Simmonds, P. G., Palmer, P. I., Rigby, M., McCulloch, A., O'Doherty, S., & Manning, A. J. (2021). Tracers for evaluating computational models of atmospheric transport and oxidation at regional to global scales. *Atmospheric Environment*, 246, [118074].
<https://doi.org/10.1016/j.atmosenv.2020.118074>

Peer reviewed version

License (if available):
CC BY-NC-ND

Link to published version (if available):
[10.1016/j.atmosenv.2020.118074](https://doi.org/10.1016/j.atmosenv.2020.118074)

[Link to publication record in Explore Bristol Research](#)
PDF-document

This is the author accepted manuscript (AAM). The final published version (version of record) is available online via Elsevier at <https://doi.org/10.1016/j.atmosenv.2020.118074>. Please refer to any applicable terms of use of the publisher.

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
<http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>

Tracers for evaluating computational models of atmospheric transport and oxidation at regional to global scales.

P. G. Simmonds^{a*}, P. I. Palmer^b, M. Rigby^a, A. McCulloch^a, S. O'Doherty^a, and A.J. Manning^c.

^a School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom.

^b School of GeoSciences, University of Edinburgh, Edinburgh, EH9 3FF, United Kingdom.

^c Meteorological Office, Fitzroy Road, Exeter, Devon, EX1 3PB, United Kingdom.

*Corresponding author.

E-mail address: petergsimmonds@aol.com

Abstract

Atmospheric tracers are effective tools for characterizing dispersion and for testing computational models of atmospheric transport. Atmospheric trace gas measurements are now used widely to infer geographical surface flux distributions. However, robust flux estimates critically rely on well-validated knowledge of atmospheric chemistry, loss processes and transport, without which we are not fully realizing the potential of atmospheric measurements collected on the ground, or from aircraft and satellites. This challenge has taken on renewed importance in the shadow of the Paris Agreement that will likely take advantage of atmospheric trace gas measurements to help improve national and global greenhouse gas emission budgets. We describe a wide range of existing and new potential atmospheric tracers for improving our understanding of atmospheric dispersion. We consider the investigation of atmospheric transport over two scales: 1) short-to-medium length scale (on the order of 1-1000 km) to improve our understanding of convection and boundary layer transport processes, and 2) hemisphere-to-global length scale (on the order of 1000-10,000 km), where large-scale mixing, cross hemisphere transport and stratosphere-troposphere exchange are important. Although we note the possibility of using “tracers of opportunity,” our primary focus is on deliberate-release tracers, and we explore the use of cyclic perfluorocarbons, hydrofluorocarbons, hydrochlorofluorocarbons, hydrofluoroethers and novel tracers of deuterium-substituted halocarbons. We examine how we might exploit existing instrumentation already deployed at remote global monitoring sites as well as requirements for new instrumentation. To guide the discussion, we provide example scenarios for how experiments might be set-up, covering regional to global spatial scales for the evaluation and improvement of atmospheric transport models. However, we stress that appropriate three-dimensional modelling studies and preliminary experiments would need to be carried out to determine the specific details of any real-world experiment.

Key Words: Deliberate-release tracers. Atmospheric transport, dispersion and oxidation.

1. Introduction

Natural and anthropogenic greenhouse gases, ozone depleting substances and air pollutants are widely recognised as a potential threat to the long-term stability of the Earth's climate, the ozone layer and human health. Studies of these gases have focused attention on the important role of atmospheric dispersion in the fate of these chemicals, as they are distributed throughout the global atmosphere (Johnson, 1983). Numerous computational models have been developed to simulate the transport and dispersion of pollutants from their sources (Wang et al., 1998; Draxler and Hess 1998; Stein et al., 2015, Pisso et al., 2019). Fundamental to the evaluation and validation of these various models is the deliberate release and atmospheric measurement of known quantities of tracer compounds. The earliest attempts at tracing dispersion plumes involved smoke and fluorescent particles (Pasquill, 1974). These simple methods were subsequently replaced by experiments using more sophisticated tracers, such as deuterated methanes, sulphur hexafluoride (SF₆) and cyclic perfluorocarbons (c-PFCs), which have the desirable properties of being non-toxic, non-depositing, having low water-solubility and, most importantly, having a very small atmospheric background concentration (Lovelock and Ferber, 1982; Martin et al, 2011). These studies provided valuable data on which to test and refine atmospheric transport models, especially the role of turbulent mixing, under a limited number of meteorological conditions up to distances of ~100 kms. Unfortunately, SF₆ has become progressively less useful as a tracer due a very large Global Warming Potential (GWP) of 23500 over a 100-year time horizon (Myhre et al., 2013) and the substantial increase in its atmospheric background concentration (Rigby et al., 2010, Simmonds et al., 2020).

In this paper, we discuss deliberate-release tracers (DRTs) as a realistic option for continued evaluation and improvement of atmospheric chemical transport models in the future and propose a subset of compounds that could be viable for this purpose. There are several reasons why such a thought experiment is timely:

- a) Transport model uncertainties have the potential to severely bias top-down estimates of greenhouse gas fluxes at global (e.g. Houweling et al., 2010; Chevallier et al, 2014) and regional (e.g. Bergamaschi, et al., 2015; Palmer et al, 2019) scales. Without improvement, these model uncertainties will prevent the full value of new greenhouse gas measurement systems from being realised.
- b) There is much debate about the magnitude and variability of the atmosphere's oxidising capacity, which is poorly constrained by existing measurements and models, but which determines the lifetime of many key greenhouse gases, ozone depleting substances and air pollutants (e.g. Montzka et al., 2011; Patra et al., 2014; Rigby et al., 2017, Turner 2017).
- c) Particularly due to the growth in satellite missions, billions of dollars have been spent on observing systems for measuring greenhouse gases, ozone depleting substances and air pollutants.
- d) Previous DRT experiments were carried out on a campaign basis in limited areas of the world. Given the spatial and temporal heterogeneity of atmospheric transport, this potentially leaves certain small-scale processes (e.g. convection), or large-scale transport phenomena (e.g. inter-hemispheric or stratosphere-troposphere exchange), poorly characterised.

85 We examine DRTs to investigate atmospheric transport at two broad scales: short-to-
 86 medium range transport (on the order of 1-1000 km), where understanding of processes such
 87 as convection, turbulent mixing, stratification, boundary layer transport, entrainment to the
 88 free-troposphere and the role of the residual boundary layer are the target, and hemisphere-to-
 89 global spatial scales (on the order of 1000-10,000 km), where large scale transport and
 90 oxidation are the subject of investigation. For the sake of discussion, we provide ourselves
 91 with a set of broad constraints and specifications for possible experiments at these two scales
 92 as outlined in the following paragraphs, although we acknowledge a wide range of
 93 experimental setups is of course possible.

94 In the absence of DRTs, some natural sources have been exploited for studying
 95 atmospheric dispersion. Radon that is naturally emitted from the land surface has been widely
 96 used as a tracer, particularly for assessing vertical transport (Feichter and Crutzen, 1990;
 97 Jacob and Prather, 1990; Aoshima et al., 2005; Karstens et al., 2015, Grossi et al., 2016;
 98 Williams et al., 2016). However, there remain substantial uncertainties regarding the
 99 magnitude and variability of radon flux (which is influenced by factors such soil moisture,
 100 Karstens, et al. 2015), which will limit the accuracy of model calibration efforts based on
 101 radon measurements. Furthermore, because of its relatively short half-life (~4 days), it is only
 102 suitable for small-scale tracer studies.

103 Other examples of natural experiments include the study of volcanic eruptions and
 104 large wildfires e.g., Black Saturday 2009 (Glatthor et al, 2013) or the 2019 bushfires in
 105 Southeast Australia. However, in general emissions from these events are highly uncertain and
 106 furthermore, they often involve atmospheric chemistry that is poorly constrained by the
 107 available observations, or they may even perturb atmospheric mixing. Consequently, to probe
 108 atmospheric transport using such “natural” phenomena, researchers have either relied on
 109 estimating the photochemical age of air, taking advantage of e-folding lifetimes of multiple
 110 tracers determined by a common loss process (e.g., Parrington et al, 2013), or used a model to
 111 study the physical age of air (Finch et al, 2014, Butler et al, 2018).

112 An alternative approach to the use of DRTs or natural sources is to use an
 113 anthropogenic “tracer of opportunity”, where emissions are thought to be well known. Gases,
 114 such as methyl chloroform (CH_3CCl_3), have been used for this purpose to estimate global
 115 hydroxyl radical concentrations (e.g., Prinn et al., 1987). The influence of uncertainties in the
 116 emissions of these tracers can be substantial, particularly where there is sparse measurement
 117 coverage and there is the potential for un-reported emissions biasing results (Palmer et al.,
 118 2003; Rigby et al., 2017). However, in future, such studies may be possible, if researchers can
 119 identify a compound or compounds that are only produced by a small number of cooperative
 120 industries, who could supply robust estimates of release rates to the atmosphere.

121 We should also note the Chernobyl nuclear accident which prompted the development
 122 of several new atmospheric dispersion models and also provided an opportunity to test
 123 existing atmospheric transport models (ATMES Report 1993). These events are of course

difficult to use for model evaluation as they are infrequent and unpredictable, and release rates are often not well known.

1.1 General considerations

The gold standard for a successful tracer dispersion experiment is the quantitative release of an atmospheric tracer that; 1) does not exist in the ambient atmosphere (i.e. zero background in at least the vicinity of the release); 2) has a well-defined atmospheric lifetime that is appropriate for the atmospheric transport process being studied; 3) can be measured with high precision at the point of detection with a suitably wide distribution of instruments; and; 4) does not have any deleterious long-term environment impact. The experiment should be complemented by comprehensive meteorological measurements over the course of the experiment and a select number of computational models should be compared in evaluating the experimental data.

