI	RS	0.45	0.26	0.60	0.33	0.41	0.60	0.63	0.83	0.72	0.78	0.70	0.76	0.55	0.38	0.68	1.00
	p-value	4.E-03	0.09	2.E-05	0.03	0.02	3.E-05	7.E-06	2.E-11	9.E-08	2.E-09	3.E-07	4.E-09	2.E-04	0.08	3.E-06	--

Table S10. Temporal trend for deposition of OPEs in Devon Ice Cap based on natural logarithm of flux versus year for 1979-2015. Doubling time was calculated for those OPEs which displayed first order kinetics ($p < 0.05$).

OPE	R ²	Degrees of freedom	Slope ± standard error (y ⁻¹)	p-value	Doubling time ± standard error (y)
Devon Ice Cap, first order kinetics*					
TEP	0.286	35	0.036 ± 0.010	0.0008	19 ± 5.2
TnBP	0.587	35	0.043 ± 0.0062	5.1 × 10 ⁻⁸	16 ± 2.3
TiBP	0.311	35	0.026 ± 0.0066	0.0004	27 ± 6.8
TCEP	0.519	35	0.040 ± 0.0065	7.2 × 10 ⁻⁷	18 ± 2.9
TCPP	0.342	35	0.064 ± 0.015	0.0002	11 ± 2.6
TDCPP	0.289	35	0.030 ± 0.0081	0.0007	23 ± 6.2
TPP	0.163	35	0.041 ± 0.016	0.015	17 ± 6.6
iDeDPP	0.637	35	0.068 ± 0.0088	5.6 × 10 ⁻⁹	10 ± 1.3
TOTP	0.311	35	0.036 ± 0.0093	0.0004	19 ± 4.9
T2iPPP	0.210	35	0.044 ± 0.015	0.0064	16 ± 5.4
TPPO	0.0644	35	0.022 ± 0.0145	0.14	
TBOEP	0.0949	35	0.016 ± 0.0083	0.068	
EHDPP	0.0624	35	0.012 ± 0.0082	0.14	
T35DMPP	0.0208	29	-0.013 ± 0.016	0.45	
DTBPPP	0.0185	35	0.0098 ± 0.013	0.44	

* TPPO, TBOEP, EHDPP, TXP and DTBPP did not display first order kinetics in the Devon Ice Cap

Table S11. Correlation matrix for OPE concentrations and particle concentrations after log transformation. Significant ($p < 0.05$) correlations in shaded cells. Excluded are substances with detection frequencies $< 50\%$: in Devon Ice Cap, these were TBPO, TDBPP, DOPP, TEHP, TTBPP, TBDPP and in the Mt. Oxford icefield these were TEEDP, TOTP, TXP. The particle concentrations are separated into size bins with partcnt2 corresponding to 2.4 to 4.5 micron and partcnt3 corresponding to 4.5 to 10 micron.

