

Global warming potentials and radiative efficiencies of halocarbons and related compounds: a comprehensive review

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- **Global Warming Potentials and Radiative Efficiencies of**
- 2 Halocarbons and Related Compounds: A Comprehensive

3 Review

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28 Abstract

29 In the mid-1970s it was recognized that, as well as being substances that deplete stratospheric 30 ozone, chlorofluorocarbons (CFCs) were strong greenhouse gases that could have substantial 31 impacts on radiative forcing of climate change. Around a decade later, this group of 32 radiatively active compounds was expanded to include a large number of replacements for 33 ozone-depleting substances such as chlorocarbons, hydrochlorocarbons, 34 hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), 35 bromofluorocarbons, and bromochlorofluorocarbons.

36 This paper systematically reviews the published literature concerning the radiative 37 efficiencies (REs) of CFCs, bromofluorocarbons and bromochlorofluorocarbons (halons), 38 HCFCs, HFCs, PFCs, SF₆, NF₃, and related halogen containing compounds. In addition we 39 provide a comprehensive and self-consistent set of new calculations of REs and global 40 warming potentials (GWPs) for these compounds, mostly employing atmospheric lifetimes 41 taken from the available literature. We also present Global Temperature change Potentials 42 (GTPs) for selected gases. Infrared absorption spectra used in the RE calculations were taken 43 from databases and individual studies, and from experimental and *ab initio* computational 44 studies. Evaluations of REs and GWPs are presented for more than 200 compounds. Our 45 calculations yield REs significantly (> 5%) different from those in the Intergovernmental 46 Panel on Climate Change Fourth Assessment Report (AR4) for 49 compounds. We present 47 new RE values for more than 100 gases which were not included in AR4. A widely-used 48 simple method to calculate REs and GWPs from absorption spectra and atmospheric lifetimes 49 is assessed and updated. This is the most comprehensive review of the radiative efficiencies 50 and global warming potentials of halogenated compounds performed to date.

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97 **1** Introduction

Concern was raised in the 1970s that emissions of chlorofluorocarbons (CFCs), a class of compounds developed for a range of industrial and domestic uses, could lead to stratospheric ozone depletion [*Molina and Rowland*, 1974]. This concern was realized a decade later with the discovery of the Antarctic ozone hole [*Farman et al.*, 1985] and a less severe but globalscale stratospheric ozone depletion [e.g., *Stolarski et al.*, 1992].

103 At about the same time, it was also recognized that the CFCs were strong absorbers of 104 infrared radiation and that sustained emissions could lead to accumulations in the atmosphere 105 which would have significant climate impacts [Ramanathan, 1975; Wang et al., 1976]. This 106 climatic role was re-emphasized during the 1980s, and expanded to more classes of gases, 107 including chlorocarbons, hydrochlorocarbons, hydrochlorofluorocarbons (HCFCs), 108 hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and the bromofluorocarbons and 109 bromochlorofluorocarbons (referred to here as halons) [e.g., Hansen et al., 1989; Ramanathan 110 et al., 1985; Ramanathan et al., 1987]. These studies indicated that the increase in 111 atmospheric concentrations of CFCs and related compounds was contributing a decadal 112 radiative forcing which was around 30-40% of that due to the increase in carbon dioxide 113 concentrations. Furthermore, it was noted that this share could increase, if the growth in 114 emissions of the CFCs and related molecules was unconstrained.

115 The landscape for considering the climate impact of halocarbons (organic compounds 116 containing one, or more, halogen atom) changed as a result of global environmental 117 agreements under the auspices of the United Nations. First, the Montreal Protocol on 118 Substances that Deplete the Ozone Layer 119 (http://ozone.unep.org/new_site/en/montreal_protocol.php) - signed in 1987 and entered into 120 force two years later - and its subsequent amendments and adjustments, led to the phasing out 121 of production and emissions (with some exceptions) of CFCs, chlorocarbons and halons; it also included a schedule for the phasing out of emissions of HCFCs. Then, the Kyoto 122 123 Protocol to the United Nations Framework Convention on Climate Change (UNFCCC) 124 (http://unfccc.int/kyoto protocol/items/2830.php) - signed in 1997 and entered into force in 125 2005 - set limits on the emissions of a "basket" of greenhouse gases by developed countries. 126 The basket of greenhouse gases included a number of PFCs and hydrofluorocarbons (HFCs), 127 the latter being most commonly used as CFC replacements. The initial Kyoto Protocol 128 covered emissions in the so-called first commitment period of 2008-2012. The Doha Amendment to the Kyoto Protocol covers emissions in a second commitment period of 20132020, and added nitrogen trifluoride to the basket of greenhouse gases.

131 Some of the issues concerning the halocarbons can be illustrated by reference to 132 Figure 1 [WMO/GAW, 2011], which shows quasi-global average atmospheric concentrations 133 of 10 of the more abundant halocarbons. During the 1980s, the halocarbon abundance and 134 growth was dominated by two CFCs (CFC-11 (CCl₃F) and CFC-12 (CCl₂F₂)). There were 135 also significant contributions from CFC-113 (CCl₂FCClF₂), methyl chloroform, and carbon 136 tetrachloride. During the 1990s there was a dramatic change in the growth rates of the three CFCs and methyl chloroform. The changes were driven by the effects of the Montreal 137 Protocol which led to rapidly declining emissions of these gases. The influence of the 138 139 atmospheric lifetime of the different gases is also clear from Figure 1. Methyl chloroform has 140 a relatively short lifetime (5 years) and its atmospheric concentration responds rapidly to 141 decreased emissions. In contrast, CFC-12 and CFC-113 have atmospheric lifetimes of 100 142 and 85 years, respectively, and their atmospheric concentrations respond more slowly to 143 decreased emissions. CFC-11 has an atmospheric lifetime of 45 years and its atmospheric 144 concentration is more responsive than CFC-12 but less responsive than methyl chloroform to 145 decreased emissions. The fact that the atmospheric concentrations of carbon tetrachloride (35 year lifetime) have only declined modestly over the past 30 years reflects continued emissions 146 147 from developing nations [WMO, 2011].

148 Figure 1 shows that concentrations of HCFC-22 (CHClF₂), an important interim 149 replacement for several CFCs, continue to grow, despite being controlled by the Montreal 150 Protocol – its concentration is now close to that of CFC-11. HFC-134a (CH₂FCF₃), which is 151 included within the Kyoto Protocol, has been the fastest growing HFC, mainly because of its 152 use as a replacement for CFC-12 in refrigeration and vehicle air-conditioning applications. Its 153 relatively short lifetime (13.4 years) compared to the CFCs means that for the same emission 154 rate the atmospheric abundance of HFC-134a would be much lower than the CFCs it replaces 155 (see section 2.4). Estimating future atmospheric concentrations of HCFCs and HFCs is 156 challenging as it requires estimation of future emissions which are difficult to predict. For 157 example, future concentrations of HFC-134a will depend on the growth of the global vehicle 158 fleet and the impact of legislation and improved technology which would limit the use of HFC-134a or its leakage from that fleet. If the current emission rate $(149\pm27 \text{ kt yr}^{-1} \text{ in } 2008 \text{ km})$ 159 [WMO, 2011]) were maintained, the tropospheric concentration of HFC-134a would stabilize 160

161 at 120 ± 20 ppt within a few decades. In addition to the gases shown in Figure 1, there are 162 other halogenated alkanes (e.g., HFC-125 (CF₃CF₂H), HFC-143a (CF₃CH₃), HFC-152a 163 (CH₃CHF₂), HFC-32 (CH₂F₂), HFC-245fa (CHF₂CH₂CF₃), C₂F₆, and C₃F₈) that have been 164 detected in the atmosphere at levels of 1-10 ppt.

While the Montreal Protocol was designed to protect the ozone layer, its impact on climate change has been substantial, since it also controlled the atmospheric abundance of species that are powerful greenhouse gases – indeed it can be argued that it had a greater influence on the radiative forcing of climate change than the Kyoto Protocol [e.g., *Velders et al.*, 2007].

170 To make the multi-gas approach embedded in the UNFCCC operational, the Kyoto 171 Protocol from 1997 adopted a framework whereby emissions of non-CO₂ greenhouse gases 172 were placed on a "CO₂-equivalent" scale. As will be discussed in section 2, there is no unique 173 way of assigning a CO_2 -equivalence to an emission of a non- CO_2 gas, but the Kyoto Protocol 174 adopted one available metric, the Global Warming Potential with a 100-year time-horizon (GWP(100)). The Protocol uses values of GWP(100) for specific gases as reported in the 175 176 Intergovernmental Panel on Climate Change (IPCC) Second Assessment Report (SAR) [IPCC, 1995]. It has not, so far, taken into account either revisions to those GWP values (as a 177 178 result of improved understanding, and changing background concentrations of gases) or the expansion of the list to include additional species (including, for example, hydrofluoroethers 179 180 (HFEs)) that have been catalogued in subsequent IPCC reports [e.g., IPCC, 2001; 2007] and 181 World Meteorological Organization (WMO) / United Nations Environment Programme 182 (UNEP) Scientific Assessment of Ozone Depletion [WMO, 2003; 2007; 2011]. In addition the 183 parties to the UNFCCC have not considered in any detail and depth the use of alternative 184 metrics to the GWP(100). For the second commitment period of the Kyoto Protocol, which is 185 covered by the Doha Amendment, a draft decision (which is described in UNFCCC Decision 186 2/CMP.8 (http://unfccc.int/resource/docs/2012/cmp8/eng/13a01.pdf) which itself refers to 187 Decision 4/CMP.7 (http://unfccc.int/resource/docs/2011/cmp7/eng/10a01.pdf)) has been made 188 to adopt the GWP(100) values reported by the IPCC's Fourth Assessment Report in the Errata 189 Table 2.14 of Working Group 1 to the report (see 190 http://www.ipcc.ch/publications and data/ar4/wg1/en/errataserrata-errata.html#table214), but this decision has not been confirmed at the time of writing. 191

192 The GWP values for specific gases given in successive IPCC and WMO Ozone 193 Assessment reports are drawn from a range of sources which use a variety of techniques to derive the input parameters (and in particular the "radiative efficiency" (RE) – which is, 194 195 broadly, the "greenhouse" strength of a particular gas, on a per molecule basis – see section 196 2.2) needed to calculate the GWP. In addition, rather simplified considerations have 197 sometimes been adopted to take into account discrepancies between values reported in the 198 literature (e.g., averaging available values rather than assessing which are likely to be the 199 more reliable).

200 The primary aim of this review is to provide a comprehensive and consistent analysis 201 of the input parameters required to calculate values of the GWP and other metrics for a large 202 number of CFCs, chlorocarbons, hydrochlorocarbons, HCFCs, HFCs, PFCs, HFEs and other 203 related halogenated substances (including, for example, nitrogen trifluoride (NF₃) and sulphur 204 hexafluoride (SF_6)). The particular emphasis will be on the method of calculation of the 205 radiative efficiency. The review will also consider, in much less detail, atmospheric lifetimes, 206 another important input parameter for the calculation of GWPs and other metrics -207 atmospheric lifetimes are, for the most part, taken from the existing literature, without 208 detailed analysis. This then enables us to provide an extensive and self-consistent set of 209 GWPs for halocarbon gases; we also provide tabulations of values for an alternative metric 210 (the Global Temperature change Potential (GTP) – see section 4.2) for selected important 211 gases.

In addition to their direct radiative effects, some halocarbons cause additional (indirect) effects on the climate system by influencing the abundance of other climaticallyimportant gases – for example, stratospheric ozone, which is influenced by the CFCs and the halons. Such indirect effects are discussed elsewhere [e.g., *Daniel et al.*, 1995; *WMO*, 2011] and are not covered here.

Section 2 provides the necessary background concepts, section 3 presents the methodology we adopt to generate a consistent set of REs and lifetimes of the halocarbons, and related halogenated substances, including a discussion of the sensitivity of these parameters to uncertainties. Section 4 provides tabulations of the radiative efficiencies, lifetimes, GWPs and GTPs. Section 5 presents our conclusions.

223 2 Background concepts

The computation of GWPs and similar metrics for a particular gas requires various inputs and model calculations. The two basic input parameters for the GWP calculations are, as will be described in section 2.5, the RE and the lifetime of the gas. The calculation of these two parameters requires, in turn, much additional information. Figure 2 summarizes the main steps required which are discussed in more detail below.

229 **2.1 Molecular radiative properties**

230 The first stage in the determination of the RE is knowledge of the fundamental spectroscopic 231 properties of a molecule. Here we are most concerned with its properties at thermal infrared (IR) wavelengths (i.e., wavelengths at which the Earth and its atmosphere emit significant 232 amounts of infrared radiation) of roughly 4 to 200 µm (2500 to 50 cm⁻¹). We will mostly work 233 234 in terms of the frequency-like variable, wavenumber (the inverse of wavelength, normally auoted in cm⁻¹). The emission of infrared radiation by the Earth and atmosphere and the 235 radiative properties of the atmosphere are strong functions of wavenumber. Hence it is 236 237 necessary to determine the spectroscopic properties of the target molecule as a function of wavenumber. A general introduction to atmospheric radiative transfer can be found in *Pettv* 238 239 [2006] and introductions to general molecular spectroscopy can be found in Hollas [2004] 240 and Atkins and Friedman [2010]. Fundamentally, the molecules of interest here absorb and 241 emit radiation by transitions between their vibrational-rotational energy levels. The 242 characteristic wavenumber of absorption is determined by the spacing of the vibrational energy levels, with the transitions between particular vibrational-rotational energy levels 243 leading to that absorption being spread by typically 50 cm⁻¹ around this characteristic 244 wavenumber. For example, one of the simplest molecules, CF₄ absorbs over a narrow range 245 of wavenumbers near 1300 cm⁻¹ which is associated with the stretching of the carbon-fluorine 246 247 bonds in the molecule. Molecules containing the carbon-chlorine bond absorb characteristically around 800 cm⁻¹. The more complex the structure of the molecule, the 248 249 greater the number of possible modes of vibrations (including different stretching and bending modes) and hence the more complex the infrared absorption spectrum becomes. Figure 3 250 251 shows IR spectra of representative halocarbons and illustrates the increased number of IR 252 absorption bands observed with larger, more complex and less symmetric molecules.

253 In principle, it would be desirable to characterize the strength of each discrete 254 vibrational-rotational transition, and indeed this is necessary for some atmospheric 255 greenhouse gases such as water vapor and carbon dioxide, where the absorption spectrum 256 consists of many sharp individual spectral lines with rapid variations of absorption with 257 wavenumber. However, for halocarbons the individual transitions are so close together (as a result of the large masses of the atoms), and sufficiently broad, that under atmospheric 258 259 conditions the individual transitions merge together leading to a spectrum that consists of broad absorption bands (see Figure 3). The spectrally-resolved absorption cross-sections 260 (units of cm² molecule⁻¹ with typical peak cross-sections of order 10⁻¹⁸-10⁻¹⁷ cm² molecule⁻¹ 261 for the molecules considered here) can be integrated over infrared wavenumbers to give the 262 integrated cross-section (typical values for halocarbons are of the order of 10^{-16} cm² 263 molecule⁻¹ cm⁻¹). The integrated cross-section gives a useful measure of the overall strength 264 265 of IR absorption but the variation of absorption with wavenumber (i.e., the absorption 266 spectrum) must be known for calculation of the potential climate impact [e.g., Pinnock et al., 267 1995; Wallington et al., 2010].