In practice, the physical properties of a particular tracer will need to be carefully considered for the desired application, and appropriate compromises made. The use of highly exotic, potentially long-lived, tracers (as in previous experiments, e.g. Lovelock and Ferber, 1982) require that only small amounts need to be released to over-power the local background for small-scale experiments. However, over time, the persistent increase in the background concentration may make such an experiment more challenging. In contrast, shorter-lived tracers could be released in larger amounts or over more sustained periods without substantially adding to the background concentration. For this type of study, lifetime is critical. A trace gas with a short e-folding lifetime (τ) of, say, seconds to an hour has the advantage of being easily identified above any ambient background, which, in general, would be low. However, such a gas would only be detectable over short length and time scales. Conversely, a trace gas with a long τ of, say, several months to years (longer than hemispheric-scale mixing) can be considered to be well-mixed in the atmosphere. This has the advantage that we can observe that trace gas far from the point of release, but the potential disadvantage, from the point of view of a small-scale experiment, that continued release would add to the background concentration, which would then need to be well characterised. Figure 1 illustrates that, between these two extremes is a collection of compounds with ‘Goldilocks’ lifetimes. In this illustrative example of short-to-medium tracer release experiment, these lifetimes range from several hours to several days that will generate an observable value above ambient but also be removed from the atmosphere on timescales corresponding to a spatial scale of 100s km. Finally, if hemispheric to global scale investigation is required, it would be in fact desirable to achieve a detectable increase in the global background, which would be monitored over time to investigate large-scale transport phenomena.

Throughout this paper we define tracer concentrations in ppt (parts per trillion, 1×10^{-12} mol/mol) and ppq (parts per quadrillion, 1×10^{-15} mol/mol).

In the tables 1-6, we use our judgement to identify atmospheric chemistry tracers that are suitable for a specific application. In practice, collecting proof-of-concept atmospheric measurements and 3-D atmospheric modelling would be required to determine if a tracer is appropriate for a specific application. We have described these applications as “small-scale campaign” for tracers that are longer-lived than our Goldilocks window, and therefore may not be appropriate for sustained long-term release because they add to global backgrounds and may have negative environmental impact; “small-scale” for Goldilocks compounds that probe small-scale (1-1000 km) atmospheric transport phenomena, and “hemispheric-global scale” (1,000-10,000 km) for compounds that would be mixed over hemispheric to global scales.

Figure 1. Schematic that illustrates the Goldilocks atmospheric e-folding lifetime (τ) of DRTs for a short-to-medium range tracer release experiment. The coloured bar represents the spectrum of possible lifetimes ranging from (sub) seconds on the left-hand scale to years on the right-hand scale, with the associated measurement challenges denoted at points along the spectrum.

1.2 Potential short-to-medium range Deliberate Release Tracer (DRT) experimental setup.

Previous short-to-medium range studies (length scales on the order of 1-1000 km) have used single release points and an extensive network of surface-based measurements (Draxler et al., 1991, Nodop et al., 1998) and/or aircraft sampling (Methven et al., 2006). It is also possible that, given the nature and the spatial and temporal scales associated with, for example, convective systems, a rapid deployment measurement strategy may be required that brings together mobile technologies (Figure 2). We are considering convective systems in the broadest sense associated with a range of spatial scales, e.g. pyro-convection triggered by large fires (e.g., the 2009 Black Saturday bushfires), natural convective urban dome flow driven by urban heat

islands, and large inland lakes that result in differential surface heating. Some of these examples are reasonably predictable (influence of cities and lakes) and even large fires typically persist for several days over the same regions each year.

In the case of convective systems, data would be collected in order to develop more robust, improved parameterisations of, for example, entrainment and detrainment associated with sub-grid scale eddies. A field campaign focus would rely mostly on aircraft measurement of vertical gradients, although ground-based *in situ* instruments could play a smaller role in the overall experiment, where tall towers, located at some observing sites, could also provide some information on vertical mixing. Given the horizontal gradients in vertical wind speed associated with convection and the responsible surface heating (e.g. large fires), aircraft measurements may be restricted to the edges of convective cells, which can help characterize the role of eddies and larger-scale detrainment of rising air into the horizontal mean flow.

Gradients of selected trace gases within the cell can be obtained via remote sensing technologies, e.g. multi axis differential optical absorption spectroscopy (Hönninger et al, 2004), either onboard the aircraft or from the ground. Other balloon-borne technologies, such as AirCore, may provide information about vertical gradients within the convective cell (Karion et al., 2010). Past work has emphasized the importance of correctly describing vertical gradients of atmospheric tracers when using atmospheric models to infer surface fluxes of CO₂ from atmospheric data, (e.g. Stephens et al, 2007).

A technical challenge faced by this kind of experiment is that DRTs would need to be measurable using instruments that can be integrated on a range of instrument platforms. This is non-trivial and represents an additional constraint on the range of tracers that could be used for this kind of DRT experiment.

Figure 2. Schematic of an experimental setup to study atmospheric dispersion associated with rapid convective mixing. Figure is not drawn to scale, but indicative length scales for the convective system range from 1 – 1000 km.

Similar experimental designs would also be relevant for studying atmospheric transport of emissions from urban hotspots, e.g. cities and industry complexes. Accurate modelling of atmospheric dispersion of urban emissions is critical if we are to use *in situ* and downwind atmospheric measurements to quantify city-wide GHG emissions that represent a significant fraction of regional and global budgets (Whetstone, 2018 and references therein). For these urban experiments we face similar measurement challenges to those associated with rapid vertical mixing, although we can take advantage of substantial urban and peri-urban infrastructures.

To estimate the emission rate required for a short-to-medium scale DRT experiment, which is not dominated by convection, we use a Gaussian plume model to describe the atmospheric dispersion of different compounds over several hundred km. We acknowledge these models were not designed to study plumes beyond a few km from the emission release, where atmospheric dispersion is not well approximated by turbulent diffusion, and consequently provide only illustrative calculations to help estimate the necessary release rates. We use this model to determine the emission rate that would maintain 1 ppt of a particular compound at distances less than 1000 km from the point of emission. This is a conservative criterion that ensures we have more than sufficient sensitivity of that compound using currently available instruments. For our illustrative calculations, we assume a surface release height and a mean wind speed of 5 m/s. We also assume neutral atmospheric stability (Pasquill atmospheric stability class D) that describes the level of atmospheric turbulence, and

we have assumed DRT candidates are significantly affected by dry deposition or wet scavenging.

1.3 Potential Hemispheric to Global scale DRT experiment

The measurement requirements for a long range or global experiment (length scales on the order of 1,000-10,000 km) are more stringent due to the generally greater role of atmospheric mixing over these long distances. Therefore, very substantial quantities of tracer would need to be injected into the atmosphere at considerable cost (but perhaps not inconsistent with the current expenditure on satellite observing systems), and the potential for environmentally damaging consequences. The quantities of tracer required are defined by the scale of the dispersion. While local dispersion studies might release a few kilograms (kg) of tracer, regional and transcontinental experiments may require hundreds of kg of tracer to be released, as demonstrated by the Ferber et al., 1986 (CAPTEX), Draxler et al., 1991 (ANATEX), and Graziani et al., 1998 (E; Nordop et al., 1998 ETEX) regional studies. To conduct a global experiment with a detectable global tracer mixing ratio of, say, 1ppt would involve the release of thousands of tons of tracer with the formidable challenge of logistics and the obvious cost implications.

There are two principal approaches to minimising these challenges, both involving the analytical detection of the tracer after extensive dilution. First, is the collection of large volumes of air with selective removal of potentially interfering gases, particularly water and carbon dioxide prior to enrichment of the tracer by cryogenic and/or adsorbent trapping. Second, is an ultrasensitive and selective detection method that can uniquely quantify the tracers in the likely presence of other trace gases which might interfere with or otherwise compromise their detection. Current analytical technologies with the necessary sensitivity include mass spectrometry, gas chromatography with specific detectors, coupled gas chromatography-mass spectrometry (GC-MS) (Miller et al., 2008).

To address the challenge of evaluating models at large scale, we explore possible DRTs that could be used in an experiment where; 1) one or more DRTs are released to the atmosphere continuously, from multiple release points around the world, over a period of years or longer; 2) the atmospheric mole fraction of the DRTs is measured at multiple locations around the world, using existing and/or new measurement infrastructure; 3) the DRT background is small compared to the enhancements due to the new release; 4) costs are to be kept as low as possible, perhaps comparable with global expenditure on greenhouse gases (GHG), ozone depleting substances (ODS) and air quality (AQ) measurement infrastructure (i.e. hundreds of millions of dollars). Funding for such a project would necessarily require international collaboration. Several configurations of such a global scale experiment could be envisaged, for example, where tracers with differing lifetimes are released from different locations, or multiple tracers are co-emitted, to disentangle the influence of chemical loss versus atmospheric mixing and advection.

Figure 3 shows a hypothetical global tracer release experiment, where tracers are emitted from a small number of locations in both hemispheres. Current Advanced Global Atmospheric Gases Experiment (AGAGE) stations are shown (Prinn, et al., 2018), where detectors could be installed. Optimal release and other potential measurement locations would need to be investigated using 3D atmospheric chemical transport model studies. With the appropriate distribution or release points and monitoring sites, a global-scale experiment could potentially also be used to evaluate regional-scale atmospheric transport processes. For example, if a tracer was released within a few hundred km of a measurement station (e.g. the European release in Figure 3), it may be possible to learn about short-timescale atmospheric transport processes, as the air is advected directly from the release point to the receptor, whilst simultaneously learning about global scale transport and chemistry, by monitoring changes in background concentrations. Whether these scales could accurately be disentangled would require further modelling investigation. By using a compound with a finite lifetime, it may be possible to learn about global atmospheric oxidative capacity simultaneously with atmospheric transport. Again, an appropriate global 3D model study would be required to ensure that these factors could be disentangled in an experiment involving single, or multiple DRTs.

Figure 3. A hypothetical global-scale tracer release experiment with (arbitrarily distributed) tracer release location shown as red squares, and the current AGAGE network shown as blue circles.

To estimate the emission rate required for a global-scale DRT experiment, for each compound, we estimated the continuous emission rate required to increase the background mole fraction by 1 ppq (see Appendix A for calculation method). To first order, these values can be linearly scaled, depending on the available measurement detection limits, so a target mole fraction increase of 1 ppt would require one thousand times the emission rate presented in the tables. We assumed no mixing to the stratosphere, but uniform mixing throughout the troposphere. If hemispheric scale transport was the primary target, lower emission rates may be possible, due to the smaller effective mixing “volume”.

2. Tracer candidates for DRT experiments

In the sections that follow, we first discuss the current status of the c-PFCs, which have been used in previous studies, then we examine if there are other potential tracers amongst the industrially produced hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), hydrochlorofluorocarbons (HCFCs) and unsaturated hydrofluorocarbons (HFOs). Finally, we discuss the possibility of developing novel tracers using stable isotopes of existing compounds which are routinely measured by ground-based monitoring stations, as currently operated by AGAGE and the National Oceanographic and Atmospheric Administration (NOAA).