		TEP	TnBP	TiBP	TPPO	TCEP	TEEDP	TCPP	TDCPP	TPhP	EHDPP	TOTP	iDeDP P	TBOEP	T35D MPP	TEHP	DTBPPP	T2iPP P	
a) Devon Ice Cap																			
measured partcnt2, ppm	R _s	0.26	0.50	0.31	0.054	0.51	-0.11	-0.047	0.28	-0.17	0.27	0.11	0.44	0.12	0.06	0.17	0.00	-0.21	
	p-value	0.073	0.0003	0.033	0.72	0.0002	0.55	0.75	0.053	0.25	0.069	0.44	0.0019	0.45	0.73	0.48	1.00	0.20	
measured partcnt3, ppm	R _s	0.25	0.54	0.32	0.11	0.55	-0.100	-0.057	0.28	-0.14	0.31	0.13	0.50	0.11	0.02	0.03	-0.09	-0.23	
	p-value	0.092	0.0001	0.027	0.46	5E-04	0.58	0.70	0.053	0.36	0.032	0.37	0.0003	0.48	0.91	0.90	0.59	0.16	
b) Oxford icefield																			
		TEP	TnBP	TiBP	TPPO	TCEP	TCPP	TDCPP	TPhP	EHDPP	iDeDP P	TBOEP	TEHP	DTBPP	T2iPPP	TBDPP	DIPI		
measured partcnt2, ppm	R _s	0.44	0.76	0.25	-0.069	0.68	0.16	0.19	0.52	0.29	0.34	0.57	0.63	0.68	0.082	0.56	0.49		
	p-value	0.0032	5.1E-9	0.11	0.66	5.9E-7	0.30	0.22	4.3E-4	0.062	0.030	9.2E-5	8.61E-7	0.61	1.0E-4	9.3E-4	0.32		
measured partcnt3, ppm	R _s	0.52	0.80	0.29	-0.063	0.80	0.25	0.30	0.54	0.33	0.43	0.65	0.71	0.69	0.14	0.58	0.51		
	p-value	3.8E-4	1.8E-10	0.063	0.69	3.0E-10	0.11	0.054	2.1E-4	0.031	0.0050	2.9E-6	1.2E-7	4.3E-7	0.36	6.0E-05	5.3E4		