The most common way for determining the absorption cross-sections of halocarbons is 268 via laboratory measurements using Fourier Transform Infrared Spectrometry. Measurements 269 270 are made at typically 0.5 cm⁻¹ or better spectral resolution. In general, the absorption cross-271 sections for halocarbons are only rather weakly dependent on temperature and pressure over 272 the atmospherically relevant range and this dependence is generally neglected in RE 273 calculations and likely uncertainties are about ±5% [Highwood and Shine, 2000]. The 274 absorption cross-section measurements are typically assessed to have an accuracy of 275 approximately ±5% [e.g., Ballard et al., 2000b; Clerbaux et al., 1993; Pinnock et al., 1995].

276 More recently, absorption cross-sections have begun to be determined by quantum mechanical electron structure calculations (we will refer to these as *ab initio* methods), which 277 278 in principle only rely on the basic laws of nature. In practice, however, *ab initio* calculations 279 involve approximations to solving the Schrödinger equation and residual errors remain [e.g., Blowers et al., 2007; Bravo et al., 2010b; Papasavva et al., 1997]. The ab initio methods 280 281 show considerable promise, but it has been found that they need empirical corrections 282 (particularly for the wavenumbers of the main vibrational modes) to agree with laboratory 283 measurements. In addition, their capabilities have not been assessed for the full range of 284 molecules considered here. Nevertheless they have already proven to be useful adjuncts to

laboratory measurements and can provide data at wavenumbers that are difficult to study in
the laboratory and allow rapid surveying of a broad range of compounds for which laboratory
samples may not be easy to procure.

288 **2.2** Radiative forcing and radiative efficiency - concepts

289 Once the absorption cross-sections have been obtained, the next step is to compute the impact 290 that the addition of a particular halocarbon to the atmosphere has on the radiation budget. The 291 resulting change in the radiation budget is generally referred to as "radiative forcing" (RF), 292 but there are a number of nuances to the definition of RF that need to be elaborated on. Also, in general, radiative forcing (in units of W m^{-2}) refers to the effect of a specified change in the 293 concentration of a species, often over some given time period. In this review, we focus on the 294 295 radiative forcing per unit change in halocarbon mixing ratio - this is referred to as radiative efficiency (RE) (W m⁻² ppb⁻¹). RE assumes that the RF is linear in mixing ratio – this is 296 normally appropriate in the case of small perturbations in mixing ratio about current 297 298 concentrations and is also appropriate for gases, such as the ones we consider here, which 299 have low background concentrations.

300 IPCC Assessment Reports [e.g., Forster et al., 2007] have addressed the rationale for 301 using RF, outlined caveats in its use, and also defined possible alternative definitions of RF 302 [see also discussions in e.g., Fuglestvedt et al., 2010; Hansen et al., 2005]. Studies using 303 climate models indicate that there is a direct relationship between global-averaged RF and the 304 (equilibrium) global-mean surface temperature change, and so RF has been essentially used as 305 a proxy for surface temperature change. RF is normally defined at the tropopause including 306 stratospheric temperature adjustment [Forster et al., 2007], the rationale being that the tight 307 coupling between the surface and troposphere means that they behave as a single 308 thermodynamic system; hence it is the change in the input of energy into this system that 309 drives the climate change.

Instantaneous RF [e.g., *Forster et al.*, 2007] is defined as the change in net irradiance at the tropopause, following (for example) a change in a greenhouse gas concentration. Earlier studies indicated that the instantaneous RF had less utility (i.e., models indicated a less close relationship between it and the resulting surface temperature change) than RF with stratospheric temperature adjustment. Part of the rationale for this is that, following a perturbation, the response time of the stratosphere is fast (around a few months) compared to 316 the decadal time scale for the temperature of the surface-troposphere system to respond. It is 317 found that for a number of forcings, the RF including stratospheric temperature adjustment 318 has a closer relationship with modeled surface temperature change, than the instantaneous RF. 319 For this definition of forcing, stratospheric temperatures are assumed to adjust in response to 320 the change in greenhouse gas concentration - this change in temperature leads to a further 321 change in the irradiance, as the downward emission by the stratosphere to the troposphere is 322 dependent on this temperature. Some gases (notably CO_2) lead to a cooling of the stratosphere 323 which makes the stratospheric-adjusted forcing less than the instantaneous forcing. For others 324 (including many halocarbons) the reverse is true, as the stratosphere warms – see section 3.3.2 325 for further discussion.

Early studies [Jain et al., 2000; Myhre and Stordal, 1997; Naik et al., 2000; Pinnock et 326 327 al., 1995] quantified the difference between the instantaneous and stratospheric-adjusted RF 328 for a range of halocarbons, indicating that the instantaneous forcing is typically 5-10% lower 329 than the stratospheric-adjusted RF. One drawback with the stratospheric-adjusted RF is that 330 its calculation is computationally much more demanding; in this review, because of the large 331 number of gases involved, we calculated instantaneous RE and then applied a correction, 332 based on the available literature, to account for the effect of stratospheric adjustment (see 333 section 3.3.2).

334 More recently, there has been much work investigating alternative definitions of 335 forcing [e.g., Andrews and Forster, 2008; Forster et al., 1997; Gregory et al., 2004; Hansen 336 et al., 2005] – for example, fixing surface temperatures (sometimes sea-surface temperature 337 only) but allowing tropospheric temperatures, humidity and cloudiness to adjust, in addition to the stratosphere. The rationale here is that there are so-called "fast feedbacks" or "rapid 338 339 adjustments" operating in the troposphere that can change, for example, cloudiness in the 340 absence of surface temperature change. Hence it is conceptually attractive to separate climate 341 responses that operate on day-to-month timescales and are independent of changes in surface 342 temperature from the "traditional" climate feedbacks (for example, water vapor feedback, ice 343 albedo feedback and various cloud feedbacks) which are mediated by surface temperature 344 change and hence act on decadal to century timescales.

These rapid tropospheric adjustments can be particularly important for other forcings, such as those resulting from black carbon aerosols. Few model results are available on the effect of tropospheric adjustments for the gases considered here. Computation of such 348 forcings requires long simulations using sophisticated climate models, and results would 349 likely depend significantly on the climate model chosen. In addition, because of the inherent "unforced" natural variability in such climate models, it would be necessary to impose a large 350 forcing (in excess of 1 W m^{-2}) to easily extract a reliable signal from the model; this is many 351 times the present-day RF of the most abundant CFC (CFC-12 – about 0.17 W m⁻² [Forster et 352 al., 2007]) and orders of magnitude more than most other gases considered here, raising 353 354 concerns about the linearity of the rapid tropospheric adjustments. Since research on these 355 more advanced definitions of forcing is still at an early stage, and also because of the 356 computational demands of performing these calculations, we believe it premature to adopt 357 them here as a framework.

358 An additional and related issue concerns the so-called climate efficacy. An underlying 359 assumption in early work in this area was that the global-mean surface temperature response to an RF of, say, 1 W m⁻², was the same irrespective of the cause of the forcing. Climate 360 model simulations now indicate that this assumption is not strictly justified. Efficacy is a 361 measure of the ability (per W m⁻²) of a particular forcing to change surface temperature 362 relative to, for example, a 1 W m⁻² forcing due to a change in carbon dioxide. Relatively little 363 research has been performed on the efficacy of the halocarbons. Forster and Joshi [2005] 364 365 found an efficacy of CFC-12 (using the stratosphere adjusted forcing) to be 0.94 in their model. Hansen et al. [2005], by contrast, found an equivalent value (for a combination of 366 367 CFC-11 and CFC-12) of 1.3, but also demonstrated that the efficacy depends on the definition 368 of forcing that is adopted. An additional issue for the short-lived halocarbons, is that the 369 efficacy likely depends on the spatial distribution of the halocarbon [Joshi et al., 2003] which 370 in turn depends on the halocarbon's lifetime (see section 2.4) and the distribution of 371 emissions. Given these uncertainties, we assume an efficacy of 1 throughout this review, 372 although it is in principle possible to include non-unity values of efficacy within the GWP and 373 GTP metrics.

2.3 Calculation of radiative efficiency

The calculation of radiative efficiency requires, in addition to the absorption spectrum for the halocarbon in question, a calculation of atmospheric irradiances, accounting for atmospheric properties, such as the amounts, distributions and radiative properties of other infraredabsorbing components (water vapor, carbon dioxide, ozone, clouds, etc.), and temperatures. As the RE is a globally- and annually-averaged quantity, in principle it should be calculated 380 locally and, say, monthly, and then averaged to produce the global and annual mean. In 381 practice, it is possible, with about 5-10% accuracy, to calculate the RE using a globally-382 averaged atmospheric profile or using two or three profiles representative of the tropics and 383 mid/high latitudes [Freckleton et al., 1998; Myhre and Stordal, 1997]. Myhre et al. [2006] found that for calculations of the CFC-12 RE, the use of two atmospheric profiles (one for 384 385 tropics and one extra-tropics) represents global simulations with a horizontal resolution of $2.5^{\circ} \times 2.5^{\circ}$ within 1%. In addition, there are several possible choices of tropopause definition 386 that impact on the calculated forcing at the 5% level [Freckleton et al., 1998]. 387

388 The radiative transfer models that can be used for such calculations vary in 389 complexity. The most complex (line-by-line (LBL) models) perform calculations at high (typically 0.01 cm⁻¹) spectral resolution and resolve explicitly the individual spectral lines of 390 391 atmospheric gases such as water vapor, carbon dioxide and ozone. These are computationally 392 expensive and parameterized models are often used (for example to compute the effect of 393 stratospheric adjustment). Narrow Band Models resolve the infrared spectrum at typically 10 cm⁻¹ resolution, while computationally-fast Wide Band Models (suitable for use in climate 394 395 models) may resolve the thermal infrared region into typically 5 to 10 spectral intervals. 396 Intercomparisons of such models both for greenhouse gases in general [e.g., Collins et al., 397 2006; Oreopoulos et al., 2012] and for halocarbons in particular [e.g., Forster et al., 2005; 398 Gohar et al., 2004; Jain et al., 2000] are of importance in assessing the capabilities of the 399 parameterized models. When these models are combined with vertical profiles of temperature, 400 cloudiness and greenhouse gas concentrations, it is necessary to ensure that the model's 401 global-and-annual outgoing longwave radiation, and the impact of clouds on the outgoing 402 longwave budget, are in reasonable agreement with satellite observations; otherwise, biases in 403 the resulting RE calculations can occur.

In addition to the direct use of radiative transfer models to calculate REs, it is possible 404 405 to use these models to produce simple techniques to compute the radiative forcing directly from the absorption cross-sections. Pinnock et al. [1995] used a narrow-band model to 406 407 compute the RE per unit absorption cross-section as a function of wavenumber, using a global 408 and annual mean atmosphere. This then indicates the spectral regions at which halocarbon 409 radiative forcing is most effective. As shown in Figure 5 and discussed in section 3.3.1, where an update to the Pinnock et al. [1995] method is presented, molecules are most effective if 410 they absorb in the 800-1200 cm⁻¹ spectral region (a so-called "atmospheric window"), but can 411

412 remain effective outside this region. If a halogenated compound absorbs at a wavelength 413 where there is already substantial atmospheric absorption (for example by carbon dioxide near 414 670 cm^{-1}) then the additional absorption by this compound will not contribute significantly to 415 radiative forcing.

416 Hence, if the spectrally-varying radiative forcings calculated by *Pinnock et al.* [1995] 417 are multiplied by the absorption cross-sections representing a real halocarbon (averaged to the 418 same spectral resolution as the radiation calculations) then an estimate of the RE can be 419 achieved easily by summing over all wavenumbers, using a spreadsheet for example, without 420 the need for a complex radiation code. Pinnock et al. [1995] demonstrated for a wide range of 421 halocarbons that this simple technique could generate instantaneous REs that were accurate to 422 within 0.3%, relative to full calculations using the same radiation code that was used to 423 generate the values in the simple technique, and using the same atmospheric profile. (It is 424 emphasized that this is not the technique's absolute accuracy, as this is dependent on the 425 accuracy of the radiation code and its input parameters). Consequently, the method developed 426 by Pinnock et al. is simple and effective, and has been widely used.

427 A further consideration in calculating the RE is that the horizontal and vertical 428 distribution of the molecule must be specified - often the baseline assumption is that the 429 molecule is well-mixed within the atmosphere (both horizontally and vertically); corrections 430 to approximately account for the departure from this assumption are then applied – see section 431 2.4 and 3.3.4. However, it should be noted that for short-lived gases in particular, there is no 432 unique value of RE, as its value depends to some extent on the geographical (and seasonal) 433 distribution of emissions, as these in turn influence the horizontal and vertical distribution of 434 the gas.

435 **2.4 Atmospheric lifetimes**

The global atmospheric lifetime (yr) of a gas is defined in the IPCC Third Assessment Report [*IPCC*, 2001] as "the burden (Tg) divided by the mean global sink (Tg/yr) for a gas in steady state (i.e., with unchanging burden)." The report also identifies two important consequences of this definition, namely that: (i) "when in steady state (i.e., source strength = sink strength) the atmospheric burden of a gas equals the product of its lifetime and its emissions"; and (ii) "the integrated atmospheric abundance following a single emission is equal to the product of the steady-state lifetime for that emission pattern and the amount emitted [*Prather*, 1996]". 443 As will be discussed in section 2.5, the most frequently used climate metrics consider the444 impact of a pulse emission of a gas.

445 The global atmospheric lifetime has also been referred to as simply as "lifetime", or 446 "turnover time" [Bolin and Rodhe, 1973; IPCC, 1995] reflecting the fact that it characterizes 447 the time required to turn over the global atmospheric burden of the gas in question. It is sometimes thought of as the decay time (e-fold) following a perturbation, with its magnitude 448 449 determined by chemical or photolytic loss rates. While conceptually appealing, this approach 450 applies rigorously only for a gas whose local chemical lifetime is constant in space and time, 451 such as for the noble gas radon, whose lifetime is fixed by the rate of its radioactive decay 452 [IPCC, 2001]. In reality the chemical losses of pollutants vary in time and space and, if the 453 magnitude of emissions are sufficient (e.g., for methane), the emissions themselves can 454 influence the chemistry of the atmosphere and hence the pollutant's lifetime. As discussed in 455 sections 3.3.3 and 3.3.4, many halocarbons have short lifetimes, are not well mixed in the 456 atmosphere, and the spatial and temporal emission pattern needs to be accounted for in 457 assessments of their radiative efficiencies.