While we provide this selection of tracers as a guide, there is a subset of specific candidates that we consider to be ‘preferred tracers.’ This is based on the criteria of being gases at ambient temperature, with a range of suitable lifetimes and being appropriate for both short-to-medium and hemispheric-to-global length scales. Our greatest uncertainty is their cost and we stress that estimates are our best guesses, in the absence of well-defined industrial prices and availability. We assume that investigators will design their own experiments and may well select their own ‘preferred tracers’ based on different specific requirements.

2.1 Cyclic perfluorocarbons: past, present and future

Lovelock and Ferber (1982) first proposed the adoption of c-PFCs for atmospheric studies and to evaluate air pollution model calculations. Historically, these c-PFCs have been successfully used in many dispersion studies (Martin et al., 2011 and references therein). The continuing attraction of these c-PFCs, as potential tracers, is their exquisitely sensitive detection by negative ion chemical ionization mass spectrometry (NICI-MS) with little or no interference from other trace atmospheric gases (Begley et al., 1988; Simmonds et al., 2002; Ren et al., 2014). Although these c-PFCs do have many desirable properties they also have large global warming potentials (GWPs) and very long atmospheric lifetimes (several thousand years) and have been referred to as “persistent” molecules, since essentially everything that has been produced and released is still in the atmosphere.

When the atmospheric background concentration of the c-PFCs were first measured (see Table 1) they had mixing ratios of several ppq (Simmonds et al., 2002; Watson et al., 2018). Unfortunately the atmospheric background concentrations of several perfluorocarbon tracers (see Table 1) are believed to have increased to about 10 ppq due to emissions from various industrial applications, and their release in several major tracer experiments (Draxler et al., 1991, Straume et al., 1998; Nordop et al., 1998; Kim et al., 2002), (see Table 1). Assuming we can accurately determine the current atmospheric background concentration of these specific c-PFCs, we could still design experiments which release sufficient amounts of tracer to overpower this non-zero background, thereby providing a substantial enhancement which can be measured with high precision (Begley et al., 1988). Based on the release of a novel perfluorocarbon tracer (i.e. with zero background concentration) and a 1L sample volume it should be possible to determine a tracer atmospheric mixing ratio of 10 ppq with high precision, assuming quantitative trapping and detection of the tracer. Obviously increasing the sample volume from 1L will proportionally increase the minimum detection

level and consequently reduce the amount of tracer released over a specific dispersion distance.

Fortunately, there are some potential new c-PFCs (listed in Table 1), that are available commercially, with currently very few industrial applications and which have not been used extensively as tracers. We note that there are other isomers in this class of perfluorocarbons, that could also be produced commercially and might be suitable as future tracers. Provided that we can confirm, from new measurements, that their current atmospheric mixing ratios are in the low ppq range, then these tracers are potentially useful for small-to-medium scale dispersions. Precisions of 2-10 % should be achievable for these new c-PFCs, at the 0.1-10 ppq level, based on the previous measurements of c-PFCs (Simmonds et al., 2002). Nevertheless, these c-PFCs do have some practical limitations. First, the current price of individual c-PFCs range from \$250-\$400/kg (based on purchase of greater than 200 kg), which might preclude these tracers being used in larger scale applications, simply on cost. Second, they are liquids at ambient temperatures requiring more sophisticated release technologies than gaseous tracers. Third, existing GC-MS instruments at global monitoring sites operate in electron-ionization (EI) mode and as such do not have the ultrasensitive detection capability of NICI-MS. Therefore, new or modified instrumentation, would be required at monitoring sites.

The very low detection limits (ppq) of the PFCS have previously make them particularly attractive as tracers for regional scale experiments such, as ETEx, where several hundred kg of tracer were released. For very large-scale or global experiments, where many tons of tracer are required, PFCs are more problematic as their persistent accumulation would have a detrimental impact on the environment. Furthermore, a principal toxic degradation product of PFCs is hydrogen fluoride (HF) which would be a potential environmental hazard. Fortunately, HF is rapidly scavenged from the atmosphere as a consequence of its high reactivity and water solubility leading to high dry and wet deposition velocities. Estimated half-lives of 14 and 12 hours for dry and wet deposition, respectively, have been calculated (Environment-Agency.UK, 2004).

There is also another group of perfluorinated cycloalkanes, known as ‘adamantanes’, consisting of three connected cyclohexane rings (examples are listed in Table 1), which may be suitable for use as tracers, that are only available in very small commercial quantities and consequently would be expected to have a near zero background concentration (Simmonds and Moore, 1985). At present, there are no reported detailed measurements of these compounds, however, we expect that it should be possible to achieve similar precisions to the c-PFCs with current instrumentation. In general, the c-PFCs and adamantanes would not be the preferred tracers of choice for the “Goldilocks” scenarios (section 1.1), because repeated releases would lead to a persistent and growing background concentration, due to their very long atmospheric lifetimes and therefore we only propose that they are used on a campaign basis.

386 .

387

Chemical name and abbreviation (Previously used c-PFC tracers)	Molecular Formula	Boiling Point (°C)	Molecular Weight*	Previously observed mixing ratio (ppq)	** Estimated 2020 atmospheric mixing ratio (ppq)	Emission rate to increase tropospheric mole fraction by 1 ppq within 1 year (tonne yr ⁻¹)	Potential DTR application
Perfluorodimethylcyclobutane (PDCB)	C ₆ F ₁₂	45	300	^a 2.7 ± 0.2, ^b 3 ± 0.4, ^c 0.85 ± 0.1	4.2	43	
Perfluoromethylcyclopentane (PMCP)	C ₆ F ₁₂	48	300	^a 6.3 ± 0.2, ^b 8 ± 0.6, ^c 6.8 ± 1.4	11.6	43	
Perfluoromethylcyclohexane (PMCH)	C ₇ F ₁₄	76	350	^a 5.5 ± 0.2, ^b 8 ± 0.9, ^c 4.6 ± 0.4	10.4	50	
Perfluoro-1,2-dimethylcyclohexane (o-PDMCH)	C ₈ F ₁₆	102	400	^a 0.73 ± 0.09, ^b 1 ± 0.4,	1.48	57	
Perfluoro-1,3-dimethylcyclohexane (m-PDMCH)	C ₈ F ₁₆	102	400	^a 8.7 ± 0.3, ^c 6.8 ± 0.5	11.9	57	
Perfluoro-1,4-dimethylcyclohexane (p-PDMCH)	C ₈ F ₁₆	102	400	^a 6.1 ± 0.4, ^b 8 ± 0.8, ^c 2.1 ± 0.4	10.4	57	
Potentially new c-PFC tracers							
Perfluoroethylcyclohexane (PECH)	C ₈ F ₁₆	102	400			57	Small-scale campaign
Perfluoro-1,3,5-trimethylcyclohexane (PTMCH)	C ₇ F ₁₄	127	450			64	Small-scale campaign
Perfluoropropylcyclohexane (PPCH)	C ₉ F ₁₈	114	450			64	Small-scale campaign

Perfluoroisopropylcyclohexane (if-PPCH)	C ₉ F ₁₈	130	450			64	Small-scale Campaign
Perfluoro-1,3-diethylcyclohexane (PDECH)	C ₁₀ F ₂₀	142	500			71	Small-scale campaign
Perfluoroperhydroindane	C ₉ F ₁₈	118	412			58	Small-scale campaign
Perfluorodecalin	C ₁₁ F ₂₀	142	512			73	Small-scale campaign
<u>Adamantanes</u>							
Perfluoroadamantane (tricyclo[3.3.1.1 ^{3,7}]decane, hexadecafluoro)	C ₁₀ F ₁₆	Not reported	424.08			60	Small-scale campaign
Perfluoromethyladamantane	C ₁₁ F ₁₈	Not reported	474.09			67	Small-scale campaign
Perfluoro-1,3-dimethyladamantane	C ₁₂ F ₂₀	Not reported	524.1			74	Small-scale campaign

389

390 Table 1. Cyclic perfluorocarbons (c-PFCs) previously used as tracers and other potential candidate c-PFC tracers. *All form stable molecular
391 anions under NICI-MS. (^a Simmonds et al., 2002; ^b Watson et al., 2007; ^c Ren, et al., 2014). **Estimated background concentration assuming
392 growth rate of ~ 1ppq yr⁻¹. Current atmospheric mixing ratios for the new potential c-PFCs have not been determined, but we assume that they
393 are < 10 ppq.
394 Not reported: All are liquids with assumed boiling points > 100°C.

2.2 Industrial chemicals as potential tracers.

We first discuss DRTs that can already be produced in appropriate quantities for our experiments, and that have e-folding lifetimes of < 30 years. Having oxidation by OH as the dominant loss process for candidate tracers allows the global troposphere to reduce the abundance of material reaching higher altitudes and may enable such compounds to be used to infer OH concentrations. However, as noted above, further work is necessary to understand how well we can separate the influences of atmospheric chemistry and transport on observed variations of individual trace gases. Using multiple DRTs with different e-folding lifetimes may be necessary to achieve this separation.

Table 2 lists eleven hydrofluorocarbons (HFCs) (selected from the larger list of Burkholder, 2018, Appendix A, Table A1) and propyl and isopropyl fluoride as potential tracers which, at present, have very limited commercial applications. The two propyl fluorides (estimated lifetimes ~ 1 day) and HFC-41, HFC-134, HFC-161, HFC-143, HFC-236ea and HFC-263fb are all gases at ambient temperature and are preferred, as their release could be accurately controlled using precision regulators fitted to high pressure gas cylinders. With the exceptions of HFC-134 and HFC-236ea, they all have e-folding lifetimes of less than 4 years. To our knowledge there have been no reported measurements of their current atmospheric mixing ratios and we assume that they are < 10 ppq. Most importantly, they could be measured with current instrumentation, that already exists at the AGAGE and NOAA network of monitoring sites. From previous measurements of other HFCs, precisions are quite variable, depending on the compound (Prinn et al., 2018). However, based on previous results, we would expect to achieve precisions of 1-2 % for mixing ratios of ~ 1 ppt. For mixing ratios of 10-100 ppq precisions would be on the order of 3-10 %. While these precisions are achievable with current AGAGE instrumentation, they will clearly be dependent on the type of instrumentation deployed.