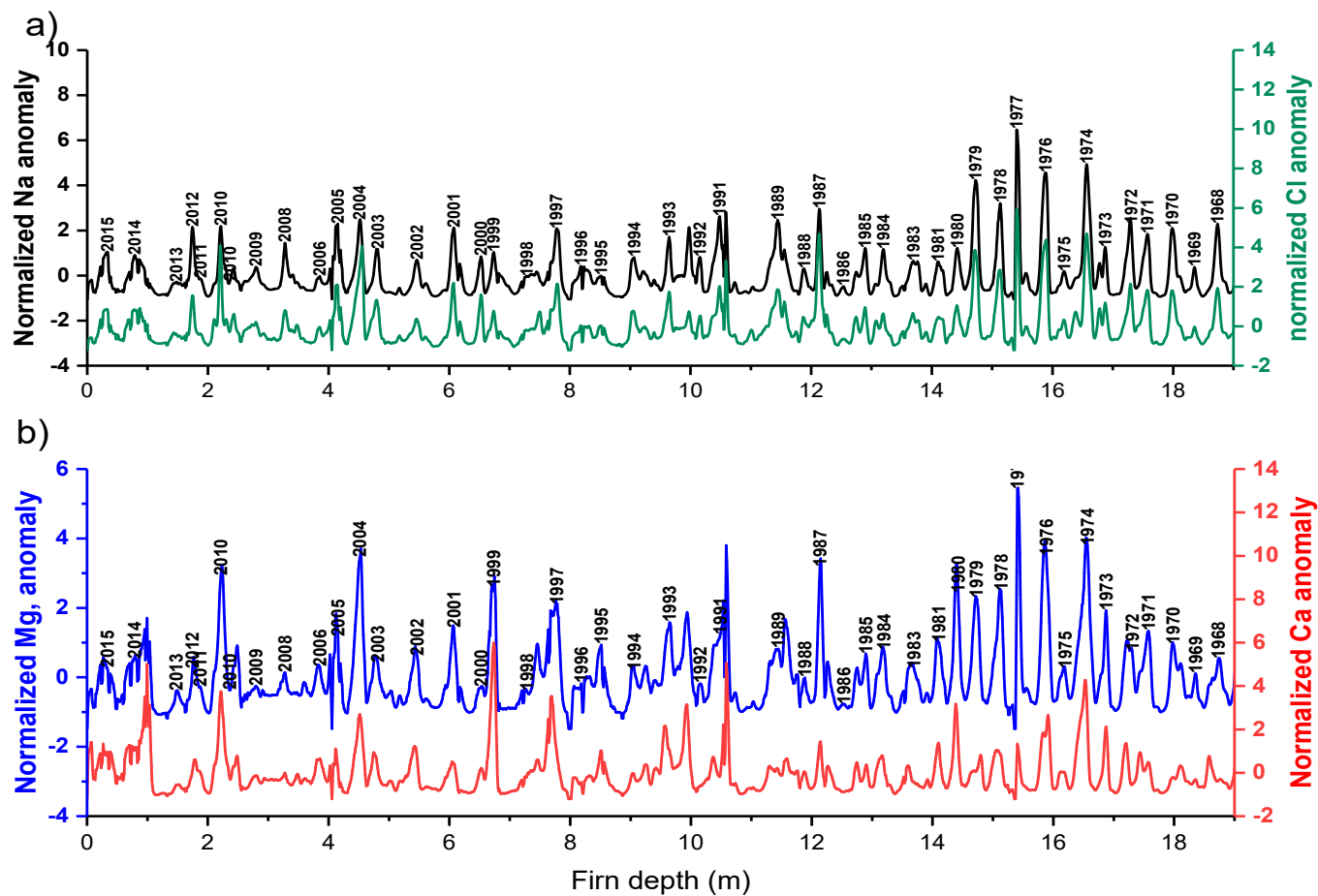
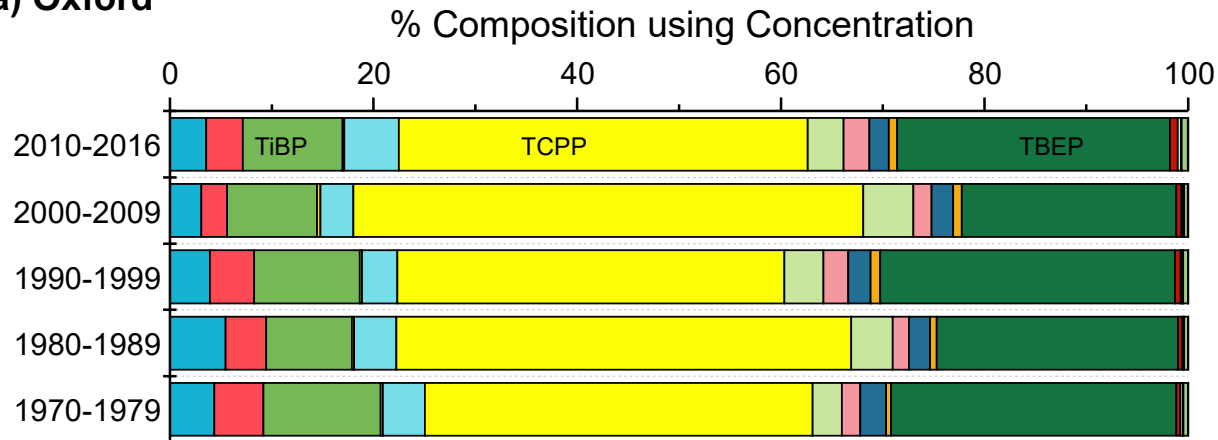


Figure S1. Major ions measured in 1 cm intervals in firn core, 0.5 cm to 19.165 cm depth in Devon Ice Cap ice core, expressed as normalized anomaly* with labels corresponding to winter maxima year: a) sodium (Na), Chloride (Cl) and b) magnesium (Mg) and

Calcium (Ca). * normalized anomaly = $\frac{(X - \mu)}{\sigma}$ where X is data point, μ and σ are average and standard deviation, respectively, for the entire length of the core. Three-point moving average smoother applied.