458 Halocarbons are removed from the atmosphere by two main mechanisms; reaction 459 with OH radicals and photolysis. As a crude guide to understanding how the molecular 460 structure of a halocarbon affects its reactivity towards OH radicals, for a given carbon 461 backbone (e.g., C₂, C₃, n-C₄, etc.) the more fluorine atoms in a haloalkane the longer its 462 lifetime and the more bromine or iodine atoms the shorter its lifetime. For molecules containing hydrogen such as HCFCs, HFCs, HFEs and hydrochlorocarbons, the primary 463 464 removal mechanism in the troposphere is reaction with the hydroxyl radical OH. Lifetimes 465 range from a few days to millennia, depending on the structure of the molecule - to first 466 order, the more heavily halogenated a molecule, the longer its lifetime, although the precise 467 arrangement and nature of those halogens in the molecule plays an important role [Atkinson et 468 al., 2008; Sander et al., 2010]. Unsaturated molecules containing >C=C< double bonds react rapidly with OH radicals. Including one, or more >C=C< double bond is a particularly 469 470 effective method of reducing the atmospheric lifetime of halocarbons. For example, CF₃CF₂CH₃ (HFC-245cb) has a lifetime of 47.1 years while CF₃CF=CH₂ (HFC-1234yf) has a 471 472 lifetime of 10.5 days.

For CFCs and halons, the primary destruction mechanism is ultraviolet photolysis in the stratosphere. CFCs are inert in the troposphere as sufficiently short wavelength ultra475 violet radiation does not penetrate in to the troposphere. Indeed, it is their chemical inertness 476 that made the CFCs so attractive in industrial and domestic usages. It is interesting and worth 477 noting that when detection of CFCs in the atmosphere was first reported, the conclusion 478 included the comment "The presence of these compounds [CFC-11 and CFC-12] constitutes 479 no conceivable hazard" [Lovelock and Maggs, 1973]. Halons have atmospheric lifetimes in 480 the approximate range of 10 to 70 years, while CFCs have atmospheric lifetimes ranging from 481 about 45 to more than a thousand years. Calvert et al. [2008] have reviewed the mechanisms 482 in the atmospheric photolysis of haloalkanes. Absorption at ultra-violet wavelengths involves an $n \rightarrow \sigma^*$ transition with a non-bonding electron of the halogen promoted into an anti-483 484 bonding sigma orbital of the C-X bond. Ultra-violet absorption spectra for haloalkanes (RX) 485 of similar carbon backbone structure move to lower energy (longer wavelength absorption) 486 along the series X = F, Cl, Br, to I, reflecting a trend of lower electron affinity of the halogen 487 atom [Calvert et al., 2008]. Absorption by C-F and C-Cl bonds only occurs at wavelengths 488 below approximately 240 nm. CFCs, HFCs, HCFCs, chlorocarbons, and hydrochlorocarbons 489 do not photolyze in the troposphere as sufficiently short wavelength ultra-violet radiation does 490 not reach the troposphere. In contrast to C-F and C-Cl bonds, C-I bonds absorb strongly at 491 tropospherically relevant wavelengths and iodine-containing haloalkanes have atmospheric 492 lifetime of days, or less, with respect to photolysis in the troposphere (e.g., 4.9 days for CH₃I, 4.3 days for C₂H₅I, 4.9 hours for CH₂ICl, and 4.9 minutes for CH₂I₂ [Calvert et al., 2008]). 493 494 Absorption by C-Br bonds at tropospherically relevant wavelengths is generally weak but 495 photolysis can contribute to determining the atmospheric lifetime of some bromoalkanes such 496 as CHBr₃ [*Calvert et al.*, 2008]. Because of the inherent strength of the C-F bond, the PFCs 497 are chemically inert and, are the longest lived of the halocarbons, with lifetimes ranging from 498 about a thousand years to approximately 50,000 years for CF₄.

499 The atmospheric lifetime plays a further role in the determination of the radiative 500 efficiency, because it helps determine the degree of heterogeneity in the distribution of the 501 halogenated molecules in the atmosphere. For molecules with lifetimes of less than a few 502 months, the atmospheric distribution is dependent on where and when the gases are emitted, 503 reflecting the spatial and temporal distribution of OH radicals which determines the local 504 atmospheric lifetimes. Since the radiative efficiency of a gas depends on its location (in 505 general, a gas at low latitudes is more effective, as more radiative energy is available to be 506 absorbed at high temperatures), a unique radiative efficiency cannot be defined for such short-507 lived molecules without a detailed knowledge of the spatial and temporal emission pattern. In 508 addition, the vertical profile of a gas is also influenced by the atmospheric lifetime. Mixing 509 processes are most efficient within the troposphere with molecules mixed vertically on the 510 typical timescales of days to weeks. Within the stratosphere the vertical profile of a particular 511 species depends strongly on the relationship between the timescales for transport within the 512 stratosphere and the rate at which the molecule is destroyed. Jain et al. [2000] and Naik et al. 513 [2000] [see also Freckleton et al., 1998] used chemical transport models to simulate the 514 distributions of a range of halocarbons, and quantify the difference in the RE between using 515 these distributions and the assumption that the gases are well mixed. Their results were used 516 by Sihra et al. [2001] to develop a simplistic method to approximately account for the effect 517 of atmospheric lifetime on the radiative efficiency. This will be further discussed in section 518 3.3.4. (A non-constant atmospheric profile of a species can also result when the rates of 519 surface emissions are growing rapidly, because of the multi-year timescale for the molecule to 520 reach deep into the stratosphere.)

521 The products of the reactions that destroy halocarbons could in principle themselves be climatically-important gases. However, it is well established that the atmospheric 522 523 degradation of halocarbons gives oxygenated compounds which have relatively short 524 atmospheric lifetimes and are typically removed by wet and dry deposition on a time scale of days or weeks [Wallington et al., 1994b]. The oxidation products do not accumulate in the 525 526 atmosphere and do not contribute significantly to radiative forcing of climate change.

527 2.5

Climate impact metrics

528 A key objective of this review is to provide values for the GWP and GTP metrics for the 529 halocarbons. The rationale and challenges in developing climate impact metrics have been 530 reviewed in detail by Fuglestvedt et al. [2010] and so only a relatively brief discussion is 531 given here.

532 One of the prime drivers of the development of emission metrics is the need for their 533 use in multi-gas climate policies (such as the Kyoto Protocol) where emissions of different 534 compounds must be placed on a common scale, usually referred to as a "CO2-equivalent" 535 scale. There is no unique method of doing this, and the choice of method should be consistent 536 with the climate policy that the metric aims to serve [e.g., Plattner et al., 2009]. The Kyoto 537 Protocol's choice of the GWP(100) has been a matter of much discussion and debate [e.g., 538 Fuglestvedt et al., 2003; Manne and Richels, 2001; O'Neill, 2000; Shine, 2009]. One often 539 cited reason for its original use and retention has been the lack of a widely-accepted 540 alternative, and, latterly, the difficulties that might arise within policymaking if the metric 541 (more specifically, the numerical value that converts a given emission to a CO_2 -equivalent 542 emission) was substantially changed.

543 There are a number of elements that have to be considered in metric design. What kind 544 of emission is considered - for example, a pulse or a sustained emission? What "impact" is 545 considered - for example, radiative forcing, surface temperature change, sea-level rise, 546 economic impact, or the rate of change of these quantities? Which indirect effects and 547 feedbacks should be included? Is the impact considered integrated over some time period, or 548 at one particular time? Is the impact given as global mean or with a regional resolution? What 549 time period is considered? And, of significance to their wider acceptability, particularly 550 within the policymaking community, how transparent are the formulations of the metrics?

551 Here we present results for two metrics. The GWP (with time horizons of 20, 100 and 552 500 years) is presented to be consistent with reporting in previous IPCC assessments and its 553 wide usage. The GWP definition we use here is as used in the first IPCC Assessment Report 554 [IPCC, 1990] which itself was based on then-recent studies suggesting ways of 555 intercomparing the climate effect of emissions of different gases [Derwent, 1990; Fisher et 556 al., 1990; Lashof and Ahuja, 1990; Wuebbles, 1989]. The GWP represents the time-integrated 557 radiative forcing due to a pulse emission of a gas. It can be presented as the absolute GWP (AGWP – with units of, for example, W $m^{-2} kg^{-1}$ vear) or, more normally, as a ratio to the 558 559 AGWP of CO_2 . One difficulty is that the AGWP of CO_2 has been subject to periodic revision 560 in IPCC assessments, as a result of atmospheric changes (the RE of CO₂ decreases as CO₂ concentrations increase) and changes in understanding of how long CO₂ concentrations 561 562 remain perturbed following a pulse emission. Hence the GWP of a halocarbon may change 563 solely because of a change in AGWP of CO₂ rather than revisions to its own lifetime and 564 radiative efficiency, as happened, for example, in the IPCC Third Assessment Report IPCC 565 [2001]. The precise method used here to determine the AGWPs, and hence the GWPs, will be presented in section 3.5. 566

567 The GTP [*Shine et al.*, 2005a] is also chosen for presentation here, partly because it 568 has attracted more attention than other alternative metrics, including at the policymaking level 569 [e.g., *Plattner et al.*, 2009] and partly because it has a quite different basis from, and hence 570 provides an alternative perspective to, the GWP. The GTP represents the temperature change 571 due to a pulse emission of a gas, at some time (here 20, 50 and 100 years are chosen) in the 572 future. Hence it is an "end-point" metric (unlike the GWP, which is a time-integrated metric) 573 and hence retains less of a memory of the effect of emissions of short-lived species. It has 574 been suggested that the GTP may be more suitable for target-based climate policies [e.g., 575 Shine et al., 2007], such as envisaged under the Copenhagen Accord of the UNFCCC, where the aim is to keep surface temperature change, relative to pre-industrial times, below 2 576 577 degrees C. The GTP method requires, in addition to the lifetime and radiative efficiency, 578 some model to represent the response of global-mean surface temperature to radiative forcing, 579 and hence requires the specification of additional parameters compared to the GWP. As with the GWP it can be presented as an absolute quantity (with units of, for example, K kg⁻¹) or as 580 581 a ratio to the absolute Global Temperature change Potential (i.e., AGTP) of CO₂.

Since *Fuglestvedt et al.* [2010], there has been a significant literature on climate emission metrics including discussions of how these "physical" metrics relate to metrics which incorporate, additionally, an economics element [e.g., *Boucher*, 2012; *Johansson*, 2012; *Tol et al.*, 2012], the relationship amongst metrics (for example, *Peters et al.* [2011] discuss the similarities of the GWP with a time-integrated GTP) and evaluations of the sensitivities of GWPs and GTPs to uncertainties in input parameters and background scenarios [e.g., *Reisinger et al.*, 2011; *Reisinger et al.*, 2010].

589

590 **3 Data and method**

591 **3.1 Absorption cross-sections**

592 3.1.1 Laboratory measurements of infrared absorption cross-sections

Analytical infrared instrumentation usually only covers the mid-infrared region, 4000-400 cm^{-1} , and the majority of available IR absorption spectra — including most of the spectra covered in this review — were measured within this wavenumber range. As will be shown in detail in section 3.3.1, the effectiveness of the absorption in contributing to RE varies strongly with wavenumber, peaking at 300-600 and 750-1000 cm⁻¹, significant at 1100-1300 cm⁻¹, and of minor importance for wavenumbers above 1500 cm⁻¹ [*Pinnock et al.*, 1995].

599 Infrared spectra are measured in transmittance, which is defined as the ratio of spectral 600 intensity transmitted through the sample at a given wavenumber \tilde{n} , $I_{tr}(\tilde{n})$, to the incoming 601 spectral intensity, $I_0(\tilde{n})$. Transmittance is related to the wavenumber and temperature 602 dependent absorption cross section, $\sigma(\tilde{n}, T)$, through the Beer-Lambert-Bouguer law:

$$\frac{I_{tr}(\tilde{n})}{I_0(\tilde{n})} = e^{-S(\tilde{n},T)nd}$$

604 where *n* is the molecule concentration (molecule cm⁻³), and *l* is the sample optical path length 605 (cm). The absorption cross section (cm² molecule⁻¹) is then given by:

$$\mathcal{S}\left(\tilde{n},T\right) = \frac{1}{n \times l} \times \ln\left[\frac{1}{\tilde{r}}\frac{I_{0}\left(\tilde{n}\right)}{I_{tr}\left(\tilde{n}\right)}\right] \stackrel{\text{ij}}{=} \frac{\ln(10)}{n \times l} \times \lg\left[\frac{1}{\tilde{r}}\frac{I_{0}\left(\tilde{n}\right)}{I_{tr}\left(\tilde{n}\right)}\right] \stackrel{\text{ij}}{=} \frac{\ln$$

607 where ln is the napierian logarithm and lg is the common decadic logarithm.

608 The strength of an absorption band is given by the integral:

609
$$S(\tilde{n}_1, \tilde{n}_2, T) = \bigcup_{\tilde{n}_1}^{\tilde{n}_2} S(\tilde{n}, T) \times d\tilde{n}$$

610 where $S(\tilde{n}_1, \tilde{n}_2, T)$ is the integrated absorption intensity (in units of cm² molecule⁻¹ cm⁻¹) over 611 the wavenumber range \tilde{n}_1 to \tilde{n}_2 .

612 The absorption cross section depends on temperature for several reasons. First, 613 infrared absorption occurs from a range of rotational energy levels, and the relative 614 populations of these levels are strongly temperature dependent. Secondly, and particularly for molecules containing heavier atoms and in bending vibrations, absorption will not only occur 615 616 from the vibrational ground state but also from vibrationally excited states - so called hot 617 bands. Since populations depend on the temperature, so will the measured net absorption. 618 Further, molecules often have several stable conformations with different energies and 619 slightly different infrared spectra. The conformational equilibrium and, consequently, the 620 absorption spectrum of such molecules will therefore vary with temperature. While the 621 infrared absorption bands of halocarbons narrow with decreasing temperature there is no 622 significant change in the integrated infrared absorption over the atmospherically relevant 623 range [Ballard et al., 2000b; Le Bris et al., 2011; Orlando et al., 1992]. Changes in temperature over the atmospherically relevant range result in narrowing of the absorption 624 bands by a few cm⁻¹ [Orlando et al., 1992]. The error that results from the use of a single 625 infrared spectrum measured at, or near, room temperature to calculate the RE of a molecule in 626 the whole atmosphere is comparable to, or smaller than, the uncertainties in a single 627

measurement [*Ballard et al.*, 2000b] and so the temperature dependence is often ignored inRE calculations.

630

631 3.1.2 Theoretical calculations of infrared absorption cross sections

632 Theoretical calculations can be used to provide estimates of infrared vibrational band 633 positions and the intensity of the transitions. The theory underpinning such calculations and 634 their computational intricacies lie outside the scope of this review, but an introduction to the background can be found in Atkins and Friedman [2010]. Despite the complexities of the 635 636 calculational methods, modern software packages are such that the non-specialist can use 637 them and take advantage of the insights that theoretical calculations offer. Calculations are 638 carried out using a combination of a calculational method and a basis set. Researchers have 639 used traditional molecular orbital ab initio calculations using the 2nd-order Møller-Plesset 640 (MP2) perturbation method, and more recently, the Density Functional Theory (DFT) method. The DFT method is becoming increasingly common, as it provides comparable accuracy to 641 642 MP2, but at a considerably reduced computational cost. A commonly used DFT method is the Becke, 3-parameter, Lee-Yang-Parr method, commonly known as B3LYP. The basis sets 643 644 used in modern calculations are comprised of Gaussian-type orbitals, which have 645 characteristics similar to s-, p-, d-, etc. hydrogenic atomic orbitals. Basis sets are described 646 with specific notation; common examples are, in order of increasing basis set size, 6-31G, 6-31G* and 6-31G**. A calculation might be described as B3LYP/6-31G**, which would mean 647 that the calculation had been carried out using the B3LYP method combined with the 6-648 649 31G** basis set. There is always a tension between achieving the most accurate description of 650 a molecule — which requires a large basis set — and the need to reduce the computational cost of the calculation — which requires a small basis set. 651

In principle, calculations should be carried out for all possible conformers of a compound, with the final spectrum being a weighted sum of the spectra of the individual conformers. The contribution of each conformer to the overall spectrum is determined by its relative population, which is calculated using the Boltzmann distribution. *Bravo et al.* [2010b] have tested the importance of including the contribution of conformers to the overall spectrum for $n-C_4F_{10}$. They concluded that the change to the RE of including the higher energy conformers was less than 1%; most calculations use the lowest energy conformer to generatethe spectrum used for RE calculations.