Table 2. Candidate HFC tracers.

Hydrofluoro-carbons	Molecular Formula	Molecular Weight	Boiling Point °C	¹ Atmospheric Lifetime (Years)	Emission rate to increase tropospheric mole fraction by 1 ppq within 1 year (tonne yr ⁻¹)	Potential DRT application
HFC-41*	CH ₃ F	34.0	-78.4	2.8	6	Hemispheric-global
HFC-161*	CH ₃ CH ₂ F	48.1	-37.1	0.2	34	Small-scale
HFC-143*	CH ₂ FCHF ₂	84.0	5.0	3.5	14	Hemispheric-global
HFC-152	CH ₂ FCH ₂ F	66.1	30.7	0.5	22	Hemispheric-global
HFC-263fb*	CH ₃ CH ₂ CF ₃	98.1	-47.6	1.2	20	Hemispheric-global
HFC-245ea	CH ₂ CHFCHF ₂	97.1	39.0	3.4	22	Hemispheric-global
HFC-245eb	CH ₂ FCHFCF ₃	134.1	23.0	3.3	22	Hemispheric-global
HFC-134*	CHF ₂ CHF ₂	102.0	-19.9	9.7	15	Hemispheric-global or small-scale campaign
HFC-236ea*	CHF ₂ CHF ₂ CF ₃	152.0	3.7	11.0	23	Hemispheric-global or small-scale campaign
HFC-338pcc	CHF ₂ CF ₂ CF ₂ CHF ₂	202.1	44.8	12.9	30	Hemispheric-global or small-scale campaign
HFC-329p*	CHF ₂ CF ₂ CF ₂ CF ₃	220.0	14.0	30.0	32	Hemispheric-global or small-scale campaign
Propyl fluoride*	CH ₃ CH ₂ CH ₂ F	62.1	-3.0	1-2 Days ¹	3207	Small-scale
Isopropyl fluoride*	(CH ₃) ₂ CHF	62.1	-10.0	1-2 Days ¹	3207	Small-scale

¹Atmospheric lifetimes reported in Burkholder (2018).

All compounds are thought to be at levels of less than 10 ppq in the atmosphere.

*Gases at ambient temperature. These are preferred tracers.

¹Estimated atmospheric lifetime.

Although these HFCs are now regulated under the Montreal Protocol their short atmospheric lifetimes would avoid long-term environmental consequences making them attractive potential tracers. A primary requirement is finding a chemical manufacturer who could produce these potential tracers in appropriate quantities for DRT experiments and at reasonable cost. We believe that the cost of HFC-tracers for short-to-medium range scales should be manageable, since they can be produced in quantity using existing technologies. However, the tracer cost of large scale or global experiments would be substantial.

By way of example, selecting HFC-41 (methyl fluoride) as a tracer in a global release experiment, we can estimate the amount and cost of the tracer required to increase the tropospheric mole fraction by 1 ppt over the course of 1 year. This equates to the release of about 6000 tonnes per year. Crudely estimated, using bulk chemical processes it should be possible to produce this compound at between \$2500/tonne and \$5000/tonne (see Appendix B) Therefore, the cost of HFC-41 for such a global experiment would be about \$16 to \$28 million per year. This cost would have considerable variability depending on the ease of manufacture and the required purity. Costs would be proportionally reduced with greater instrumental precision and detection capability (e.g. to between \$16000 to \$28000 per year for a precision of 1 ppq). As we argue above, costs should be compared to global annual expenditure on trace gas measurements, which are of the order of hundreds of millions of dollars. It should be remembered that all HFCs, including HFC-41, will undergo chemical degradation via reaction with OH, eventually producing hydrofluoric acid (HF), which will be rained out of the atmosphere (Tuazon et al., 1993; Burkholder et al., 2015).

Another potential DRT, HFC-161, which falls within our “Goldilocks” zone for small to medium scale experiments (lifetime ~0.2 year), has a particular advantage in that it is not, as yet, specifically regulated by the Montreal Protocol. We estimate a required release rate of 9g/s to maintain 1 ppt at distances less than 1000 km from the point of emission. For a campaign spanning one year that emission rate equates to approximately 284 tonnes of HFC-161, and therefore a cost for a year-long experiment of around \$1 (this assumes optimistically that HFC-161 can be produced by bulk chemical processes at about \$3500/tonne). Because atmospheric dispersion is the principal loss process over distances less than 1000 km for tracers with chemical lifetimes longer than a few months, we find similar emission rates are necessary for HFC-152, propyl fluoride, and isopropyl fluoride.

In Table 3 we list thirteen hydrofluoroethers (HFEs), which have not yet been used extensively in industrial applications and could be viable tracers. The majority are low boiling liquids which would require some additional complexity to control their accurate release as a vapour. Since there also appear to be no reported atmospheric measurements for these specific HFEs, we assume that current atmospheric mixing ratios are < 10 ppq and with lifetimes, ranging from 0.8-25.4 years, they would be removed from the environment at a similar rate to the HFCs listed above. The three gaseous tracers HFE-134, HFE-245cb2, and HFE-245fa1 are preferred as their release can be more accurately controlled, compared to substances that are liquids at typical atmospheric temperatures.

These HFE-tracers can be routinely measured by commercial electron ionization-mass spectrometers (EI-MS) and ideally during the analysis, they should be separated chromatographically from possible interferences and furthermore when ionized they should not undergo extensive fragmentation, instead preferentially forming just a few high mass ions to enhance detectability. The presence of a molecular ion would be especially beneficial, as it provides the relative molecular mass of a specific HFE and allows us to discriminate between different HFEs. It will also be important to establish experimentally that there are no ions with the same mass to charge ratio (m/e) formed during the electron ionization of any co-eluting compounds. Like the HFCs, they could be easily measured at existing AGAGE and

NOAA monitoring sites which already contain automated EI-MS instruments and with similar precisions, as noted above for the HFCs. These compounds are therefore potentially excellent tracers, as they are non-toxic and would be conveniently removed by reaction with OH on relatively short timescales, thereby mitigating any long-term environmental impact. Since many related HFEs are already available commercially, we would expect that these candidate HFE-tracers can be also manufactured in quantity at reasonable cost. Current costs for commercially available HFEs range between \$5000-\$10,000/tonne. We would expect that similar pricing for the HFE's listed in Table 3 could be obtained using existing production technologies.

Table 3. Candidate HFE tracers.

Hydrofluoro-ether (HFEs)	Molecular Formula	Molecular Weight	Boiling Point °C	¹ Atmospheric Lifetime (Years)	Emission rate to increase tropospheric mole fraction by 1 ppq within 1 year (tonne yr ⁻¹)	Potential DRT application
HFE-245cb2*	CH ₃ OCF ₂ CF ₃	150.1	5.6	2.5	26	Hemispheric-global
HFE-254cb2	CH ₃ OCF ₂ CHF ₂	132.1	37.3	5.0	21	Hemispheric-global
HFE-245fa1*	CF ₃ OCH ₂ CHF ₂	150.1	15.1	6.5	23	Hemispheric-global
HFE-245fa2	CHF ₂ OCH ₂ CF ₃	150.1	29.2	5.5	23	Hemispheric-global
HFE-356mec3	CH ₃ OCF ₂ CHF ₂ CF ₃	182.1	54.5	2.6	31	Hemispheric-global
HFE-356pcc3	CH ₃ OCF ₂ CF ₂ CHF ₂	182.1	68	3.0	30	Hemispheric-global
HFE-347mcc3	CH ₃ OCF ₂ CF ₂ CF ₃	200.1	61	5.0	31	Hemispheric-global
HFE-347mcf	CHF ₂ OCH ₂ CF ₂ CF ₃	200.1	45.9	5.6	31	Hemispheric-global
HFE-569sf2	CH ₃ CH ₂ O(CF ₃) ₂ CF ₃	252.1	76	0.8	63	Hemispheric-global
HFE-134*	CHF ₂ OCHF ₂	118.0	6.3	25.4	17	Hemispheric-global or small-scale campaign
HFE-236ca	CHF ₂ OCF ₂ CHF ₂	168.0	Not reported	20.8	24	Hemispheric-global or small-scale campaign
HFE-38mmz1	(CF ₃) ₂ CHOCHF ₂	218.1	Not reported	21.2	32	Hemispheric-global or small-scale campaign
Perfluoro isopropyl methyl ether	(CF ₃) ₂ CFOCH ₃	200.1	29	3.6	32	Hemispheric-global

¹Atmospheric lifetimes reported in Burkholder (2018).

All compounds are thought to be at levels of less than 10 ppq in the atmosphere.

*Gases at ambient temperature. These are preferred tracers.

Not reported: Boiling points have not been reported for these specific HFEs.

It is noteworthy, that given the wide range of tracer lifetimes listed in Tables 2 and 3, those with the longer lifetimes from 10-30 years and with assumed atmospheric mixing ratios < 10 ppq could be used for both small-scale studies on a campaign basis, or hemispheric to global DRT studies.

For completeness we have also considered the possibility of using a few hydrochlorofluorocarbons (HCFCs), listed in Table 4, with short atmospheric lifetimes, existing manufacturing processes and facile determination by existing AGAGE and NOAA monitoring sites. However, we recognise that, as ODSs, with relatively small ozone depletion potentials (ODP range 0.01-0.11), they would still have a minor, but nevertheless adverse, environmental impact. From previously reported measurements of HCFCs, precision was ~ 2% for mixing ratios of about 1 ppt (Prinn et al., 2018).

Hydrochloro- fluorocarbon (HCFCs)	Molecular Formula	Boiling Point °C	¹ Atmospheric Lifetime Years	Molecular Weight	Emission rate to increase tropospheric mole fraction by 1 ppq within 1 year (tonne yr ⁻¹)	Potential DRT application
HCFC-21*	CHCl ₂ F	8.9	1.7	102.9	19	Hemispheric-global
HCFC-123	CHCl ₂ CF ₃	27.6	1.3	152.9	31	Hemispheric-global
HCFC-123a	CHClFCClF ₂	29.5	4.0	152.9	24	Hemispheric-global
HCFC-123b	CHF ₂ CCl ₂ F	29.5	6.0	152.9	24	Hemispheric-global
HCFC-132b	CH ₂ ClCClF ₂	46.8	Not reported	134.9	Unknown	Hemispheric-global
HCFC-225ca	CHCl ₂ CF ₂ CF ₃	52	1.9	202.9	37	Hemispheric-global

¹Atmospheric lifetimes reported in Burkholder (2018).