a) Oxford



b) Devon

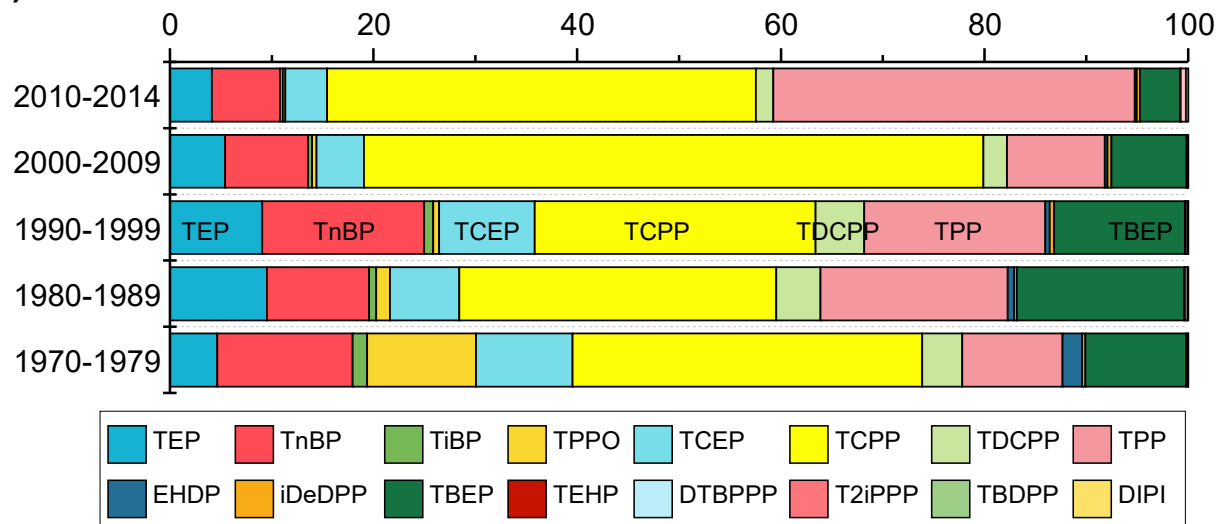


Figure S2. Multi-year binned composition of OPEs using concentration in ice cores from a) Mt. Oxford ice field and b) Devon Ice Cap.