660 Theoretical calculations are subject to quite significant errors, with contributions 661 arising from the method used and the limited size of the basis set. Fortunately, the outputs 662 from the calculations generally provide an estimate of the positions of vibrational bands that 663 differ in a systematic way from the experimentally observed band positions [Scott and 664 Radom, 1996]. The extent to which these differences have a significant impact on radiative 665 forcing efficiency calculations depends on the region of the spectrum where the transitions 666 occur. For example, compounds containing C-F bonds have strong absorptions at around 1250 cm⁻¹. In this region of the spectrum, the radiative efficiency function changes rapidly with 667 668 wavenumber (see section 3.3.1) and so small errors in the band position can have a relatively 669 large impact on calculated REs [Bravo et al., 2010b]. Different researchers have dealt with the 670 systematic errors in different ways; the errors are sometimes ignored [Blowers and 671 Hollingshead, 2009], accounted for by using a generic correction formula [Shine et al., 672 2005b], or corrected using methods specific to the particular class of compounds under consideration [Bravo et al., 2010b]. Integrated cross sections (over the appropriate 673 674 wavenumber range) are generally in good agreement (within 5%) with those determined 675 experimentally [Bravo et al., 2010b].

The output from calculations differs from experimental measurements in that rather 676 677 than providing an absorption cross section as a function of wavenumber, an integrated absorption cross section (IAC) is calculated for each vibrational band. Conversion to a cross 678 679 section can be achieved simply by dividing by the appropriate wavenumber interval to get an 680 average cross section over that interval; for example, *Pinnock et al.* [1995] calculate REs using a 10 cm⁻¹ interval, so IACs are simply divided by 10 cm⁻¹ to get the average cross 681 682 section over this interval for use in their calculations [Bravo et al., 2010b]. An alternative 683 approach is to 'spread' some of the absorption into neighboring wavenumber intervals. Bravo et al. [2010b] showed that spreading 50% of absorption equally into regions above and below 684 the central interval did not have a significant effect on calculated radiative forcing efficiencies 685 686 for a number of PFCs using the Pinnock method. However, the impact is likely to be more 687 significant if a narrower wavenumber interval is chosen for the calculations.

688 For comparison with experiment, the integrated absorption cross sections can be used 689 to simulate spectra assuming the vibrational bands are Gaussian in shape. Figure 4 shows an 690 experimentally determined spectrum of n-C₄F₁₀ from *Bravo et al.* [2010b] along with spectra 691 calculated using the B3LYP and MP2 methods. The calculated spectra have been corrected 692 for the systematic errors discussed earlier. The agreement between theory and experiment is 693 very good, particularly for calculations carried out using the B3LYP method. The spectra 694 generated in this way can also be used to calculate radiative forcing efficiencies in the normal 695 way. Again, using the Pinnock method with a 10 cm⁻¹ interval, *Bravo et al.* [2010b] found that 696 converting the IACs to spectra in this way had only a modest impact on the calculated RE.

697

698 3.1.3 Database and sources of cross-section data

699 The main sources of experimental infrared absorption cross-sections are Ford Motor Company [e.g., Sihra et al., 2001], the SWAGG project (Spectroscopy and Warming 700 701 potentials of Atmospheric Greenhouse Gases) [Ballard et al., 2000c; Highwood and Shine, 702 2000], and the two databases HITRAN-2008 (High Resolution Transmission) [Rothman et al., 703 2009] and GEISA-2009 (which is now referred to as GEISA-2011 on the GEISA website) 704 (Gestion et Etude des Informations Spectroscopiques Atmosphériques) [Jacquinet-Husson et 705 al., 2011]. Theoretical absorption data from ab initio calculations [Bravo et al., 2011a; Bravo 706 et al., 2010b] have also been included here.

707 The HITRAN-2008 database includes IR cross-sections of 31 different gases, many of 708 which are measured at a range of temperatures and pressures. Updates since the previous 709 edition, HITRAN-2004, have been described in detail in Rothman et al. [2009]. In GEISA-710 2009, IR spectra of 39 different gases are included, again for a wide range of temperatures 711 and pressures. Some of the spectra in GEISA-2009 are from the same source as in HITRAN-712 2008, and when this is the case we disregard the spectrum from GEISA-2009 to avoid 713 duplicates. Jacquinet-Husson et al. [2011] describes the GEISA-2009 database and the 714 updates that have taken place since the 2003 edition.

The absorption cross-sections available in the literature have been summarized (Tables 2, 4, 6, 8, 10, 12 and 14) and the spectra which have been used in the calculation of new best estimate REs are highlighted. Each available spectrum has been evaluated and if several cross-sections exist from the same laboratory group, only the latest published spectrum has been used in our calculations. In particular, spectra from *Sihra et al.* [2001] supersede those from *Pinnock et al.* [1995] and *Christidis et al.* [1997] since the methodology of the Ford 721 laboratory measurements improved over time. Furthermore, cross-sections from laboratory 722 measurements are favored over theoretical calculations, but the latter have been used if 723 experimental spectra are not available for a compound and when significant differences in 724 experimental data exist. The spectrum that was recorded nearest room temperature and 725 atmospheric pressure was used when more than one spectrum was available from a source, as 726 described further in section 3.6.1. The format of theoretical ab initio data differ from 727 experimentally measured infrared spectra; theoretical data consist of values of the central 728 wavenumber and the strength at the vibrational band center. To calculate the radiative efficiencies from these data, they were spread to the 1 cm⁻¹ bin size of our spectrally-varying 729 radiative efficiency data (see section 3.3.1). All the cross-sections used in this study have 730 731 been converted to the same format as in HITRAN (more information about this format can be 732 obtained at the HITRAN web site at http://www.cfa.harvard.edu/hitran), and many of the 733 cross-sections are available in the supplementary material.

734

735 **3.2 Atmospheric lifetimes**

736 The processes that remove halocarbons from the atmosphere have been described recently 737 [WMO, 2011]; this publication included a discussion of the rationale for recent changes to the 738 recommendations for the lifetimes of a number of species. It is outside of the scope of this 739 review to re-examine these recommendations; we confine ourselves to a summary of the 740 major atmospheric loss processes for halocarbons, which include chemical reaction and 741 photolysis, as well as uptake by the oceans and terrestrial ecosystems. In addition, there are examples of compounds — e.g., SF_5CF_3 , — where dissociative electron attachment may also 742 743 be important [Takahashi et al., 2002].

The global atmospheric lifetime of a gas was defined in section 2.4 as its burden divided by its loss rate. Under locally defined conditions, lifetimes can be determined as the inverse of a (pseudo-)first-order loss process. For loss of compound Y by reaction with X, we can write the loss rate as:

748
$$-\frac{\mathrm{d}[\mathrm{Y}]}{\mathrm{d}t} = k_{\mathrm{X}}[\mathrm{Y}][\mathrm{X}].$$

In this process, the pseudo-first-order rate constant for the loss of Y is equal to $k_X[X]$, and the lifetime of Y with respect to reaction with X, τ_X , is $1/(k_X[X]) = 1/k'_X$, with an assumption (or 751 approximation) that [X] is constant. Integration over space and time yields a global and 752 annual average lifetime of Y with respect to reaction with X. In the troposphere, the dominant 753 oxidant is the hydroxyl radical, OH. For well-mixed compounds (lifetimes greater than a few 754 months) lifetimes with respect to OH are determined relative to the lifetime of methyl 755 chloroform, CH₃CCl₃. The lifetime of a gas is given as the product of the CH₃CCl₃ lifetime 756 and its rate constant for reaction with OH divided by the OH rate constant of the gas; see WMO [2011], Prather and Spivakovsky [1990], Spivakovsky et al. [2000] and Montzka et al. 757 758 [2011] for further detailed discussion.

For photolytic processes, a photolysis rate constant, J, is defined with units of s⁻¹, and is given by the expression:

761
$$J = \int_{\lambda_1}^{\lambda_2} I(\lambda, z) \sigma(\lambda, T) \phi(\lambda, T) d\lambda$$

where $I(\lambda, z)$ is the wavelength-dependent intensity of solar radiation at altitude *z* (sometimes known as the actinic flux), $\sigma(\lambda, T)$ is the wavelength- and temperature-dependent ultraviolet/visible absorption cross section of the molecule of interest, $\phi(\lambda, T)$ is the wavelength- and temperature-dependent photolysis quantum yield, and λ_1 and λ_2 define the wavelength range over which the calculation is carried out. Integration over space and time yields a global and annual average lifetime with respect to photolysis, τ_J .

For a molecule destroyed by both chemical reaction and photolysis (and other processes), the overall global atmospheric lifetime, τ_{total} can be written as a combination of the global and annual average lifetimes with respect to the various loss processes:

771
$$1/\tau_{\text{total}} = 1/\tau_{\text{X}} + 1/\tau_{J} (+ 1/\tau_{\text{other}}).$$

As discussed in section 2.4, loss by chemical reaction within the troposphere is dominated by the reactivity of the hydroxyl radical, OH. For water soluble compounds such as perfluorinated esters, uptake by the oceans may also be important [*Kutsuna et al.*, 2005]. Compounds with lifetimes with respect to reaction with OH that are greater than a few years will reach the stratosphere, where destruction via photolysis and reaction with O(¹D) may also contribute. Fully fluorinated compounds have lifetimes typically of several thousands of years and their loss is dominated by photolysis in the mesosphere and thermosphere, while CFCs have lifetimes in the range 50-1000 years and are degraded by photolysis and reaction with $O(^{1}D)$ in the stratosphere [*Ravishankara et al.*, 1993].

781 The calculation of atmospheric lifetimes is complicated. Concentrations of reacting 782 species show strong temporal and spatial variability, and it may be difficult to be confident of 783 the absolute concentrations of these species. The intensity of solar radiation varies strongly 784 with altitude, and the absorption cross sections and quantum yields may show significant 785 dependence on temperature. There are also chemical feedbacks which can affect the lifetime. 786 Given the spatial and temporal variability of reaction partners and photolysis and the potential 787 for chemical feedbacks, it is necessary to use atmospheric models to accurately determine 788 lifetimes, which adds significantly to the complexity of the lifetime determination [Prather, 789 2007]. There are no unique lifetimes for the shorter lived gases, as their lifetimes depend on 790 the location of emissions and the chemical and physical conditions of the atmosphere. As 791 discussed in section 3.6.3, there are often significant uncertainties associated with 792 atmospheric lifetimes.

793

794 **3.3 Radiative forcing efficiency**

795 3.3.1 Spectrally-varying radiative efficiency

796 The radiative efficiency calculations carried out here are based on the simple method outlined 797 by Pinnock et al. [1995] in which a radiative transfer code is used to derive a wavelength-798 dependent RE for a unit absorption cross-section. With this method the instantaneous REs can 799 be estimated directly from the absorption spectrum of a molecule without using a radiative 800 transfer model, as explained in section 2.3. Pinnock et al. [1995] showed that results from 801 their simple method agreed to within 0.3% with results from a narrowband model. This 802 virtually eliminates the computational time needed and makes it straightforward to perform 803 RE calculations for a large number of compounds. Additionally, when comparing the 804 calculated REs between different compounds, uncertainties related to the absorption spectra 805 are the only factor affecting the comparison, as uncertainties related to the use of different 806 radiative transfer models can be ruled out. The Pinnock method is derived assuming the 807 molecule causing the forcing to be well mixed in the atmosphere. The resulting RE has to be 808 modified to take into account any non-uniformity in the horizontal and vertical distribution; 809 the method by which this is done here is described in sections 3.3.3 and 3.3.4, and is

810 particularly important for emissions of short-lived gases. In principle, the RE should be 811 calculated (in a similar manner to the lifetime, as discussed in section 3.2) by calculating the 812 forcing locally and averaging in space and time to yield the global and annual average RE.

813 The method proposed by *Pinnock et al.* [1995] (plus the lifetime correction) is 814 applicable for all compounds with low atmospheric concentrations and therefore weak 815 absorption, such as the halogenated compounds considered here. When this requirement is 816 met, the compound's radiative forcing per spectral interval is proportional to the product of its 817 absorption cross section and its number column density. Pinnock et al. [1995] included a 818 weak absorber with the same cross section at all wavelengths in a narrowband model to 819 calculate the instantaneous, cloudy-sky, RF per unit cross section as a function of 820 wavenumber.

821 We present here a revised calculation of the instantaneous, cloudy-sky, RF per unit cross section to reflect improvements in the radiative transfer calculations in the period since 822 823 the Pinnock et al. [1995] curve was derived. Figure 5 illustrates the progression from the 824 original to our final revised Pinnock curve. First we employ the same radiative transfer code 825 (the Reading Narrow Band Model (NBM)) as used in *Pinnock et al.* [1995] to reproduce the 826 original Pinnock curve, using the (rather dated) global-mean atmospheric profile presented in 827 that paper – the specification of cloud amount was especially crude. We then recalculated the 828 Pinnock curve, incorporating many minor updates to the NBM and in particular the use of a 829 more modern global-mean atmosphere, based on European Centre for Medium-Range 830 Weather Forecasts (ECWMF) and International Satellite Cloud Climatology Project (ISCCP) data [Freckleton et al., 1998]. Figure 5 (top) shows in particular a decrease in the Pinnock 831 curve in the 800-1200 cm⁻¹ region, which mostly reflects an improved characterization of 832 cloud (the longwave cloud forcing increased from 12 to 21 W m⁻² between the old and the 833 new global-mean atmosphere). At other wavenumbers, the new and old Pinnock curves agree 834 835 well. Next, we recalculated the Pinnock curve using area-weighted results using one tropical 836 and two extratropical profiles [Freckleton et al., 1998], rather than a single global-mean 837 profile. The most marked effect (see red curve on Figure 5 (top)) of using the new profiles is an increase in the Pinnock curve between 100 and 500 cm⁻¹, which reflects the fact that the 838 839 extratropical profiles are cooler (moving the peak of the Planck function to lower wavenumbers) and drier. At wavenumbers greater than 800 cm⁻¹ there are only small 840 841 differences between the single and three atmosphere curves. Mixing ratios of other well842 mixed gases used in the NBM were 389 ppm for CO_2 , 1800 ppb for CH_4 and 323 ppb for 843 N₂O, reflecting contemporary values.