All compounds are thought to be at levels of less than 10 ppq in the atmosphere.

*Gas at ambient temperature. Preferred tracer.

Not reported: Lifetime has not been assessed.

In addition to the selection of HFCs and HFEs, there are a significant number of unsaturated hydrofluorocarbons (HFOs) with atmospheric lifetimes on the order of days (listed in Table 5 and selected from Burkholder, 2018, Appendix A, Table A1). For example, CH₂=CF₂ (HFO-1132a, τ=4 days) and CF₃CH=CH₂ (HFO-1243zf, τ=7.0 days) that could be used for the small-scale DRT dispersions (see Sect. 1.2) and which would be rapidly scavenged from the atmosphere. To our knowledge, there are no reported measurements of these compounds. However, some HFOs, HFO-1234yf, HFO-1234ze(E), and HFO-1233zd(E) have recently been detected in the atmosphere with mixing ratios in the ppq range (Vollmer et al., 2015).

Table 5. Candidate HFOs tracers.

Unsaturated Hydrofluoro Carbons	Molecular Formula	Boiling Point °C	¹ Atmospheric Lifetime (Days)	Molecular Weight	Potential DRT application
HFO-1123	CHF=CF ₂	-51.0	1.4	82.02	Small-scale
HFO-1141	CH ₂ =CHF	-72.0	2.1	46.04	Small-scale
HFO-1132a	CH ₂ =CF ₂	-83.0	4.0	64.0	Small-scale
HFO-1234zf	CF ₃ CH=CH ₂	-18.0	7.0	96.05	Small-scale

¹Atmospheric lifetimes reported in Burkholder (2018).

All compounds are thought to be at levels of less than 10 ppq in the atmosphere.

Note: All are gases at ambient temperature. These are all preferred tracers.

We could also consider the whole range of volatile organic compounds (VOCs) as potential tracers, although in practice many VOCs could be compromised by the probability of unexpected industrial releases not connected with a tracer release. Nevertheless, saturated, olefinic, and oxygenated hydrocarbons (C₂-C₃), and many other classes of VOCs are all potentially plausible tracers, with lifetimes generally on the order of days, that would only be suitable for very short-range DRT experiments. However, there may be practical limitations regarding their compatibility with existing analytical instruments, caused by potential losses during sample processing, as well as a high background concentration, availability and cost. In this paper we have initially restricted our selections to readily available non-toxic compounds which can be produced by existing commercial manufacturing processes. A consideration of all possible VOCs as tracers is beyond the scope of this paper.

2.3 Novel tracers of deuterium-substituted halocarbons

The use of deuterated methanes as effective tracers for long range atmospheric transport has already been reported (Alej et al., 1987), however, these compounds are not available commercially in large quantities, as far as we know. We believe that using current EI-GC-MS technologies it should be possible to deploy several deuterium-substituted low molecular weight halocarbons (listed in Table 6), as potential atmospheric tracers. Precisions determined from previous AGAGE measurements of undeuterated chlorinated solvents at high ppt levels were in the range 0.2-0.5% (Prinn et al., 2018). We would expect to obtain equivalent precisions for the deuterated analogues at high ppt levels. However, reducing the tracer concentration to ppt or sub-ppt would most likely lower precisions to ~5-10%. Some of these compounds are already available commercially in small quantities as standards for Nuclear Magnetic Resonance (NMR) studies. As with many of the previous tracers, these deuterium-substituted compounds could be measured at globally distributed sites operated by AGAGE and NOAA. Furthermore, it should be possible to synthesise several homologues of the same compound by varying the deuterium substitution e.g. (CD₃Cl, CD₂HCl, CDH₂Cl). Each homologue would be uniquely identified by their mass/charge ratio (m/e) and the concentration determined by GC-MS, if several deuterium-substituted related tracers were used, for example, in a small-scale campaign.

Table 6 Novel tracers.

Estimated atmospheric lifetimes are based on lifetimes of non-deuterated homologues.
 All compounds are thought to be at levels of less than 1 ppq in the atmosphere.
 *Gases at ambient temperature. These are preferred tracers.

Deuterium substituted and other isotopes	Molecular Formula	Boiling Point °C	Estimated Atmospheric Lifetime (Years)	Molecular Weight	Emission rate to increase tropospheric mole fraction by 1 ppq within 1 year (tonne yr ⁻¹)	Potential DRT application
Chloromethane-d*	CD ₃ Cl	-11.6	1.0	53.5	12	Small-scale campaign
Dichloromethane-d	CD ₂ Cl ₂	40	< 0.5	86.9	29	Small-scale campaign
Chloroform-d	CDCl ₃	60.9	0.5	120.4	39	Small-scale campaign
1,2-dichloroethane-d	C ₂ D ₄ Cl ₂	83	0.1-0.3	103.0	73	Small-scale Campaign
Fluoromethane-d*	CD ₃ F	-78	1.0	37.0	8	Small-scale campaign
Fluoroethane-d*	CD ₃ CD ₂ F	-37	<1.0	53.1	12	Small-scale campaign

While these deuterium-substituted tracers are attractive for small-scale studies due to their relatively short atmospheric lifetimes, some do contain chlorine, with associated environmental consequences and they suffer from a potentially high cost of manufacture. For example, deuterated chloroform (CDCl₃) is about \$400/kg and other deuterium-labelled tracers would be much more expensive (currently at about \$50,000-\$60,000/kg). However, these estimates are based on gram quantities in speciality chemical catalogues and we would assume that there would be a significant price reduction for bulk syntheses. However, we still caution that availability and cost is still a major issue for this class of possible tracers. Consequently, we would only envisage them being used in small-scale experiments, where minimal quantities of tracer may be required.

With respect to all of the tracers discussed above in sections 2.1, 2.2, and 2.3, there are two main issues still to be solved in order to select appropriate tracers for specific dispersion and transport studies; 1) new measurements of atmospheric background mixing ratios are required for many of the potential candidate tracers that have not been accurately measured for many years. For completely novel tracers it is reasonably safe to assume that the background mixing ratio will be zero or at least not detectable with current instrumentation; 2) the more difficult problem is the cost of acquiring substantial quantities of high purity tracers. We should stress that catalogue prices for potential tracers are very

expensive (\$1000s per kg) however, as noted previously these are speciality chemical prices for small quantities and from discussions with representatives of the chemical industry we are confident, that due to economies of scale, prices would be much lower with bulk chemical manufacturers. Lastly regulatory controls under the Montreal and Kyoto Protocols and their amendments may require special dispensation if large tracer releases are anticipated, although a short atmospheric lifetime would argue for a fast removal rate from the atmosphere, thereby eliminating any atmospheric accumulation issues or any long-term detrimental impact on the environment.

3. Existing and new instrumentation.

3.1 Current instrumentation:

Existing networks such as those operated by AGAGE and NOAA already contain sophisticated automated GC-MS instruments for the routine measurement of a wide range of organic compounds (Prinn et al., 2018; Montzka, et al., 2019). Importantly, the majority of the potential tracers listed in Tables 2, 4, 5 and 6 could be measured by existing AGAGE instrumentation with some modifications and we believe that both field and laboratory-based instrumentation, operated by NOAA, could also measure a substantial number of the potential tracers. However, to specifically determine the c-PFCs tracers, existing GC-MS instruments which currently operate in EI-mode, would need to be converted to the NICI-mode of ionization, or new GC-MS instruments would have to be developed.

NOAA also collects weekly air samples in paired flasks at 16 baseline sampling sites for halocarbon and trace gas measurements under the HATS program and hourly (in situ) GC-ECD measurements are made at 5 of the sites (South Pole, Samoa, Mauna Loa, Niwot Ridge and Barrow) of a subset of gases. In addition, NOAA/ESRL/GML CCGG cooperative air sampling network collects flask samples at 87 active sites in 38 countries (www.esrl.noaa.gov). We believe that flask samples collected by NOAA could measure a substantial number of the potential tracers, using their current instrumentation. As part of a collaborative effort special ‘tracer’ flasks could also be collected using the NOAA infrastructure and analysed by AGAGE and NOAA laboratory-based instrumentation. Importantly, NOAA and AGAGE measurements are co-located at some of the same sites within their sampling networks so rigorous intercomparisons can be made.

Many other global monitoring sites also have well established flask sampling facilities and laboratory-based analytical instruments to measure these potential tracers. (Dunse et al., 2005; Saito et al., 2010; Barletta, et al., 2011; Yokouchi et al., 2018; Schuck et al., 2018, 2020; Droste et al., 2020). We envisage that in any hemisphere-to-global length scale experiment, these sites could work collaboratively with existing AGAGE and NOAA observatories to substantially increase the number of scientific measurements with a much larger spatial coverage.

3.2. New instrumentation

We accept that some of the potential tracers noted above may be excluded on practical grounds, as strictly regulated, too expensive or simply unavailable. However, even for viable tracers existing instrumentation may need to be modified to optimise their detection. Some new instrumentation may also need to be developed for atmospheric studies involving novel tracers, such as advanced airborne samplers and sample collection equipped drones. There is clearly a requirement here for the development of new fast response instruments which can determine several tracers in near real-time, with also modest power and weight demands, so they can be easily deployed as airborne sensors. Fast analysis GC instruments which can resolve several tracers may have a role here. Whole air sample bottles and samplers containing sequential adsorbent traps do allow for the subsequent analysis of several tracers on return to the laboratory, but in the case of adsorbent samplers are constrained by longer sample collection times.

There is another powerful spectroscopy technique, with reported sub-ppt level sensitivities, that could provide additional instrumentation for tracer dispersion studies. Photo-acoustic spectrometers have been developed which are highly sensitive for certain compounds and one report describes the detection of perfluorocarbon tracers leaking from oil-filled cables (Zajarevich et al., 2013). However, photo-acoustic spectrometers will require further development and modifications to make them suitable for routine field-portable and airborne use (Xiong et al., 2017; Tomberg et al., 2018).