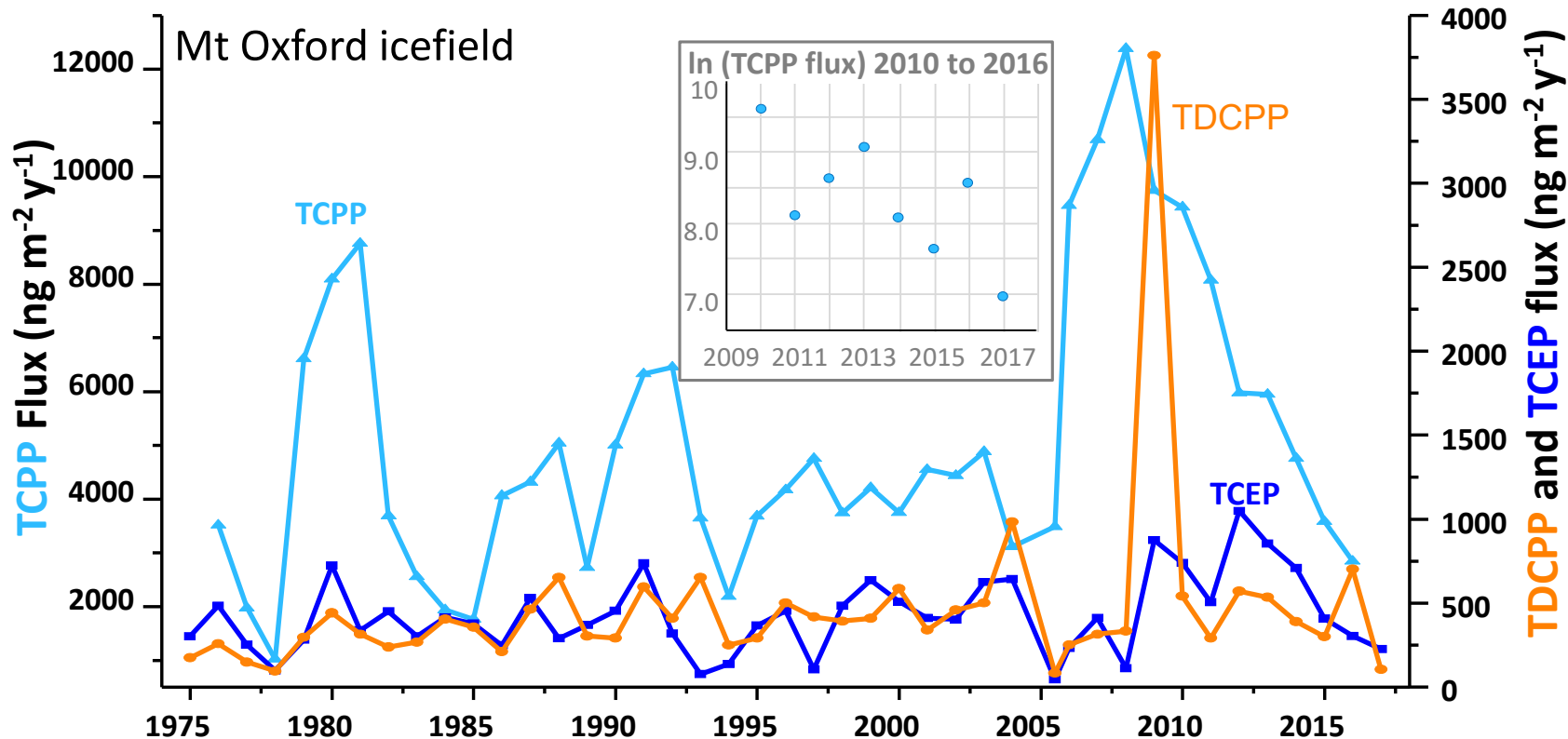


Figure S3. Annual flux (ng m^{-2}) of TCPP, TCEP, and TDCPP in Mt. Oxford icefield core from 1975 to 2017. Magnitude of TCPP corresponds to left y-axis and TDCPP, TCEP to the right y-axis. Inset shows first order decline in TCPP flux from 2010 to 2017, elimination half-life of $2.9 \pm 1.2 \text{ y}$ ($r^2 = 0.51$, $p = 0.047$). Note: Measurement in 2017 is 5.5 months of accumulation and not a full year.