844 Since we wanted our new Pinnock curve to be based on a LBL code (as it is inherently more accurate and also at higher spectral resolution than the original (10 cm^{-1}) curve) we next 845 generated a Pinnock curve using the Oslo LBL model [Myhre et al., 2006], employing their 846 two (tropical/extratropical) atmosphere approach. Figure 5 (middle) shows a comparison of 847 the NBM and LBL (averaged to 10 cm^{-1} resolution) Pinnock curves – there is excellent 848 agreement between the two models. Figure 5 (bottom) shows the final Pinnock curve, using 849 the LBL but now averaged to 1 cm⁻¹ resolution. The effect of using the improved spectral 850 851 resolution was found to have a negligible impact (<1-2%) on the RE calculations for most of 852 the compounds presented in section 4. However, for a few compounds, this effect was 853 stronger, as illustrated in Figure 6. The largest effect was for CF₄ because its main absorption 854 band is at the edge of the atmospheric window. For this compound the RE was underestimated by about 8% when using 10 cm⁻¹ resolution compared to 1 cm⁻¹ resolution of 855 856 the LBL Pinnock curve.

An Excel spreadsheet with both the updated 1 and 10 cm⁻¹ resolution LBL Pinnock curves is available in the supplementary material.

859

860 3.3.2 Stratospheric temperature adjustment

861 Generally, halocarbons warm the lower part of the stratosphere because their strongest absorption bands normally occur in the atmospheric window region. For these wavelengths, in 862 863 the stratosphere, the extra absorption of upwelling radiation by the halocarbon from the 864 surface and troposphere exceeds the amount of extra radiation emitted by the halocarbon. 865 Hence, there will be an increased heating rate of the stratosphere. When stratospheric temperature adjustment is applied, the increased heating rate leads to a warming of the 866 867 stratosphere. In the new equilibrium state, the higher stratospheric temperatures lead to an 868 increase in the amount of radiation emitted downwards into the troposphere so that the 869 stratosphere-adjusted forcing is higher than the instantaneous forcing. (The reverse is true for 870 CO_2 forcing, since it acts to cool the stratosphere so that the stratosphere-adjusted forcing is 871 smaller than the adjusted forcing.).

872 Since the Pinnock et al. function used for calculating REs in this study does not take 873 into account the stratospheric temperature adjustment, we have applied a factor to convert 874 from instantaneous to adjusted forcing. Based on several studies [Forster et al., 2005; Jain et 875 al., 2000; Myhre and Stordal, 1997; Naik et al., 2000; Pinnock et al., 1995], we have 876 increased the calculated instantaneous RE for most compounds by 10% to account for 877 stratospheric temperature adjustment. It should be kept in mind that the effect of stratospheric 878 temperature adjustment can be quite variable for each compound [e.g., *Pinnock et al.*, 1995], 879 particularly for gases which absorb outside the atmospheric window. For a few selected gases 880 (CFC-11, CFC-12, HFC-41 and CF₄) we have carried out explicit calculations, using the Oslo 881 LBL model, to estimate the ratio between the RE including stratospheric temperature 882 adjustment and the instantaneous RE. For CFC-11 and CFC-12, which have their main 883 absorption bands in the atmospheric window region, the REs were 9.1% and 10.5% higher, 884 respectively, when taking the stratospheric temperature adjustment into account. HFC-41 is a 885 special case because its main absorption band overlaps strongly with ozone and our result 886 from the LBL calculation shows a decrease in RE of 5.0% when accounting for stratospheric 887 temperature adjustment (some of the radiation which would have been absorbed by ozone in 888 the stratosphere is instead trapped by CH₃F in the troposphere leading to a cooling of the 889 stratosphere). As stated in section 3.3.1, CF₄ absorbs strongly at the edge of the atmospheric 890 window (near 1,300 cm⁻¹), and our results show an increase in RE of 10.5% due to 891 stratospheric temperature adjustment for this compound. Based on these results and on 892 previous literature [e.g., Myhre and Stordal, 1997; Pinnock et al., 1995] we consider a 10% 893 increase a good approximation for most gases.

894

3.3.3 Simulations of atmospheric distributions and lifetimes

The effect of non-uniform vertical profiles on radiative forcing has been investigated in several studies [e.g., *Freckleton et al.*, 1998; *Jain et al.*, 2000; *Naik et al.*, 2000; *Sihra et al.*, 2001], and is described in section 2.4. To further investigate and reduce the uncertainties associated with the correction factors for compounds which are mainly lost in the troposphere through reaction with OH, and normally have a relatively short lifetime, a number of simulations have been carried out with a 3-D Chemistry-Transport Model (CTM) in combination with a radiative transfer model. The models chosen for this purpose are the global offline Oslo CTM2 model [*Berglen et al.*, 2004; *Søvde et al.*, 2008] and the Oslo
broadband radiative transfer model [*Myhre and Stordal*, 1997].

905 The setup of the CTM simulations is similar to the studies of Acerboni et al. [2001] 906 and Sellevag et al. [2004b] where a total of 6 short-lived halocarbons were implemented in 907 the Oslo CTM2. Here we have implemented the following 9 halocarbons in the model, which 908 were chosen to represent a range of atmospheric lifetimes (~10 days to 5.2 years): HFC-909 1234yf (CF₃CF=CH₂), HFE-356mmz1 (CH₃OCH(CF₃)₂), HFE-254eb2 (CH₃OCHFCF₃), 910 HFC-161 (CH₃CH₂F), CH₃Br, HCFC-123 (CF₃CCl₂H), HFC-152a (CH₃CHF₂), HFC-143 911 (CH₂FCHF₂) and HFC-32 (CH₂F₂). The compounds were assumed to only react with the 912 hydroxyl radical (OH), which is the main loss for most short-lived halocarbons, and their 913 reaction rate coefficients were taken from the NASA/JPL database [Sander et al., 2010]. In a 914 reference simulation, the geographical distribution of the emissions was the same as for CFC-915 11 [McCulloch et al., 1994], while in a sensitivity simulation the emission distribution was set 916 the same as for black carbon (BC) [Bond et al., 2004; van der Werf et al., 2006] with the 917 purpose of studying the impact of having a larger share of the emissions occurring at lower 918 latitudes near the equator. It should be kept in mind that the sensitivity simulation is 919 considered a rather extreme case as halocarbons are industrial chemicals and their emission 920 distribution is more likely to follow that for other industrial compounds, such as CFC-11, than 921 for species like black carbon which has significant non-industry related sources. In both cases, 922 the anthropogenic emissions of other compounds were taken from the RETRO [2006] 923 database for year 2000. The model was run repeatedly for the meteorological year 2000 with 924 uniform annual emissions, and a sufficient amount of spin-up time was allowed to obtain 925 chemical steady-state at levels that yield globally averaged surface mixing ratios of approximately 1 ppb. The model has been driven by meteorological forecast data from the 926 927 ECMWF IFS model cycle 36, as explained by Søvde et al. [2011], and run at a horizontal resolution of approximately $2.8^{\circ} \times 2.8^{\circ}$ (T42) and 60 vertical layers distributed from the 928 929 surface to 0.1 hPa.

Figure 7 shows the calculated atmospheric distribution of HFC-161, which has a lifetime with respect to OH of 84 days in the reference simulation. In the sensitivity simulation with a "BC-like" emission distribution, the global burden is smaller, and hence the lifetime is shorter (71 days), due to the higher concentrations of OH found near the tropics. Due to the relatively short lifetime of HFC-161, the distribution of surface concentrations 935 reflects the regions of emissions quite well (Figure 7, top). The reference simulation reveals 936 large concentrations in the northern hemisphere, and particularly over the industrial areas in 937 US and Europe, while the sensitivity simulation shows a weaker gradient between the 938 hemispheres, and with surface maxima over Southeast Asia and the biomass burning regions 939 in Africa. Furthermore, the vertical profile is different between the two runs with a stronger 940 decay of mixing ratios with altitude in the simulation with "CFC-11-like" emission 941 distribution compared to the simulation with "BC-like" emission distribution.

942 The Oslo CTM2 simulated distributions of the halocarbons have been used for RF 943 calculations with the Oslo broadband model [Myhre and Stordal, 1997]. In the radiative 944 transfer calculations we also use 60-layer meteorological data from the ECMWF-IFS model, but with a reduced horizontal resolution of $5.6^{\circ} \times 5.6^{\circ}$ (T21). Annual mean cloudy-sky RF 945 946 (with stratospheric temperature adjustment included) has been calculated using the radiative 947 transfer model (based on monthly-mean data), which has been run both with a constant global 948 and annual mean vertical profile (so that the global and annual mean surface mixing ratio is 949 used at all heights, latitudes, longitudes and times), and with the monthly mean atmospheric 950 distribution calculated by Oslo CTM2. A quantification of the importance of using realistic 951 vertical profiles rather than constant profiles was then obtained by calculating the fractional 952 difference between the resulting RF from the two radiative transfer simulations.

953 In addition to the model runs explained above, simulations were carried out with the 954 Oslo LBL model to quantify the effect of a non-uniform vertical profile for compounds which 955 are mainly lost by photolysis in the stratosphere. Such compounds (i.e., mainly CFCs and 956 halons) are well-mixed in the troposphere but their mixing ratios decay with increasing 957 altitude in the stratosphere. Hence, they have a different vertical profile, and their atmospheric 958 concentrations are also much less influenced by the horizontal distribution of emissions, than 959 the compounds with lifetimes governed by OH destruction. The three compounds Halon-960 1211, CFC-11 and CFC-12 were chosen for the LBL model experiments because they span a 961 relatively wide range of lifetimes (16 to 100 years [WMO, 2011]), and because vertical 962 profiles of these compounds were available from CTM simulations. The vertical profiles of 963 the two CFCs were taken from Myhre and Stordal [1997] while the Halon-1211 profiles were fit to the annual mean output from Oslo CTM2, averaged separately over the tropics and the 964 965 extra-tropics. For all three compounds the mixing ratios were assumed to decrease 966 exponentially above the tropopause in the radiation code.

967 To validate the vertical profiles of CFC-11 mixing ratio used in the Oslo radiative 968 transfer model (results presented in section 3.3.4), we have compared these data with a 969 recently derived climatology from the MIPAS satellite instrument [Hoffmann et al., 2008] in 970 Figure 8. This MIPAS data set has been thoroughly validated against several other satellite 971 observations, as well as airborne and ground-based measurements [Hoffmann et al., 2008]. 972 For comparison the CFC-11 vertical profiles from the Oslo CTM2 simulations are also 973 included in Figure 8, although these results are not used here directly (only the Halon-1211 974 profiles were used, as explained above). It should be noted that the mixing ratios of CFC-11 975 calculated by Oslo CTM2 are largely governed by the top and bottom boundary conditions 976 taken from the Oslo 2-D stratospheric chemistry model [Stordal et al., 1985] which is based 977 on WMO recommendations. CFC-11 has a relatively long lifetime of about 45 years [WMO, 978 2011] and its main loss is photolysis in the stratosphere. As a consequence, CFC-11 is well-979 mixed throughout the troposphere, while its concentration decreases with height in the 980 stratosphere. This reduction with height has a major impact on the compound's radiative 981 forcing [e.g., Freckleton et al., 1998], and it is therefore important that the models include 982 realistic vertical profiles. The comparison between the Oslo radiation code and the Oslo 983 CTM2 model shows that the assumption of an exponential decay of CFC-11 mixing ratios 984 above the tropopause in the radiation code works relatively well (Figure 8). Furthermore, the 985 CFC-11 vertical profiles employed in both models are in relatively good agreement with the 986 climatology derived from MIPAS observations. Some discrepancies can be seen, especially 987 near the tropical tropopause region, but it should be noted that differences between 988 climatologies derived from satellite observations are also evident [Hoffmann et al., 2008] 989 (their Figure 11), and that tropical stratospheric measurements of CFC-11 is a major source of 990 uncertainty [Minschwaner et al., 2012] (see also their Figure 6). The vertical profiles are 991 shown separately for the tropics (30°S-30°N) and the extra-tropics (90°S-30°S and 30°N-992 90°N) in Figure 8 due to the different tropopause heights. These two regions are also the same 993 as used in the two-atmosphere setup of the Oslo radiation code.

994

995 3.3.4 Fractional correction versus lifetime

Results from the experiments described in section 3.3.3 are shown in Figure 9 together with
results from previous studies [*Acerboni et al.*, 2001; *Jain et al.*, 2000; *Sellevag et al.*, 2004b].
Our calculations differ from previous studies in three important respects. First, a number of

999 hypothetical "HFC-1234yf-like" molecules were studied. These compounds all had the 1000 infrared spectrum of HFC-1234yf but had different atmospheric lifetimes ranging from 1001 approximately 1 day to 7 years. Variation of the lifetime within the model was achieved by assuming rate coefficients for reaction with OH radicals in the range $4.3 \times 10^{-15} - 3.5 \times 10^{-11}$ 1002 cm³ molecule⁻¹ s⁻¹. The results are shown by the filled circles in Figure 9. Second, the 1003 1004 literature values for the rate coefficients for reactions of OH radicals with the remaining 8 1005 compounds were used, but this time we did not use the actual absorption spectra for the 1006 compound for the radiative transfer calculations. Instead, we chose to span the vertical axis, 1007 representing the fractional correction, by repeating the RE calculation 6 times for each gas, using different absorption bands which were either within or at the borders of the atmospheric 1008 1009 window region. More specifically, these bands were centered at wavenumbers of 631 (absorption band of CF₄), 714 (C₂F₆), 948 (SF₆), 1116 (C₂F₆), 1250 (C₂F₆), and 1283 (CF₄) 1010 1011 cm⁻¹. Figure 9 shows the fractional correction for the mean (filled squares) and standard deviation (vertical lines) of these 6 bands for each of the 8 gases. It should be noted that the 1012 1013 fractional correction depends primarily on lifetime, but to some extent also on the position of 1014 the absorption bands; absorption bands inside the atmospheric window region has the weakest 1015 correction. Third, the correction factors for compounds with stratospheric photolysis as the primary loss mechanism have been calculated using a two-atmosphere approach, and are 1016 shown by the red symbols in Figure 9. 1017

1018 Several interesting features can be seen in Figure 9. The lifetimes calculated by the 1019 Oslo CTM2 are shorter when the geographical distribution of emissions was "BC-like" rather than "CFC-11-like", especially for lifetimes shorter than approximately 0.5 years. This is not 1020 1021 surprising as the levels of OH are highest near the tropics (where a large share of the "BClike" emissions takes place) because of higher humidity and more incoming solar radiation at 1022 1023 low latitudes. Another interesting feature is that the fractional correction is weaker (i.e., closer to 1) in the run with "BC-like" emissions than the reference run with "CFC-11-like" 1024 1025 emissions for lifetimes longer than about 0.003 years, or 1 day, while it is stronger for 1026 lifetimes shorter than 1 day. One reason for this is the higher RF for well-mixed greenhouse gases near the equator than at higher latitudes, because of higher temperatures [Shine and 1027 1028 Forster, 1999].