4. Conclusions

We have listed about 50 potential candidate tracers in Tables 1-6 for testing the ability of atmospheric chemical transport models to determine trace gas dispersion over small and large transport scales, and, potentially, large-scale atmospheric oxidation. Tracers which are gases at room temperature are preferred, as their release rate can be more accurately controlled from high pressure cylinders. Several gaseous candidate tracers are identified in each table with a range of convenient atmospheric lifetimes for the different dispersion scales. We expect that tracers, with a knowledge of their atmospheric lifetimes and costs, will be selected on the anticipated transport distances and the overall duration of the transport and dispersion study. We have proposed several c-PFC compounds, similar to those that have previously been used as DRTs, but which, to our knowledge, have not yet been used extensively as DRTs, or in industrial applications. These compounds may be used on a campaign basis for the investigation of small-scale transport. However, their long lifetimes and high GWPs may prevent larger scale, or more sustained release. Alternatively, we have identified several compounds that could be mass produced using existing chemical technologies. We have listed several HFCs, HFEs, HCFCs, HFOs and some novel deuterium-substituted halocarbon tracers that could conceivably be produced in substantial quantities, for use in long-term, small-scale studies, or even hemispheric to global investigations, provided costs could be met, or instrumental precisions improved. For tracer mixing ratios of 1ppt, current precisions of AGAGE instrumentation are excellent at 1-2%. To determine tracer mixing ratios in the 10-100 ppq range would require further instrumental development

with the ability to accurately process larger sample volumes. We acknowledge that there are substantial costs in obtaining tonnage quantities of tracer for hemispheric and global length scale experiments, although for smaller scale studies we believe that costs should be manageable by taking advantage of bulk chemical production processes. We argue that the costs associated with these studies be compared against current expenditure on trace gas observing systems, which require well-validated atmospheric models for interpretation.

Appendix A. Calculation of global emissions required to increase mole fraction by 1 ppq

For each tracer with a lifetime on the order of months to years, we provide an estimate of the emission rate required to raise tropospheric baseline mole fractions by 1 fmol mol⁻¹ (ppq). We assume that gases mix uniformly only within a 1-box troposphere, containing of 1.4 x 10²⁰ mol of air (M_{atm} , about 80% of the total atmosphere). For an emission rate, Q (in kg yr⁻¹), the rate of increase in the burden (in kg), B , of a gas with lifetime (in yr), τ , and molecular weight, m , is given by:

$$\frac{dB}{dt} = Q - \frac{B}{\tau} \quad (1)$$

This is a linear ordinary differential equation (e.g. Riley, Hobson and Bence, 1997, pp381), the solution of which, for a constant emission rate and an initial atmospheric burden of zero, is:

$$B(t) = \tau Q \left(1 - e^{-\frac{t}{\tau}} \right) \quad (2)$$

where t is the time (in yr) since the beginning of the release. Rearranging, and substituting burden for mole fraction, χ , where $\chi = B/(mM_{atm})$, we obtain:

$$Q = \frac{\chi m M_{atm}}{\tau \left(1 - e^{-\frac{t}{\tau}} \right)} \quad (3)$$

Note that the emission rate is linearly related to the target mole fraction, so the tabulated values can be scaled to mole fraction detection limit of the measurements (e.g. a multiple of 1000 would be required to raise the mole fraction from 1 ppq to 1 ppt).

Appendix B. Examples of Approximate Costs of Fluoroalkane Tracers

Fluoromethane (HFC-41) from chloromethane and hydrogen fluoride:

At 90% efficiency, requires 1.65 tonnes of chloromethane per tonne of product and 0.65 tonnes of anhydrous hydrogen fluoride (aHF).

Chloromethane is available in China at USD200 to USD800 per tonne in bulk and anhydrous HF is offered at USD1530 per tonne (www.alibaba.com April 2020).

Resulting raw material cost would be between USD1330 and USD 2320 per tonne of HFC-41. Assuming that raw materials account for half of the price of the product, bulk

quantities of HFC-41 could be available for 2500 to 5000 USD/tonne (rounded from 2660 to 4640).

Fluoroethane (HFC-161) from ethene and hydrogen fluoride:

At 90% efficiency, requires 0.65 tonnes of ethene 0.46 tonnes of aHF.

Ethene is globally priced at USD1100/tonne (Platts Global Ethylene Price Index, www.spglobal.com/platts April 2020). Coupled with the aHF cost and requirement, this gives a raw material cost of USD1420/tonne of HFC-161. Again, if this is half of the final price, bulk HFC-161 could be available for 3000 USD/tonne (rounded from 2840).

Author contributions

P.G.S lead author and all co-authors contributed to writing the paper. M.R and P.I.P specifically wrote the major modelling sections and also contributed to the introduction they were also responsible for atmospheric model simulations.

Competing interests

We confirm that there are no competing interests.

Acknowledgements.

This study was supported by various grants from the Department for Business, Energy & Industrial Strategy (BEIS, UK formerly the Department of Energy and Climate Change (DECC)), the National Aeronautical and Space Administration (NASA, USA), and the National Oceanic and Atmospheric Administration (NOAA, USA). P. Palmer is supported by the EU H2020 VERIFY project, grant 776810 funded under the Research and Innovation Action H2020-SC5-4-2017 370. We specifically acknowledge the cooperation and support of the AGAGE community, and constructive inputs from the TransCom community. We thank Dr Steve Montzka for providing detailed information on NOAA flask sampling programmes. We also thank Dr R Derwent for valuable discussions on certain aspects of the paper.

References.

Alei, M.; Cappis, J.H.; Fowler, M.M.; Frank, D.J.; Goldblatt, M.; Guthals, P.R.; Mason, A.S.; Mills, T.R.; Mroz, E.J.; Norris, T.L.; Perrin, R.E.; Poths, J.; Rokop, D.J.; and Shields, W.R. Determination of Deuterated Methane's for use as Atmospheric Tracers. Atmos. Environ. 1987, 21, 909-915.

Aoshima, H., Hashiguchi, Y., Moriizumi, J., Yoshioka, K., Kim, Y.S., Lida, T., A study of atmospheric radon transport as a tracer of pollutants over the Japan Sea. Radioactivity in the Environment, 7, 567-572, 2005. ([doi.org/10.1016/S1569-4860\(04\)07068-8](https://doi.org/10.1016/S1569-4860(04)07068-8)).

ATMES Report 1993. EVALUATION OF LONG-RANGE ATMOSPHERIC TRANSPORT MODELS USING ENVIRONMENTAL RADIOACTIVITY DATA FROM THE CHERNOBYL ACCIDENT: Publication No. EU14147 EU of the Commission of the European Communities. 1993. Ed, B. Klug, G. Graziani, G. Grippa, D. Pierce and C. Tassone.

Barletta, B., Nissenson, P., Meinardi, S., Dabdub, D., Sherwood Rowland, F., VanCuren, R.A., Pederson, J., Diskin, G.S., and D. R. Blake, D.R. Atmospheric Chemistry and Physics HFC-152a and HFC-134a emission estimates and characterization of CFCs, CFC replacements, and other halogenated solvents measured during the 2008 ARCTAS campaign (CARB phase) over the South Coast Air Basin of California: *Atmos. Chem. Phys.*, 11, 2655–2669, 2011. (doi:10.5194/acp-11-2655-2011).

Bergamaschi, P., Corazza, M., Karstens, U., Athanassiadou, M., Thompson, R. L., Pison, I., Manning, A. J., Bousquet, P., Segers, A., Vermeulen, A. T., Janssens-Maenhout, G., Schmidt, M., Ramonet, M., Meinhardt, F., Aalto, T., Haszpra, L., Moncrieff, J., Popa, M. E., Lowry, D., Steinbacher, M., Jordan, A., O'Doherty, S., Piacentino, S., and Dlugokencky, E.: Top-down estimates of European CH₄ and N₂O emissions based on four different inverse models, *Atmos. Chem. Phys.*, 15, 715–736, <https://doi.org/10.5194/acp-15-715-2015>, 2015.

Begley, P., Foulger, B., and Simmonds. P., 1988. Femtogram detection of perfluorocarbon tracers using capillary chromatography-electron capture negative ion mass spectrometry. *J. of Chromatog.* 445, 119-125. Cooke, K.M., Simmonds, P., Nickless, G., and Makepeace, A.W.P., 2001. The use of capillary gas chromatography with negative ion-chemical ionization mass spectrometry for the measurement of perfluorocarbon tracers in the atmosphere. *Anal.Chem.*, 73, 4295-4300.

Burkholder, J.B., R. A. Cox, R.A and A. R. Ravishankara, A.R. Atmospheric Degradation of Ozone Depleting Substances, Their Substitutes, and Related Species. *Chem. Rev.* 2015, 115, 10, 3704–3759.

Burkholder, J. B.: Appendix A: Summary of abundances, lifetimes, ozone depletion potentials (ODPs), radiative efficiencies (REs), global warming potentials (GWPs), and global temperature change potentials (GTPs), in *Scientific Assessment of Ozone Depletion: 2018*, vol. 58, World Meteorological Organization, Geneva, Switzerland. [online] Available from: https://www.esrl.noaa.gov/csl/assessments/ozone/2018/downloads/AppendixA_2018OzoneAssessment.pdf (Accessed 28 July 2020), 2018.

Butler, R., Palmer, P. I., Feng, L., Andrews, S. J., Atlas, E. L., Carpenter, L. J., Donets, V., Harris, N. R. P., Montzka, S. A., Pan, L. L., Salawitch, R. J., and Schauffler, S. M.: Quantifying the vertical transport of CHBr₃ and CH₂Br₂ over the western Pacific, *Atmos. Chem. Phys.*, 18, 13135–13153, <https://doi.org/10.5194/acp-18-13135-2018>, 2018.

773 Chevallier, F., P. I. Palmer, L. Feng, H. Boesch, C. O'Dell, and P. Bousquet, "Towards robust
774 and consistent regional CO₂ flux estimates from in situ and space-borne measurements of
775 atmospheric CO₂," *Geophys. Res. Lett.*, 41, doi:[10.1002/2013GL058772](https://doi.org/10.1002/2013GL058772).

776 Draxler, R. R., and Hess G.D. 1998: An overview of the HYSPLIT_4 modeling system for
777 trajectories, dispersion, and deposition. *Aust. Meteor. Mag.*, 47, 295–30.

778 Draxler, R. R., Dietz, R.; Lagomarsino, R.J., and Start, G., 1991. Across North America
779 Tracer experiment (ANATEX): Sampling and Analysis. *Atmospheric Environment Part A*,
780 199, Volume 25, Issue 12, p. 2815-2826.