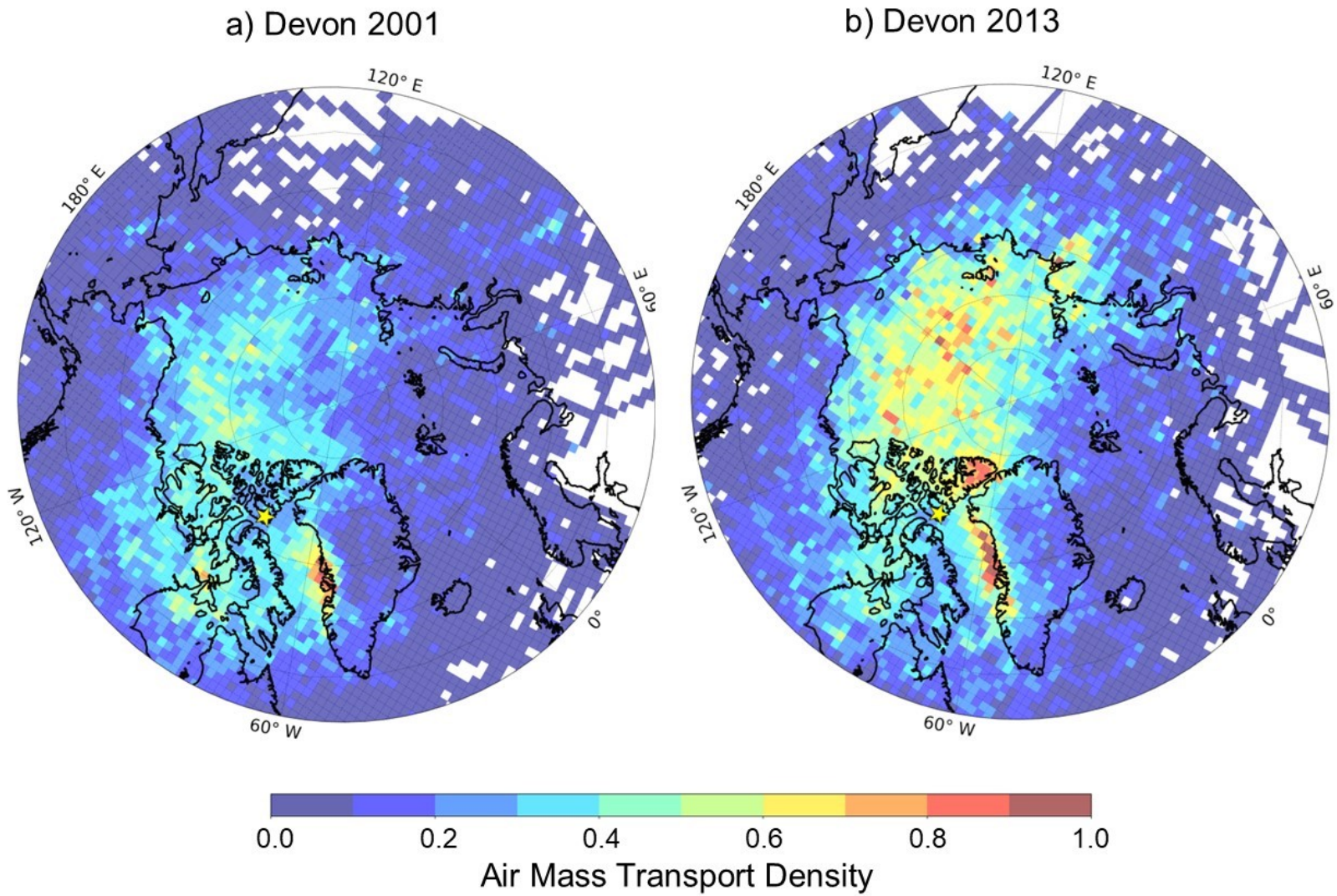


Figure S4. Air mass density back trajectory for Devon Ice Cap (star) for a) 2001 and b) 2013.