1029 For the compounds with similar lifetimes as in *Jain et al.* [2000], the fractional 1030 corrections in our reference simulation roughly agree with their corrections, except for the
1031 compound in Jain et al. [2000] that has a lifetime of 0.25 years and a fractional correction of 1032 0.61, which is closer to our results from the simulation with "BC-like" emission distribution. Part of the reason is probably that Jain et al. [2000] used a 2-D model with geographically 1033 1034 constant surface mixing ratios, while we use a 3-D model with an assumed (and likely more 1035 realistic) emission distribution. In fact, another Oslo CTM2 sensitivity simulation with 1036 surface mixing ratios fixed at 1 ppb globally (results not shown) gives a very similar vertical 1037 profile and fractional correction factor as the simulation with "BC-like" emission distribution. 1038 Interestingly, the three compounds studied in Sellevag et al. [2004b] have smaller fractional 1039 correction factors than our results, and they do not always show an increase of fractional correction proportional with the lifetime. As the models and simulation setup are quite similar 1040 1041 to this study, the differences can probably be attributed to the absorption spectra, which are 1042 different for the various compounds. Figure 9 shows that the spectral position has some 1043 influence on the fractional correction and causes a maximum deviation from the mean of 1044 $\pm 10\%$. On the other hand, the results from Acerboni et al. [2001] show slightly higher fractional correction factors than in our study, presumably because they used a constant 1045 1046 surface mixing ratio all over the globe instead of an assumed emission distribution.

1047 Sihra et al. [2001] derived an empirical curve fit (see grey curve in Figure 9) to the values in Jain et al. [2000] and this has been used in later studies [e.g., Bravo et al., 2011a; 1048 Gohar et al., 2004]. Their fit is given by $f(\tau) = 1 - 0.241 \tau^{-0.358}$, where f is the fractional 1049 correction and τ is the lifetime in years for lifetimes greater than 0.25 years. Here we have 1050 1051 derived two new empirical curve fits, one for compounds dominated by loss in the troposphere through OH reaction, and one for compounds dominated by loss through 1052 1053 stratospheric photolysis. In the latter case we have used a similar approach as Sihra et al. 1054 [2001] and derived an exponential fit, but this time only results from explicit LBL 1055 calculations discussed in section 3.3.3 have been used. We further assumed that f = 1 for very 1056 long lifetimes. The resulting exponential function is given by

1057
$$f(\tau) = 1 - 0.1826 \ \tau^{-0.3339},$$
 (1)

and is shown in Figure 9 by the red curve for $10 < \tau < 10,000$ years. Equation (1) has been used to calculate lifetime-corrected RE for some of the compounds presented in section 4. In the case for compounds dominated by tropospheric OH loss, the empirical fit was restricted to results from 3-D model experiments where a "CFC-11-like" emission distribution was assumed. This means that the results from *Acerboni et al.* [2001] and the 2-D model of *Jain et* *al.* [2000] were not considered when deriving the fit (but still shown in Figure 9 for comparison), while the results of *Sellevag et al.* [2004b] were included along with results from the present study. As we now want to include compounds with very short lifetimes, the empirical curve fit was constrained to form an *S*-shaped curve in Figure 9 with the following formula:

1068 _____, (2)

1069 where *a*, *b*, *c* and *d* are constants with values of 2.962, 0.9312, 2.994, and 0.9302, 1070 respectively. The curve was further constrained to give f = 0 for very short lifetimes and f = 11071 for very long lifetimes. The resulting *S*-shaped function is shown in Figure 9 by the dark blue 1072 curve for $10^{-4} < \tau < 10^4$ years, and has been used to calculate lifetime corrected RE values for 1073 most of the compounds presented in section 4.

1074

1075 **3.4** Discussion of impact of functional groups on spectra/radiative forcing

1076 The infrared spectra of polyatomic molecules are made up of a number of vibrational bands, 1077 each containing rotational fine structure that may, or may not, be resolved. For a non-linear 1078 molecule containing N atoms, there are 3N-6 normal vibrations, although this number of 1079 bands may not be visible in the spectrum. Bands may overlap with each other, may lie outside 1080 of the spectral range of the measurements, may be forbidden or the vibrational mode may be degenerate. For example, the tetrahedral molecule, CF₄ has a total of 9 normal vibrations, but 1081 1082 only one band is observed in its infrared spectrum (as illustrated in Figure 3). The molecule 1083 has stretching and a variety of bending vibrations, but the bending vibrations occur at lower wavenumber (ca. 400 cm⁻¹) than can usually be observed in an infrared measurement. At the 1084 1085 same time, as it contains four C-F bonds, it is expected to have four stretching normal 1086 vibrations. A simple analysis of the symmetry properties of the stretching modes shows that 1087 one is the totally symmetric (A_1) stretch, which cannot be accessed in an allowed infrared 1088 transition. The other three vibrations turn out to be three-fold degenerate (symmetry species T_2) and give rise to a single allowed transition at around 1280 cm⁻¹. Molecules with lower 1089 symmetry will exhibit more bands, as degenerate vibrations are less likely to occur. 1090

1091 In the case of CF_4 , it is clearly possible to identify the T_2 vibration as a C-F stretching 1092 vibration, which is a specific example of a group vibration. In general, a normal mode of

1093 vibration involves movement of all the atoms in a molecule and it is not always possible to 1094 assign transitions to particular group vibrations. From the perspective of determining radiative 1095 efficiencies, the majority of spectral features of importance occur in the region between 1500 and 500 cm⁻¹. This region is called the *fingerprint region* and usually contains a complicated 1096 1097 series of absorptions, and it is often difficult to clearly identify group vibrations within this region. Nevertheless, some features may be identified. Molecules containing H atoms will 1098 have C-H stretching vibrations that produce transitions in the 3000 cm⁻¹ region of the 1099 spectrum, well outside of the region of interest here. On the other hand, C-H bending 1100 vibrations are expected at around 1400 cm⁻¹ and are a common feature of many HFCs [e.g., 1101 Sihra et al., 2001]. We have already seen that C-F stretching gives rise to a band at 1280 cm⁻¹, 1102 1103 and bands in this region are observed in a wide range of fluorine-containing compounds [e.g., Bravo et al., 2010b; Sihra et al., 2001]. However, it should be noted that the electron-1104 1105 withdrawing properties of neighboring groups can have a significant influence on band position. While molecules with a relatively high fluorine content show a C-F stretching 1106 1107 feature at around 1200-1300 cm⁻¹, HFC-41 (CH₃F) shows only a feature at 1000-1100 cm⁻¹, which corresponds to the expected position for a C-F group vibration given in standard 1108 1109 spectroscopy textbooks such as Hollas [2004]. For this reason, care must be used when 1110 assigning observed bands to individual group vibrations in the spectra of heavily halogenated 1111 molecules.

1112

1113 **3.5 Description of metrics**

1114 The motivation for the choice of metrics adopted here (GWP and GTP) was given in section1115 2.5.

1116 3.5.1 The Global Warming Potential (GWP)

1117 The Global Warming Potential (GWP) is based on the time-integrated radiative forcing due to 1118 a *pulse* emission of a unit mass of gas. It can be given as an absolute GWP for gas i (AGWP_i) 1119 (usually in W m⁻² kg⁻¹ year) or as a dimensionless value by dividing the AGWP_i by the 1120 AGWP of a reference gas, normally CO₂. Thus, the GWP is defined as:

1121 ______.

1122 A user choice is the time horizon (*H*) over which the integration is performed. IPCC has 1123 usually presented GWP for 20, 100 and 500 years and the Kyoto Protocol has adopted GWPs 1124 for a time horizon of 100 years.

For a gas *i*, if A_i is the RE, τ_i is the lifetime (and assuming its removal from the atmosphere can be represented by exponential decay), and *H* is the time horizon, then the integrated RF up to H is given by:

1128

_

1129 This is an approximation that holds for long-lived gases but is less accurate for shorter lived gases whose lifetimes depend on location of emissions and physical and chemical 1130 1131 conditions of the atmosphere. Prather [2007] developed a concept of atmospheric chemistry 1132 as a coupled system across different trace species with transport between different regions and 1133 radiative feedbacks. Due to these processes a perturbation to one species in one location will lead to a global response on a wide range of time scales, often involving many other chemical 1134 1135 components. The chemistry-transport system can be linearized and represented by eigenvalue decomposition [Prather, 2007] that are perturbation patterns of trace gas abundances, also 1136 1137 known as chemical modes. Any perturbation to atmospheric composition can be expressed as 1138 a sum of chemical modes, each with a fixed decay term.

1139 The AGWP for CO_2 is more complicated, because its atmospheric response time (or 1140 lifetime of a perturbation) cannot be represented by a simple exponential decay. This situation 1141 arises because CO_2 is absorbed into the various regions of the oceans (surface water, 1142 thermocline, deep ocean) on a range of different timescales. As a consequence, following a 1143 pulse emission of CO_2 the perturbation of the atmospheric concentration of CO_2 remains 1144 significant (>20%) even after 1000 years. The decay of a perturbation of atmospheric CO_2 1145 following a pulse emission at time *t* is usually approximated by *Joos et al.* [2013]:

1146

1147 where the parameter values are a_0 =0.2173, a_1 =0.2240, a_2 =0.2824, a_3 =0.2763, α_1 =394.4, 1148 α_2 =36.54 and α_3 =4.304. The parameter values for the impulse response function (IRF) are 1149 based on a recent multi-model study [*Joos et al.*, 2013], and these values have been used here. 1150 For comparison the parameter values from *Forster et al.* [2007] were a_0 =0.217, a_1 =0.259, 1151 a_2 =0.338, a_3 =0.186, α_1 =172.9, α_2 =18.51 and α_3 =1.186 (see footnote a, Table 2.14 in *Forster* 1152 *et al.* [2007]).

38

1153

Then the AGWP_{CO2} can be given as:

1155 Note that the parameters used in calculating the AGWP are dependent on the choice of 1156 background state, but it is convention to use present-day conditions. While the models used to 1157 calulate IRF for CO_2 usually include climate carbon cycle feedbacks, usually no climate 1158 feedbacks are included for the non- CO_2 gases.

1159

1160 3.5.2 The Global Temperature change Potential (GTP)

1161 GTP is presented as an alternative to the GWP and uses the *change in global mean* 1162 *temperature for a chosen point in time* as the impact parameter. While GWP is a metric 1163 integrative in time, the GTP is based on the temperature change per unit emissions for a 1164 selected year, *t*. As for the GWP, the impact of CO_2 is normally used as reference, thus,

1165
$$GTP(t)_i = AGTP(t)_i / AGTP(t)_{CO2} = \Delta T(t)_i / \Delta T(t)_{CO2},$$

where AGTP (K kg⁻¹) is the absolute GTP. The assumed lifetime of CO_2 is the same as that given for the GWP in section 3.5.1.

In the calculations here, we represent the thermal inertia of the climate system following the method used by *Fuglestvedt et al.* [2010]. This includes a representation of the deep ocean as well as the ocean mixed layer based on a temperature response function with two time-constants derived from climate model results [*Boucher and Reddy*, 2008]. The derived GTPs are dependent on the assumed value of climate sensitivity [*Shine et al.*, 2005a; *Shine et al.*, 2007], which is implicit in the Boucher and Reddy response functions, and is equal to about 1 K (W m⁻²)⁻¹.

1175

1176 3.5.3 The reference gas CO₂

The metric values need updating due to new scientific knowledge about various properties,
but also due to changes in lifetimes and radiative efficiencies caused by changing atmospheric
background conditions.

1180 For the reference gas CO_2 , such changes (i.e., in AGWP_{CO2} and AGTP_{CO2}) will affect 1181 all the other gases. With increasing CO_2 levels in the atmosphere the marginal radiative forcing is reduced, while at the same time the ocean uptake is reduced and airborne fraction increased. These changes (working in opposite directions) lead to changes in $AGWP_{CO2}$ and $AGTP_{CO2}$. Updates to $AGWP_{CO2}$ are often presented in IPCC and WMO Ozone assessments.

1185 The radiative forcing for CO_2 can be approximated using the expression based on 1186 radiative transfer models [*Myhre et al.*, 1998]:

1187 $RF = \alpha \ln((C_0 + \Delta C)/C_0)$, where $\alpha = 5.35$ W m⁻² and *C* is the atmospheric mixing ratio 1188 of CO₂.

Based on this and for a small ΔC , the radiative efficiency of CO₂ can be approximated. The RE of CO₂ changed from 0.0147 W m⁻² ppm⁻¹ to 0.0141 W m⁻² ppm⁻¹ when atmospheric CO₂ levels increased from 364 to 378 ppm, as used by IPCC Third Assessment Report (TAR) [*IPCC*, 2001] and IPCC Fourth Assessment Report (AR4) [*IPCC*, 2007], respectively. At current CO₂ levels of ~391 ppm [*WMO/GAW*, 2012], a 1 ppm change in the CO₂ concentration (ΔC =1 ppm) gives a radiative efficiency for CO₂ of 0.013665 W m⁻² ppm⁻¹.

The airborne fraction and the impulse response function have also been updated and 1195 1196 Figure 10 shows the IRFs from the four IPCC assessment reports together with the updated 1197 IRF from Joos et al. [2013]. In this review we have updated the AGWP_{CO2} and AGTP_{CO2} values based on the new IRF and RE of CO₂. The latter value is converted from per ppb to per 1198 kg by multiplying with $(M_A/M_{CO2}) \times (10^9/T_M)$, where M_A and M_{CO2} are the molecular weight 1199 of dry air (28.97 g mol⁻¹) and CO₂ (44.01 g mol⁻¹), respectively, and $T_{\rm M}$ is the mean dry mass 1200 of the atmosphere $(5.135 \times 10^{18} \text{ kg} [Trenberth and Smith, 2005])$. The RE of CO₂ given per 1201 mass is then 1.75×10^{-15} W m⁻² kg⁻¹, and the resulting AGWPs for CO₂ (using Equation 3) are 1202 2.495×10^{-14} , 9.171×10^{-14} and 32.17×10^{-14} W m⁻² vr (kgCO₂)⁻¹ for time horizons of 20, 100 1203 1204 and 500 years, respectively. These values are higher than the $AGWP_{CO2}$ used in AR4 (calculated based on the IRF and RE of CO₂ given in AR4) by approximately 1.4, 6.0 and 1205 13%, respectively, mainly due to the change in IRF. As a consequence the GWP_{100} values 1206 presented for all compounds in section 4 will be about 6% lower than if the $AGWP_{CO2}$ from 1207 1208 AR4 was used. The AGTP_{CO2} values used in the calculations of GTPs in section 4.2, have been updated (using Equation A3 in Fuglestvedt et al. [2010]) to 6.841×10^{-16} , 6.167×10^{-16} , 1209 5.469×10^{-16} K (kgCO₂)⁻¹ for time horizons of 20, 50 and 100 years, respectively. As for 1210 $AGWP_{CO2}$ the new $AGTP_{CO2}$ values take into account the updated IRF and radiative 1211 1212 efficiency of CO₂, while the remaining parameters are taken from *Fuglestvedt et al.* [2010].