781 Droste, E. S., Adcock, K.E., Ashfold, M.J., Chou, C., Fleming, Z., Fraser, P.J., Gooch, L.J.,
782 Hind, A.J., Langenfelds, R.L., Elvidge, E.L., Hanif, N.M., O'Doherty, S., Oram, D.E., Ou-
783 Yang, C-F., Panagi, M., Reeve, C.E., Sturges, W.T., and Laube, J.C. Trends and emissions
784 of six perfluorocarbons in the Northern Hemisphere and Southern Hemisphere. *Atmos.*
785 *Chem. Phys.*, 20, 4787–4807, 2020. (<https://doi.org/10.5194/acp-20-4787-2020>).

786 Dunse, B., Wilson, S. R., Steele, L., Fraser, P. & Krummel, P. (2005). Trace gas emissions
787 from Melbourne, Australia, based on AGAGE observations at Cape Grim, Tasmania, 1995-
788 2000. *Atmospheric Environment*, 39 (34), 6334-6344. (DOI: 10.1016/j.atmosenv.2005.07.014).

789 Feichter, J and Crutzen, P.J. Parameterization of vertical tracer transport due to deep cumulus
790 convection in a global transport model and its evaluation with ²²²Rn measurements.
791 *Tellus*, 42, 100-117, 1990. (doi.org/10.1034/j.1600-0889.1990.00011).

792 Ferber, G.J., Heffter, J.L., Draxler, R.R., Legomarsino, R.J., and Dietz, R.N. 1986. Cross-
793 Appalachian tracer experiment (Captex '83). Final Report. United States: N.p.,1986, Web.

794 Finch, D. P., Palmer, P. I., and Parrington, M.: Origin, variability and age of biomass burning
795 plumes intercepted during BORTAS-B, *Atmos. Chem. Phys.*, 14, 13789–13800,
796 <https://doi.org/10.5194/acp-14-13789-2014>, 2014

797 Glatthor, N., Höpfner, M., Semeniuk, K., Lupu, A., Palmer, P. I., McConnell, J. C.,
798 Kaminski, J. W., von Clarmann, T., Stiller, G. P., Funke, B., Kellmann, S., Linden, A., and
799 Wiegele, A.: The Australian bushfires of February 2009: MIPAS observations and GEM-AQ
800 model results, *Atmos. Chem. Phys.*, 13, 1637–1658, [https://doi.org/10.5194/acp-13-1637-](https://doi.org/10.5194/acp-13-1637-2013)
801 2013, 2013.

802 Graziani, G., S. Galmarini, G. Grippa, and W. Klug, 1998: Real-time Long-range Dispersion
803 Model Evaluation of the ETEX [European Tracer Experiment] Second Release. [Joint](#)
804 *Research Center European Commission EUR 17755 EN*, 98, 303pp.

805 Grossi, C., Àgueda, A., Vogel, F.R., Vargas, A., Zimnoch, M., Wach, P., Martín, J.E., López-
806 Coto, I., Bolívar, J.P., Morguá, J.A., and Rodó, X. (2016), Analysis of ground-based ²²²Rn
807 measurements over Spain: Filling the gap in southwestern Europe, *J. Geophys. Res. Atmos.*,
808 121, 11,021–11,037, doi:10.1002/ 2016JD025196

809

810 Hönninger, G., von Friedeburg, C., and Platt, U.: Multi axis differential optical absorption
 811 spectroscopy (MAX-DOAS), *Atmos. Chem. Phys.*, 4, 231–254, [https://doi.org/10.5194/acp-](https://doi.org/10.5194/acp-4-231-2004)
 812 4-231-2004, 2004.

813 Houweling, S., Aben, I., Breon, F.-M., Chevallier, F., Deutscher, N., Engelen, R., Gerbig, C.,
 814 Griffith, D., Hungershoefer, K., Macatangay, R., Marshall, J., Notholt, J., Peters, W., and
 815 Serrar, S.: The importance of transport model uncertainties for the estimation of CO₂ sources
 816 and sinks using satellite measurements, *Atmos. Chem. Phys.*, 10, 9981–9992,
 817 <https://doi.org/10.5194/acp-10-9981-2010>, 2010.

818 Jacob, D. J. and Prather, M. J., 1990, Radon-222 as a test of convective transport in a general
 819 circulation model, *Tellus* 42B, 118–134. (doi.org/10.1034/j.100-0889.1990.00012).

820 Johnson, W.B. Meteorological Tracer Techniques for Parameterizing Atmospheric
 821 Dispersion. *J. Climate and Applied Meteorology*, 22, 931-946, 1983.

822 Karion, A., C. Sweeney, P. Tans, and T. Newberger, 2010: AirCore: An Innovative
 823 Atmospheric Sampling System. *J. Atmos. Oceanic Technol.*, 27, 1839–
 824 1853, <https://doi.org/10.1175/2010JTECHA1448.1>.

825 Karstens, U., Schwingshackl, C., Schmithüsen, D., and Levin, I.: A process-based ²²²radon
 826 flux map for Europe and its comparison to long-term observations, *Atmos. Chem. Phys.*, 15,
 827 12845–12865, <https://doi.org/10.5194/acp-15-12845-2015>, 2015.

828 Kim, HyeKyeong; Yea, Sun Kyung; Ro, Chul-Un; Lee, Chong Bum; Jang, Meongdo; Lee,
 829 Gangwoong; Yoo, Eunjin and Hanyeong, Jin-Seok Determination of Atmospheric
 830 Perfluorocarbon Background Concentrations of fL/L Range at the Western Coastal Area of
 831 Korea. *Bull. Korean Chem. Soc.* 2002, 23, 301.

832 Klee, M.S., and Blumberg L.M. Practical Aspects of Fast Gas Chromatography and Method
 833 Translation. *Journal of Chromatographic Science*, 40, 234-247, 2002.

834 Lovelock, J.E., and Ferber J.E., 1982. Exotic tracers for atmospheric studies. *Atmos Environ.*
 835 16, 1467-1471.

836 Martin, D., Petersson, K.F., and Shallcross, D.E., 2011. The use of cyclic perfluorocarbons
 837 and SF₆ in atmospheric dispersion experiments. *Q.J.R. Meteorol. Soc.*, 137. 2047-2063.

838 Methven, J, et al., (2006), Establishing Lagrangian connections between observations within
 839 air masses crossing the Atlantic during the International Consortium for Atmospheric
 840 Research on Transport and Transformation experiment, *J. Geophys. Res.*, 111, D23S62,
 841 doi:[10.1029/2006JD007540](https://doi.org/10.1029/2006JD007540).

842 Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Grealley, B. R., Mühle, J., and
 843 Simmonds, P. G.: Medusa: a sample preconcentration and GC/MS detector system for in situ
 844 measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, *Anal.*
 845 *Chem.*, 80, 1536– 1545, doi:[10.1021/ac702084k](https://doi.org/10.1021/ac702084k), [http://pubs.acs.org/doi/abs/10.](http://pubs.acs.org/doi/abs/10.1021/ac702084k)
 846 [1021/ac702084k](https://doi.org/10.1021/ac702084k), 2008.

847 Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Grealley, B. R., Mühle, J., and
 848 Simmonds, P. G.: Medusa: a sample preconcentration and GC/MS detector system for in situ
 849 measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, *Anal.*
 850 *Chem.*, 80, 1536– 1545, doi:10.1021/ac702084k, [http://pubs.acs.org/doi/abs/10.](http://pubs.acs.org/doi/abs/10.1021/ac702084k)
 851 [1021/ac702084k](http://pubs.acs.org/doi/abs/10.1021/ac702084k), 2008.

852 Montzka, S.A., Krol, M., Dlugokencky, E., Hall, B., Jöckel, P., Lelieveld, J. Small
 853 Interannual Variability of Global Atmospheric Hydroxyl. *Science*, 331, 67-69, 2011:
 854 DOI: 10.1126/science.1197640.

855 Nordop, K.; Connolly, R.; Girardi, F. The Field Campaigns of the European Tracer
 856 Experiment (ETEX): Overview and Results. *Atmos. Environ.* 1998, 32, 4095-4018.

857 Palmer, P. I., Jacob, D. J., Mickley, L. J., Blake, D. R., Sachse, G. W., Fuelberg, H. E. and
 858 Kiley, C. M., Eastern Asian emissions of anthropogenic halocarbons deduced from aircraft
 859 concentration data. *J. Geophys. Res.* 108, 24, 1-9, 2003.

860 Palmer, P. I., L. Feng, D. Baker, F. Chevallier, H. Boesch, P. Somkuti, "Net carbon emissions
 861 from African land biosphere dominate pan-tropical atmospheric CO₂ signal", *Nature*
 862 *Comm.*, <https://doi.org/10.1038/s41467-019-11097-w>, 2019.

863 Parrington, M., Palmer, P. I., Lewis, A. C., Lee, J. D., Rickard, A. R., Di Carlo, P., Taylor, J.
 864 W., Hopkins, J. R., Punjabi, S., Oram, D. E., Forster, G., Aruffo, E., Moller, S. J., Bauguitte,
 865 S. J.-B., Allan, J. D., Coe, H., and Leigh, R. J.: Ozone photochemistry in boreal biomass
 866 burning plumes, *Atmos. Chem. Phys.*, 13, 7321–7341, [https://doi.org/10.5194/acp-13-7321-](https://doi.org/10.5194/acp-13-7321-2013)
 867 [2013](https://doi.org/10.5194/acp-13-7321-2013), 2013.

868 Pasquill, F. 1974, *Atmospheric Diffusion*. Ellis Horwood Ltd, Chichester, UK.

869 Patra, P., Krol, M., Montzka, S. *et al.* Observational evidence for interhemispheric hydroxyl-
 870 radical parity. *Nature* **513**, 219–223 (2014). <https://doi.org/10.1038/nature13721>

871 Pissu, I., Sollum, E., Grythe, H., Kristiansen, N.I., Cassiani, M., Eckhardt, S., Arnold,
 872 D., Morton, D., Thompson, R.L., Groot Zwaafink, C.D., Evangeliou, N., Harald Sodemann,
 873 H., Haimberger, L., Henne, S., Brunner, D., Burkhart, J.F., Fouilloux, A., Brioude, J., Philipp,
 874 A., Seibert, P., and Stohl, A. The Lagrangian particle dispersion model FLEXPART version
 875 10.4..*Geosci. Model Dev.*, 12, 4955–4997, 2019
 876 (doi.org/10.5194/gmd-12-4955-2019).