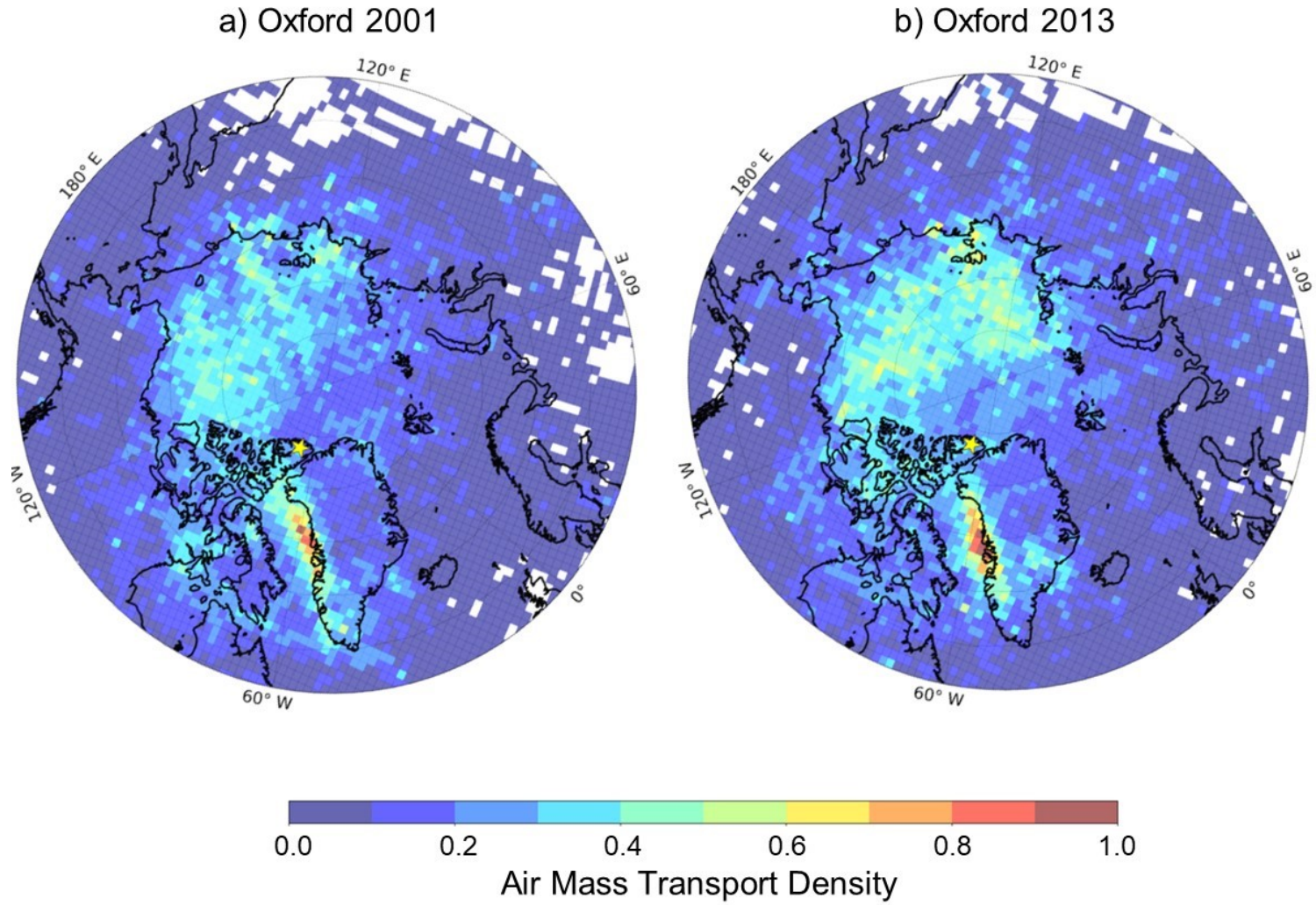


Figure S5. Air mass density back trajectory for Mt. Oxford icefield (star) for a) 2001 and b) 2013.