1214 **3.6 Uncertainty – sensitivity to assumptions**

1215 3.6.1 Absorption cross-sections

1216 Uncertainties related to the measurements of IR absorption spectra are dependent on many 1217 factors, and can differ for each compound. Some compounds have been subject to extensive 1218 laboratory measurements by several groups, such as for HCFC-22 [Ballard et al., 2000b] and 1219 HFC-134a [Forster et al., 2005], while others may lack reliable experimental cross-section 1220 data. Typical sources of uncertainties related to spectra include, but are not limited to, 1221 temperature and pressure for the measurement and in the sample, spectral range and 1222 resolution in the measurement, purity of sample, spectrometer and methods used, and noise in 1223 the measurements. A comprehensive intercomparison of laboratory measurements of 1224 absorption spectra was reported by Ballard et al. [2000b] for HCFC-22. They examined a 1225 range of sources of uncertainties and identified a limited set of aspects, related both to sample 1226 and photometric uncertainty sources, which should be given special attention when measuring 1227 other molecules. Overall, the total error in the absorption cross-section measurements for each 1228 of the five laboratory groups considered by Ballard et al. [2000b] were generally less than 5% 1229 and for the most part in the range 3-5%.

1230 Integrated absorption cross sections from theoretical calculations are often in good 1231 agreement with experimentally determined values; for example, Bravo et al. [2010b] report 1232 theoretical integrated absorption cross sections for a range of PFCs that are within 5% of the 1233 experimentally determined values. Because band overlap often makes it difficult to compare 1234 individual vibrational bands, agreement at this level may be somewhat worse than for the total 1235 integrated cross sections. As discussed in section 3.1.2, theoretical calculations generally 1236 provide infrared absorption band positions that differ systematically from those observed 1237 experimentally. These differences are wavenumber dependent and are usually only a few 1238 percent, but because band position is so important in determining radiative efficiencies, 1239 corrections for these differences are usually made.

1240 The absorption spectra used in this study have for the most part been used as reported 1241 in the literature when performing the radiative forcing calculations. However, each spectrum 1242 has been the subject of a visual inspection and in some cases it was necessary to remove noise 1243 around the baseline. As the noise often does not average out to precisely zero, inclusion of 1244 noise occurring outside the absorption bands may lead to biases in the RE calculations. 1245 Furthermore, for some compounds measurements were often available for a number of 1246 different temperatures and pressures, particularly for the HITRAN and GEISA databases. 1247 When this was the case, we used the data for which temperature and pressure were closest to 1248 room temperature, 296 K, and surface pressure, 760 Torr. Forster et al. [2005] have shown 1249 that variation of the diluent pressure over the range 0-740 Torr and temperature over the range 1250 190-296 K has no discernible (<5%) effect on the integrated absorption band intensities of 1251 HFC-134a. To sum up, we estimate an uncertainty of 5 and 10% for the experimental and ab 1252 initio absorption cross-sections, respectively.

1253

1254 3.6.2 Radiative forcing calculations

Past studies estimating halocarbon radiative forcings have differed significantly for some compounds. For instance, a recent RE estimate of the very potent greenhouse gas sulphur hexafluoride (SF₆) (0.68 W m⁻² ppb⁻¹) [*Zhang et al.*, 2011a] was more than 30% higher than the IPCC AR4 estimate (0.52 W m⁻² ppb⁻¹). As noted in section 3.6.1, differences can arise due to uncertainties related to the absorption cross-sections, but a large part of the uncertainties is usually related to the radiative forcing calculations.

1261 Multi-model studies have proved particularly useful in assessing and reducing uncertainties in the RF calculations. Forster et al. [2005] applied six detailed radiative 1262 1263 transfer models (four line-by-line models and two narrowband models) and reduced the uncertainty in the radiative forcing of HFC-134a, a compound with a RE estimate that had 1264 1265 differed significantly in the previous studies. They also concluded that for this compound the 1266 uncertainties arising from the RF calculations were larger than those caused by using different absorption cross-sections - up to 10 and 7%, respectively. Similarly, Gohar et al. [2004] 1267 1268 obtained differences of less than 12% when using two different radiative transfer models to calculate REs of four compounds which had differed significantly in the past literature. 1269

1270 The assumptions related to RF calculations includes the choice of radiation scheme, 1271 temporal and spatial averaging, cloud data, background temperature and concentrations, 1272 tropopause height, stratospheric temperature adjustment, and accounting for non-uniform 1273 vertical profile. A wide range of radiative transfer schemes exist, each varying in complexity. 1274 Broadband schemes are among the simplest and are often used in General Circulation Models

1275 (GCMs) due to the heavy computational requirements of such models. The intercomparison 1276 study of Collins et al. [2006] showed that there are often large differences in the calculated 1277 radiative forcing by well-mixed greenhouse gases between the various GCM schemes, and 1278 between the GCM schemes and the much more detailed and computationally expensive line-1279 by-line (LBL) codes. However, the LBL codes were in excellent agreement with each other, 1280 and this type of code has previously been found to agree well with observations, at least in the spectral region between 800 and 2600 cm⁻¹ [*Tjemkes et al.*, 2003], which covers the whole 1281 1282 atmospheric window. Similarly, Forster et al. [2011] generally found agreement within 5% 1283 for four longwave LBL codes (slightly larger range for shortwave LBL codes) in an 1284 intercomparison study under clear sky conditions for various cases with changes in GHG 1285 concentrations, whereas differences were substantially larger for radiative transfer codes used 1286 in GCMs. One exception for the agreement between the LBL codes was for changes in 1287 stratospheric water vapor [Maycock and Shine, 2012]. In a recent study by Oreopoulos et al. 1288 [2012], a LBL model was validated against several high-resolution spectral measurements and 1289 used as reference when comparing a number of different LBL and GCM radiative transfer 1290 codes. They concluded that the longwave radiative transfer schemes were generally in 1291 agreement with the reference results, and that the current generation schemes perform better than the GCMs from two decades ago [*Ellingson and Fouquart*, 1991]. The fact that we apply 1292 1293 a detailed LBL model, should lead to less uncertainty compared to if a narrowband or 1294 broadband code was used. In Forster et al. [2005], the estimated contribution to total RF 1295 uncertainty for HFC-134a due to radiative transfer scheme was taken to be 3%. Here, we 1296 consider this value to be too optimistic and estimate an uncertainty of ~5%. We underscore 1297 that this uncertainty is for detailed radiative transfer codes and codes which have been 1298 through careful validation in intercomparison studies such as Forster et al. [2005] and does 1299 not apply to radiative transfer codes traditionally used in GCMs.

Different methodologies in how clouds are treated lead to additional uncertainties in radiative transfer models [e.g., *Gohar et al.*, 2004]. Clouds lead to reduced upward irradiance and therefore the cloudy-sky radiative forcing is normally about 25-35% lower than the clearsky RF [*Jain et al.*, 2000]. Inter-model differences of up to 10% in the cloud radiative effects were found by *Oreopoulos et al.* [2012], while *Forster et al.* [2005] estimated an additional uncertainty of about 5% in the RE of HFC-134a due to the inclusion of clouds. The detailed radiative transfer codes used in *Forster et al.* [2005] all had a global-mean outgoing longwave radiative flux at the top of the atmosphere close to observations and they span the range of
realistic longwave cloud radiative effects [*Kiehl and Trenberth*, 1997; *Trenberth et al.*, 2009].

1309 The effect of spectral overlap is important, including in the atmospheric window 1310 where most of the halocarbons absorb. Spectral overlap with H_2O is the most important for 1311 most compounds, and according to Pinnock et al. [1995] and Jain et al. [2000], removing all water vapor lead to increases in cloudy-sky instantaneous RF typically in the range ~10-30%. 1312 However, there is less than 1% increase when reducing the water vapor by 10% [Pinnock et 1313 1314 al., 1995], indicating that the uncertainty induced by spectral overlap is negligible. On the 1315 other hand, omitting N₂O and CH₄, which was common in some models, could lead to 1316 substantially larger errors as they increase the instantaneous RF by about 10% for some 1317 compounds [Pinnock et al., 1995]. In Forster et al. [2005], one model was used to test the 1318 effect of a 0.2 K uncertainty in surface temperature and of using two different climatologies 1319 for water vapor and pressure, and found approximately 1 and 2% differences in the radiative forcings, respectively. Previous studies have also assessed uncertainties associated with 1320 1321 spectroscopic measurements in new releases of HITRAN data of the greenhouse gases H₂O, CO₂, O₃, N₂O, and CH₄ [Kratz, 2008; Pinnock and Shine, 1998]. In general, they found that 1322 1323 improvements in absorption spectra for these compounds during the preceding couple of 1324 decades had a relatively small impact on radiative forcing estimates.

1325 Another factor influencing the radiative forcing estimates is the definition of the 1326 tropopause (recall from section 2.2 that the radiative forcing is normally defined at the tropopause). Previous studies have highlighted the role of choosing an appropriate tropopause 1327 1328 height, and found differences up to 10% in the global mean instantaneous RF when testing 1329 various tropopause definitions [Forster et al., 2005; Freckleton et al., 1998; Myhre and 1330 Stordal, 1997]. The error when using more than one vertical profile to represent the global 1331 atmosphere is lower, and we have estimated this uncertainty to be $\sim 5\%$. Furthermore, the effect of global and annual averaging may lead to additional errors due to non-linearities in 1332 1333 the radiative forcing calculations. For well-mixed gases, Myhre and Stordal [1997] found only small differences (less than 1%) in RF due to temporal averaging, while spatial 1334 averaging to one global mean profile induced errors up to 10%, partly due to the strong 1335 sensitivity to tropopause height for the halocarbons. However, the use of three profiles 1336 1337 representing the tropics and the extra-tropics of each hemisphere was found sufficient by

Freckleton et al. [1998]. The RF calculations presented in this study use two or three profiles,
representing the tropics and the extra-tropics (see section 3.3.1).

As explained in section 3.3.2, stratospheric temperature adjustment typically leads to an increase in cloudy-sky RF for the halocarbons of typically about 10%. *Forster et al.* [2005] have provided an estimate of the contribution to the RF uncertainty arising from this factor, namely ~4%, based on the results of four different radiative transfer models. The two models in *Gohar et al.* [2004] differed by a maximum of 3 percentage points when calculating the increase in RF due to stratospheric temperature adjustment for four different HFCs.

1346 One of the largest sources of uncertainties in RF estimates is the effect of a non-1347 uniform vertical profile caused mainly by reaction with OH in the troposphere and photolysis 1348 in the stratosphere (section 3.3.4). Sihra et al. [2001] estimated this uncertainty to be in the 1349 order of 5-10%, while we note from Figure 9 that this number is dependent on the lifetime. The fractional correction factors for compounds that are reasonably well-mixed in the 1350 1351 atmosphere, with lifetimes typically longer than about 5 years, show less spread than the compounds with shorter lifetimes. One reason for the larger spread is differences caused by 1352 1353 the various absorption bands, but is also due to uncertainties related to the geographical 1354 distribution of emissions which influence both the fractional correction and the atmospheric 1355 lifetime. However, it should be stressed here that for the sensitivity simulation using the "BClike" emission distribution (section 3.3.3) is considered an extreme case and should be given 1356 1357 less weight. Based on previous literature and the new simulations performed in this study, we estimate an uncertainty of ~5% for compounds with lifetimes longer than about 5 years and 1358 1359 $\sim 20\%$ for compounds with shorter lifetimes.

1360 Each source of uncertainty and their estimated contribution to the total RE uncertainty 1361 is listed in Table 1. The uncertainty estimates are based on available published studies and on subjective judgment, as discussed above. Using the root-sum-square (RSS) method, we find 1362 an overall uncertainty due to radiative forcing calculations (including uncertainties in the 1363 experimental absorption spectra described in section 3.6.1) of approximately 13% for 1364 1365 compounds with lifetimes longer than around 5 years. When using properly corrected 1366 theoretical absorption spectra the total uncertainty increases to around 15%. We estimate the 1367 overall uncertainty to be valid for a 5 to 95% (90%) confidence range, which is the same confidence range used for the radiative forcing values in IPCC AR4. Our estimate of 13% 1368 1369 (valid for experimental cross-sections) is only slightly larger than the 10% uncertainty reported for long-lived greenhouse gases in AR4. Due to the large uncertainties in the fractional correction, the total RF uncertainty increases to ~23% for compounds with lifetimes shorter than around 5 years. It should also be noted that the radiation schemes used to produce our updated "Pinnock curve" is a detailed LBL code and therefore has less uncertainties than models with coarser spectral resolution, such as broadband models.

1375

1376 3.6.3 Atmospheric lifetimes

1377 Uncertainties in atmospheric lifetimes arise from a range of factors. For short-lived 1378 compounds, accurate determinations of the temperature-dependent rate coefficients for 1379 reactions with OH are needed. The NASA Data Evaluation Panel [Chemical Kinetics and 1380 Photochemical Data for Use in Atmospheric Studies Evaluation Number 17 NASA Panel for 1381 Data Evaluation:2011] indicates uncertainties in OH rate constants at room temperature of up 1382 to about 20% for the compounds considered here. Combined with uncertainties in the temperature dependence gives an overall uncertainty of about 30% in the rate coefficient of 1383 1384 the reactions at tropospheric temperatures. It is also important to note that lifetimes with respect to reaction with OH are determined relative to the lifetime of methyl chloroform, 1385 1386 which in turn is dependent on the global OH field (see section 3.4). As an example, Prather et 1387 al. [2012] have used a recently published analysis of methyl chloroform data [Montzka et al., 2011] to estimate a total lifetime for HFC-134a of 14.2 yr as against the WMO [WMO, 2011] 1388 1389 recommendation of 13.4 yr. While this change is within our stated uncertainty, the important point is that changes in our understanding of the methyl chloroform lifetime can have an 1390 1391 impact on the lifetimes of a great many compounds.

1392 For some longer-lived compounds, photolysis in the stratosphere is the dominant loss 1393 process. Estimates of lifetimes for such compounds can be made from their ultraviolet 1394 absorption cross sections and quantum yields, and the altitude-dependent actinic flux. The 1395 NASA Data Evaluation Panel provides combined cross section/quantum yield uncertainties 1396 for some of the compounds considered here. For well-studied CFCs (CFC-11 and CFC-12) 1397 these uncertainties are well-constrained and are quoted at 10%, while for halons, uncertainties 1398 of a factor of two are quoted. Combined with uncertainties in the actinic flux, it is clear that there can be very significant uncertainties in photolysis lifetimes. This can be particularly true 1399 1400 when considering very long-lived compounds such as the PFCs [Ravishankara et al., 1993].

However, it should be noted that for such long-lived species, GWPs on a one hundred year time horizon are insensitive to atmospheric lifetimes. Uncertainties in other processes such as deposition can be very large, but as *Prather et al.* [2012] point out, these uncertainties often have a relatively small impact on total lifetimes. In general, uncertainties in lifetimes are large compared to uncertainties in other parameters such as cross sections. A follow up study could assess the uncertainties in lifetimes and the combined effect of RE and lifetimes uncertainties on GWP and GTP.