877 Prinn, R. G., Cunnold, D. M., Rasmussen, R., Simmonds, P. G., Alyea, F. N., Crawford, A.,
 878 Fraser, P. J., and Rosen, R, 1987. Atmospheric trends in methyl chloroform and the global
 879 average for the hydroxyl radical, *Science*, 238, 945–950.

880 Prinn, R. G., Weiss, R. F., Arduini, J., Arnold, T., DeWitt, H. L., Fraser, P. J., Ganesan, A.
 881 L., Gasore, J., Harth, C. M., Hermansen, O., Kim, J., Krummel, P. B., Li, S., Loh, Z. M.,
 882 Lunder, C. R., Maione, M., Manning, A. J., Miller, B. R., Mitrevski, B., Mühle, J.,

883 O'Doherty, S., Park, S., Reimann, S., Rigby, M., Saito, T., Salameh, P. K., Schmidt, R.,
884 Simmonds, P. G., Steele, L. P., Vollmer, M. K., Wang, R. H., Yao, B., Yokouchi, Y., Young,
885 D., and Zhou, L.: History of chemically and radiatively important atmospheric gases from the
886 Advanced Global Atmospheric Gases Experiment (AGAGE), *Earth Syst. Sci. Data*, 10, 985–
887 1018, <https://doi.org/10.5194/essd-10-985-2018>, 2018.

888 Ren, Y.; Schlager, H., and Marin, D., 2014. The application of TD/GC/NICI-MS with an
889 Al₂O₃-PLOT-S Column for the Determination of Perfluoroalkylcycloalkanes in the
890 Atmosphere. *Chromatographia*, 77. 309-316.

891 Riley, K. F., Hobson, M. P. and Bence, S. J.: Mathematical methods for physics and
892 engineering: a comprehensive guide, Cambridge University Press, Cambridge, U.K. ; New
893 York, NY, USA., 1997.

894
895 Rigby, M., Mülhe, J., Miller, B.R., Prinn, R.G., Krummel, P.B., Steele, L.P., Fraser, P.J.,
896 Salameh, P.K., Harth, C.M., Weiss, R.F., Grealley, B.R., O'Doherty, S., Simmonds, P.G.,
897 Vollmer, M.K., Reimann, S., Kim, J., Kim, K.-R., Wang, H.J., Olivier, J.G.J., Dlugokencky,
898 E.J., Dutton, G.S., Hall, B.D., and Elkins, J.W., 2010. History of atmospheric SF₆ from 1973-
899 2008. *Atmos. Chem. Phys.*, 10. 10305-10320. Doi: 10.5194/acp-10-10305-2010.

900 Rigby, M., Montzka, S. A., Prinn, R. G., White, J. W. C., Young, D., O'Doherty, S., Lunt, M.
901 F., Ganesan, A. L., Manning, A. J., Simmonds, P. G., Salameh, P. K., Harth, C. M., Mühle,
902 J., Weiss, R. F., Fraser, P. J., Steele, L. P., Krummel, P. B., McCulloch, A. and Park, S.,
903 2017. Role of atmospheric oxidation in recent methane growth, *Proceedings of the National*
904 *Academy of Sciences*, 201616426, doi:[10.1073/pnas.1616426114](https://doi.org/10.1073/pnas.1616426114), 2017.

905 Saito, T., Yokouchi, Y., Stohl, A., Taguchi, S and Mukai., H. 2010: Large Emissions of
906 Perfluorocarbons in East Asia Deduced from Continuous Atmospheric Measurements. (DOI:
907 10.1021/es1001488).

908 Schuck, T.J., Lefrancois, F., Gallmann, F., Wang, D., Jesswein, M., Hoker, J., Bönisch,
909 H and Engel, A. Establishing long-term measurements of halocarbons at Taunus Observatory.
910 *Atmos. Chem. Phys.*, 18, 16553–16569, 2018. (DOI: 10.5194/acp-18-16553-2018).

911 Schuck, T.J., Blank, A-K., Rittmeier, E., Williams, J., Brenninkmeijer, C.A.M., Engel, A and
912 Zahn, A. Stability of halocarbons in air samples stored in stainless- steel canisters. *Atmos.*
913 *Meas. Tech.*, 13, 73–84, 2020. (DOI: 10.5194/amt-13-73-2020).

914 Simmonds, P.G and Moore, R.E. 1985. Fluorocarbon tracers and tracing method. US Patent
915 4,520,109.

916 Simmonds, P.G.; Grealley, B.R., Olivier, S., Nickless, G., Cooke, K.M., and Dietz, R.N.,
917 2002. The background atmospheric concentrations of cyclic perfluorocarbon tracers
918 determined by negative ion-chemical ionization mass spectrometry. *Atmos. Environ.*, 36,
919 2147-215.

920 Simmonds, P.G., Rigby, M., Manning, A.L., Park, S., Stanley, K.M., McCulloch, A., Henne,
 921 S., Graziosi, F., Maione, M., Arduini, J., Reimann, S., Vollmer, M.K., Mühle, J., O'Doherty,
 922 S., Young, D., Krummel, P.B., Fraser, P.J., Weiss, R.F., Salameh, P.K., Harth, C.M., Park,
 923 M-K., Park, H., Arnold, T., Rennick, C., Steele, L.P., Mitrevski, B., Wang, R.H.J and Prinn,
 924 R.G. 2020. The increasing atmospheric burden of the greenhouse gas sulfur hexafluoride
 925 (SF₆). *Atmos. Chem. Phys.*, 20, 7271–7290. <https://doi.org/10.5194/acp-20-7271-2020>.
 926

927 Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B. J. B., Cohen, M. D., and Ngan, F.
 928 NOAA'S HYSPLIT ATMOSPHERIC TRANSPORT AND DISPERSION
 929 MODELING SYSTEM. *Bulletin of the American Meteorological Society*, Vol. 96, No. 12
 930 (DECEMBER 2015), pp. 2059-2078.

931 Stephens, B.B. Weak Northern and Strong Tropical Land Carbon Uptake from Vertical
 932 Profiles of Atmospheric CO₂. *Science*, 316,1732-1735, 2007. doi: 10.1126/science.1137004.

933 Straume, A.G.; Dietz, R. N.; Koff, E.N., and Norden, K., 1998. Perfluorocarbon background
 934 concentrations in Europe. *Atmos. Environ.* 32, 4109-4122.

935 Tuazon, E.C., Atkinson, R. Tropospheric degradation products of CH₂FCF₃ (HFC-134a). *J*
 936 *Atmos Chem* 16, 301–312 (1993). <https://doi.org/10.1007/BF01032627>.

937 Tomberg, T., Vainio, M., Hietya T., and Halonen, L., 2018. Sub-parts-per-trillion level
 938 sensitivity in trace gas detection by cantilever-enhanced photo-acoustic spectroscopy.
 939 *Scientific Reports*, 8, 1848-1867.

940 Turner, A. J. C., Frankenberg, P. O., Wennberg, D. J., Jacob., 2017. Decadal trends in
 941 atmospheric methane and OH. *Proceedings of the National Academy of Sciences*, 114 (21)
 942 5367-5372; DOI: 10.1073/pnas.1616020114.

943 Vollmer, M. K., Reimann, S., Hill, M. and Brunner, D.: First observations of the fourth
 944 generation synthetic halocarbons HFC-1234yf, HFC-1234ze(E), and HCFC-1233zd(E) in the
 945 atmosphere, *Environ. Sci. Technol.*, 49(5), 2703–2708, doi:10.1021/es505123x, 2015.
 946

947 Wang, Y., D.J. Jacob, and J.A. Logan, Global simulation of tropospheric O₃-NO_x-
 948 hydrocarbon chemistry, 3. Origin of tropospheric ozone and effects of non-methane
 949 hydrocarbons, *J. Geophys. Res.*, 103/D9, 10,757-10,768, 1998.
 950 <https://doi.org/10.1029/98JD00157>.

951 Watson, T. B.; Wilke, R., Dietz, R.N., Heiser, J., and Kalb, P., 2007. The atmospheric
 952 background of perfluorocarbon compounds used as tracers. *Environ. Sci. & Technology*
 953 2007, 41, 6909-6913. Whetstone, J.R., Advances in urban greenhouse gas flux quantification:
 954 2018. The Indianapolis Flux Experiment (INFLUX). *Elem Sci Anth*, 6(1), p.24. doi:
 955 <http://doi.org/10.1525/elementa.282>, 2018.

956 Whetstone, J.R., Advances in urban greenhouse gas flux quantification: 2018. The
 957 Indianapolis Flux Experiment (INFLUX). Elem Sci Anth, 6(1), p.24. doi:
 958 <http://doi.org/10.1525/elementa.282>, 2018.

959 Williams, A.G., Chambers, S.D., Conen, F., Reimann, S., Hill, M., Griffiths, A.D., and
 960 Crawford, J. (2016) Radon as a tracer of atmospheric influences on traffic-related air
 961 pollution in a small inland city, Tellus B: Chemical and Physical
 962 Meteorology, 68:1, DOI: [10.3402/tellusb.v68.30967](https://doi.org/10.3402/tellusb.v68.30967).

963 Xiong, L., Bai, W., Chen, F., Zhao, X., Yu, F., and Diebold, G.J., 2017. Photoacoustic trace
 964 detection of gases at the parts-per-quadrillion level with a moving optical grating. PNAS,
 965 114, 7246-7249.

966 Yokouchi, Y., Saito, T., and Mukai H. 2018: Long-term high-frequency measurements of
 967 dibromomethane in the atmosphere at algae-rich and algae-poor coastal sites. Journal of
 968 Atmospheric Chemistry volume 75, pages 171–180. (DOI: [10.1007/s10874-017-9370-z](https://doi.org/10.1007/s10874-017-9370-z)).
 969

970 Zajarevich, N., Slezak, V., Peuriot, A., Villa, G., Láttaro, A., and Crivicich, R., 2013.
 971 Photoacoustic Detection of Perfluorocarbon Tracers in Air for Application to Leak Detection
 972 in Oil-Filled Cables. International J. of Thermophysics, 34, 1444-1450.

973

974

975