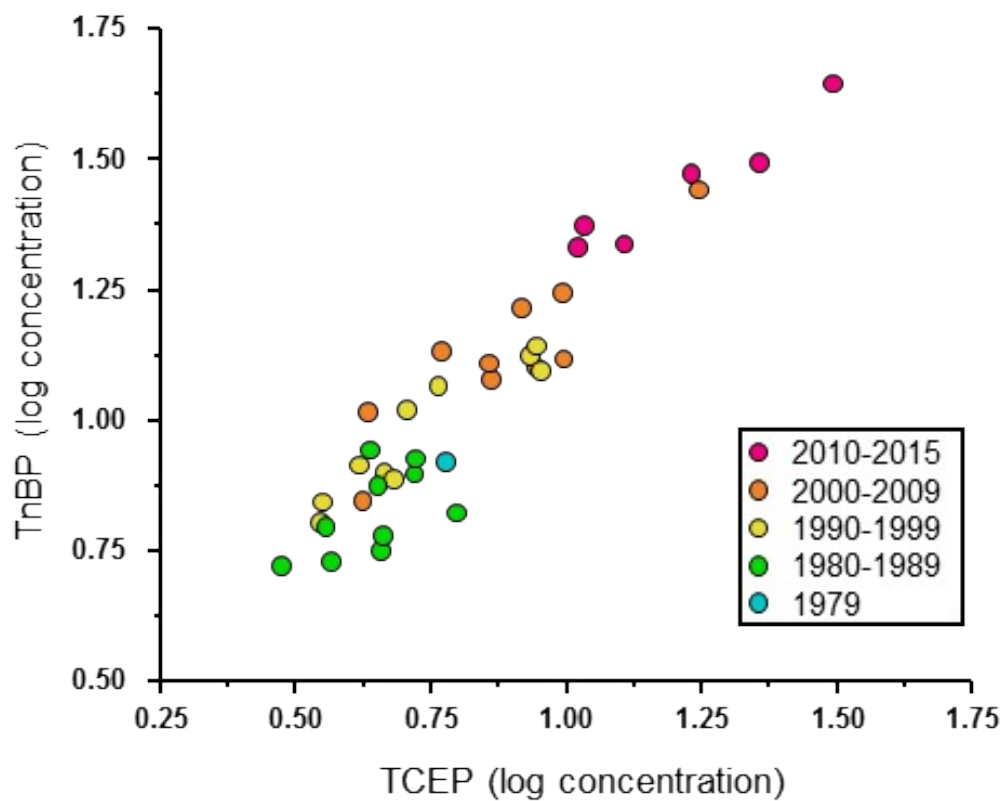


Figure S6. Correlation between log transformed concentrations of tributylphosphate (TnBP) and trichloroethylphosphate (TCEP) in Devon Ice Cap with colour shading corresponding to decade. Spearman correlation coefficient, $R_S = 0.90$ and $p < 0.001$.

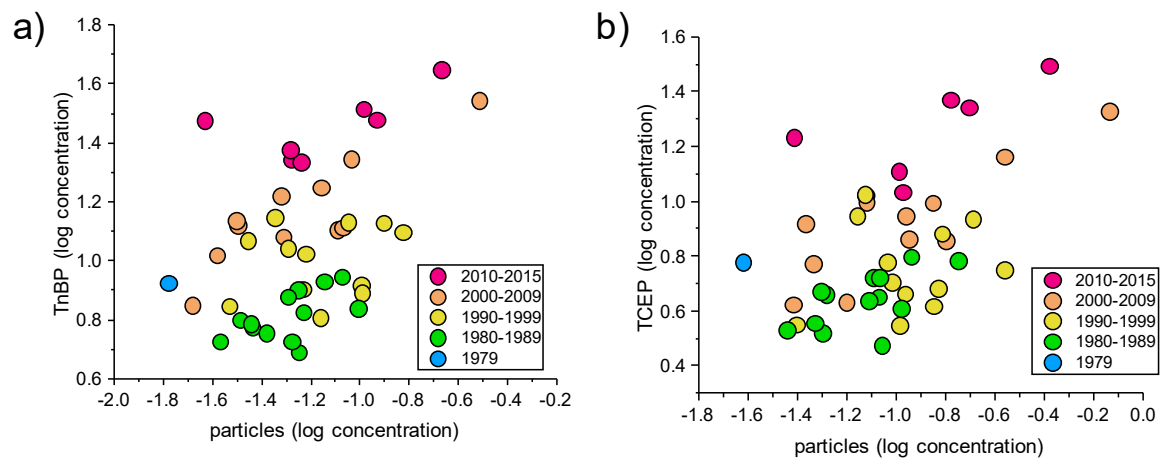


Figure S7 Correlation of log transformed a) tri-*n*-butyl phosphate (ng L^{-1} TnBP); $R_S = 0.54$, $p=6.8\text{E-}5$ and b) trichloroethyl phosphate (ng L^{-1} TCEP); $R_S = 0.55$, $p= 4.5\text{E-}5$ with particle concentration ($\mu\text{g ml}^{-1}$) in dated ice core sections from the Devon Ice Cap.

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