1408 3.6.4 GWP

Some studies have investigated uncertainty in GWP and GTP values [*Boucher*, 2012; *Olivié and Peters*, 2012; *Reisinger et al.*, 2010; *Wuebbles et al.*, 1995] and they have been either based on model comparisons or Monte-Carlo approaches. Uncertainty can also be assessed using standard methods of uncertainty propagation. For a general function, f, with two independent variables, x and y, the uncertainty in f can be approximated as

$$1414 - - (4)$$

This allows combination of different pieces of information on uncertainty (e.g., from independent studies) to assess the importance of the different components of metrics (e.g., RE versus lifetime). We use this approach for two chosen gases as examples (HFC-134a and CFC-11) and use uncertainties in RE obtained in this study with uncertainties in lifetimes from the literature. Based on Equation (4) the uncertainty for AGWP is given by

1421 assuming Gaussian distributions and no correlation between RE and τ . The derivatives of 1422 AGWP with respect to RE and τ were obtained analytically. For HFC-134a, the relative 1423 uncertainty (for the 5–95% (90%) confidence range) is estimated to be $\pm 18\%$ for τ [*Prather et* 1424 al., 2012] and $\pm 13\%$ for RE (from Table 1). Using Equation (5) with these uncertainties, the total uncertainty for AGWP_{HFC-134a} is $\pm 16\%$ for a 20 year time horizon, $\pm 22\%$ for 100 years, 1425 1426 and $\pm 22\%$ for 500 years. For CFC-11, the relative uncertainty is estimated to be $\pm 33\%$ for τ 1427 [Minschwaner et al., 2012] and ±13% for RE (from Table 1). Note that uncertainties related 1428 to indirect effects caused by e.g., the influence of CFC-11 on stratospheric ozone, are not

taken into account here. The total uncertainty for AGWP_{CFC-11} is then $\pm 15\%$ for a 20 year time horizon, $\pm 28\%$ for 100 years, and $\pm 36\%$ for 500 years.

1431 The uncertainty in the AGWP_{CO2} can be obtained using the $\pm 10\%$ estimated 1432 uncertainty in RE [*IPCC*, 2007] and uncertainty in the time-integrated IRF_{CO2} (see definition 1433 of IRF_{CO2} in section 3.5.1) of $\pm 15\%$, $\pm 25\%$, and $\pm 28\%$ for a 20, 100, and 500 year time 1434 horizon [*Joos et al.*, 2013]. The uncertainty for the product , i.e., the 1435 uncertainty in AGWP_{CO2}, is given by

1436

1437 leading to an uncertainty of AGWP_{CO2} of $\pm 18\%$, $\pm 26\%$, and $\pm 30\%$, respectively, with the 1438 uncertainty dominated by the uncertainty in the integrated IRF_{CO2} . These estimates are different from what is given by IPCC AR4 where it was stated that AGWP for CO₂ is 1439 1440 estimated to be $\pm 15\%$, with equal contributions from the CO₂ response function and the RF 1441 calculation [IPCC, 2007]. The main reason for the difference is the new uncertainty range in the IRF for CO₂ based on a multi model study [Joos et al., 2013]. Combining the uncertainty 1442 1443 in the AGWP values for HFC-134a and CFC-11 with AGWP_{CO2} (using the sum of the squares 1444 uncertainty propagation), the uncertainty in GWP_{HEC-134a} is estimated to $\pm 24\%$, $\pm 34\%$, and 1445 $\pm 37\%$ for a 20, 100, and 500 year time horizon. For CFC-11 the GWP uncertainties are $\pm 23\%$, 1446 $\pm 38\%$ and $\pm 47\%$ for a 20, 100, and 500 year time horizon.

1447 *IPCC* [2007] gives GWP uncertainties of $\pm 35\%$ for the 5 to 95% (90%) confidence 1448 range which is based on earlier IPCC assessments; i.e., the Second and Third Assessment 1449 reports [*IPCC*, 1995; 2001].

1450 The stated uncertainties for HFC-134a and CFC-11 are probably representative of 1451 those for most other CFCs, HCFCs, HFCs and perfluorocarbons with similar or longer 1452 lifetimes and with experimentally determined absorption cross-sections. For shorter-lived 1453 gases (τ less than 5 years), the uncertainties will be considerably greater (we estimate AGWP) 1454 uncertainties about at least a factor of 2 larger than those given above), and the assumption 1455 that there is no correlation between RE and τ will be less valid. In addition, for the shorterlived gases, both RE and τ will depend on the location (and time) of emission, and the validity 1456 1457 of presenting a single globally-representative value of GWPs is more questionable.

1458

1459 **4** Results and Discussion

1460 **4.1 Infrared Spectra, REs and GWPs**

1461 Absorption cross-sections and radiative efficiency estimates in the literature are reviewed in 1462 this section. In addition we present new calculations of REs and GWPs for a large number of 1463 gases based on published absorption cross-sections and the updated Pinnock curve described in section 3.3. All the REs are given for cloudy-sky and with stratospheric temperature 1464 1465 adjustment included (see definition of RE in section 2.2), unless explicitly noted in the text. 1466 When the atmospheric lifetime is available, a correction for non-homogeneous (vertical and 1467 horizontal) distribution is applied to the calculated REs, following the methods described in 1468 section 3.3.4. Each available spectrum has been evaluated and the most reliable spectra have been used in the calculations of new best estimate REs, as explained in section 3.1.3. 1469

1470 For each compound our results are compared to the values presented in AR4. In a few 1471 cases, the best estimate RE from AR4 has been retained when new calculations were not 1472 carried out due to unavailability of reliable absorption cross-section data. Best estimate RE 1473 and GWP for each compound are indicated in bold in the tables. Additionally, we provide 1474 best estimate REs and GWPs for a number of compounds which were not included in AR4, 1475 but where absorption cross-sections were available or where RE values have been published. 1476 The atmospheric lifetimes necessary for the GWP calculations have been taken from WMO 1477 [2011] unless stated otherwise in the text. Note that indirect effects caused by e.g., the 1478 influence of CFCs on stratospheric ozone, have not been studied here but are covered 1479 elsewhere [e.g., Daniel et al., 1995; WMO, 2011]. In the following, a brief discussion is given 1480 for each compound in each of the categories: chlorofluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons, chlorocarbons, bromocarbons and halons, fully fluorinated species, and 1481 1482 halogenated alcohols and ethers. Additional information, such as the REs reported in each of 1483 the individual studies, and the calculated REs of all available spectra, is given in Tables S1-S7 1484 in the supplementary material.

1485 In the following, when we refer to IPCC AR4 [IPCC, 2007] it should be noted that a number of compounds were inadvertently omitted in the printed version of AR4 WGI Table 1486 1487 2.14; we have used the erratum to this table which is available at http://www.ipcc.ch/publications and data/ar4/wg1/en/errataserrata-errata.html. 1488

1489

1490 4.1.1 Chlorofluorocarbons (CFCs)

CFCs are long-lived compounds which are mainly removed in the stratosphere by UV 1491 photolysis or reaction with excited oxygen atoms, $O(^{1}D)$. Their GWPs are generally high due 1492 to long lifetimes, and despite substantial emission reductions of CFCs during the past couple 1493 1494 of decades, their radiative forcing of climate will remain large for many decades [WMO, 2011]. The CFCs are relatively homogeneously distributed in the troposphere, but due to 1495 1496 photolysis their mixing ratios decrease with increasing altitude in the stratosphere. The IR absorption by the CFCs occurs to a large extent in the 'atmospheric window' from 800 - 1200 1497 cm⁻¹, as illustrated for CFC-11 in Figure 11. Previously published absorption cross-sections 1498 are listed in Table 2, while updated atmospheric lifetimes, REs, and GWP(100) values for 1499 1500 CFCs are presented in Table 3 and discussed below. Unless stated otherwise, the exponential 1501 fit from section 3.3.4 (Equation (1) and red curve in Figure 9) has been used to account for a 1502 non-uniform vertical profile for the compounds presented in this subsection.

1503

1504 CFC-11 (CCl₃F)

Several studies have calculated the RE of CFC-11 [Christidis et al., 1997; Fisher et al., 1990; 1505 1506 Good et al., 1998; Hansen et al., 1997; Heathfield et al., 1998; Jain et al., 2000; Myhre and Stordal, 1997; Myhre et al., 1998; Naik et al., 2000; Ninomiya et al., 2000; Pinnock et al., 1507 1995; Sihra et al., 2001]. Many of these studies report RE equal to, or close to, 0.25 W m⁻² 1508 ppb⁻¹, (range: 0.22-0.29 W m⁻² ppb⁻¹, mean: 0.25 W m⁻² ppb⁻¹), which is the value that was 1509 used in AR4. (It should be noted that the RE values for all compounds reported by Fisher et 1510 al. [1990] were given relative to CFC-11 in IPCC [1990], assuming a RE of 0.22 W m⁻² ppb⁻¹ 1511 1512 for CFC-11. WMO [1999] scaled the REs from Fisher et al. [1990] by a factor 1.14 to account for the change in the recommended forcing for CFC-11 (from 0.22 to 0.25 W m⁻² ppb⁻¹), and 1513 these values were then adopted in subsequent IPCC assessments.) Good et al. [1998] 1514 1515 estimated a value of RE using vibrational integrated absorption cross sections calculated using ab initio methods and obtained a value some 18% larger than those experimentally-derived 1516 1517 band strengths.

In the present study we have used absorption spectra from several sources [*Heathfield et al.*, 1998; *Imasu et al.*, 1995; *Li and Varanasi*, 1994; *Orkin et al.*, 2003; *Sihra et al.*, 2001] and calculated the RE of CFC-11, assuming it to be well mixed, to be in the range 0.27 – 0.29

W m⁻² ppb⁻¹ (mean: 0.28 W m⁻² ppb⁻¹) (see Tables 2-3). For CFC-11 we have carried out 1521 explicit simulations using the Oslo LBL model and derived factors to account for 1522 stratospheric temperature adjustment and lifetime adjustment (see sections 3.3.3 and 3.3.4 for 1523 1524 details and validation against satellite observations of CFC-11). The stratospheric adjustment, which is accounted for in the mean value of $0.28 \text{ W m}^{-2} \text{ ppb}^{-1}$, is assumed to increase the 1525 forcing by 9.1%, while the lifetime correction reduces this value by 7.3%. Our final value, 1526 0.26 W m⁻² ppb⁻¹ is in relatively good agreement with AR4. As noted above, the RE in some 1527 studies is given relative to the RE of CFC-11, and have been scaled in previous assessments 1528 to the former recommended CFC-11 RE of 0.25 W m⁻² ppb⁻¹. Here we choose to list the 1529 absolute REs of these studies [mainly Fisher et al., 1990; Imasu et al., 1995] as scaled to our 1530 new recommended CFC-11 RE of 0.26 W m⁻² ppb⁻¹. 1531

1532 A significant source of uncertainty related to the GWP of CFC-11 is the lifetime. In 1533 recent assessments [IPCC, 2007; WMO, 2011] the lifetime has been estimated as 45 years, 1534 based on observational studies [Cunnold et al., 1997; Volk et al., 1997] and model studies [WMO, 1999]. However, new studies, based on both models and observations, suggest a 1535 longer lifetime for CFC-11. Douglass et al. [2008] estimated a CFC-11 lifetime of 56-64 1536 1537 years using models that have realistic age of air and reproduce the observed relationship between the mean age and the fractional release. In Wuebbles et al. [2009] the lifetime was 1538 1539 estimated to be 54 and 57 years, using a 3-D and a 2-D atmospheric chemistry model, 1540 respectively. Recent studies based on satellite and ground-based observations have estimated 1541 a CFC-11 lifetime of 50 years (range: 34-67 years) [Minschwaner et al., 2012], 52 years (range: 40-66 years) [Rigby et al., 2013], and 59 years (range: 53-66 years) [Laube et al., 1542 1543 2012]. In Table 2 we choose to keep the lifetime of 45 years from WMO [2011] as our best 1544 estimate.

1545

1546 CFC-12 (CCl₂F₂)

Literature values for the RE of CFC-12 [*Fisher et al.*, 1990; *Good et al.*, 1998; *Hansen et al.*, 1997; *Jain et al.*, 2000; *Myhre and Stordal*, 1997; *Myhre et al.*, 1998; *Myhre et al.*, 2006; *Orkin et al.*, 2003; *Sihra et al.*, 2001] provide results in the range 0.30 - 0.33 W m⁻² ppb⁻¹ with a mean of 0.32 W m⁻² ppb⁻¹, while a value of 0.32 W m⁻² ppb⁻¹ was used in AR4 (based on *Myhre and Stordal* [1997]). Differences are caused by differing impact of clouds, absorption cross-section data and the vertical profile of decay of the mixing ratio in the

stratosphere [IPCC, 2001]. Detailed LBL calculations were performed by Myhre et al. [2006] 1553 who calculated a RE of 0.33 W m^{-2} ppb⁻¹. Here we have used absorption cross sections from 1554 several sources [Clerbaux et al., 1993; Myhre et al., 2006; Orkin et al., 2003; Sihra et al., 1555 1556 2001; Varanasi and Nemtchinov, 1994] to calculate an average RE due to CFC-12 of 0.32 W m^{-2} ppb⁻¹ (range: 0.29 - 0.33 W m⁻² ppb⁻¹) (Tables 2-3). As for CFC-11 we have carried out 1557 explicit simulations of CFC-12 using the Oslo LBL model and derived factors to account for 1558 1559 stratospheric temperature adjustment and lifetime adjustment. The instantaneous RE is increased by 10.5% when stratospheric temperature adjustment is taken into account, while 1560 the lifetime correction reduces the RE by 3.0%. Our final estimate (0.32 W m^{-2} ppb⁻¹) is in 1561 excellent agreement with that used in AR4. In contrast to CFC-11, the atmospheric lifetimes 1562 1563 of CFC-12 derived in the new model study by *Douglass et al.* [2008] are in good agreement with those used in previous IPCC and WMO assessments, and we here adopt the lifetime of 1564 1565 100 years which has been used since the assessment of WMO [1999].

1566

1567 CFC-13 (CClF₃)

A value of 0.25 W m⁻² ppb⁻¹ for the RE of CFC-13 has been used in the previous IPCC and WMO assessments and is from *Myhre and Stordal* [1997] who used a broadband model. The same value was calculated with a narrowband model in *Jain et al.* [2000], and was obtained in this study using absorption cross-section data from *McDaniel et al.* [1991].

1572

1573 **CFC-113** (**CCl₂FCClF₂**)

Literature measurements of the RE of CFC-113 fall in the range 0.28 - 0.33 W m⁻² ppb⁻¹ with a mean of 0.31 W m⁻² ppb⁻¹ [*Fisher et al.*, 1990; *Jain et al.*, 2000; *Myhre and Stordal*, 1997], which is the same value as in AR4 (based on *Myhre and Stordal* [1997]). We have used absorption cross-sections from a recent study by *Le Bris et al.* [2011] and from *McDaniel et al.* [1991] to obtain values of 0.31 and 0.29 W m⁻² ppb⁻¹, respectively. Our average RE (0.30 W m⁻² ppb⁻¹) is in excellent agreement with AR4.

1580

1581 CFC-114 (CCIF₂CCIF₂)

Literature measurements of the RE of CFC-114 are in the range 0.29 - 0.38 W m⁻² ppb⁻¹ 1582 (mean: 0.33 W m⁻² ppb⁻¹) [Fisher et al., 1990; Jain et al., 2000; Myhre and Stordal, 1997]. 1583 AR4 reports a RE of 0.31 W m⁻² ppb⁻¹ (based on *Myhre and Stordal* [1997]) which is the 1584 1585 same as calculated here using absorption cross-section from McDaniel et al. [1991]. Although 1586 our RE estimate is in excellent agreement with AR4, the best estimate GWP of CFC-114 is about 15% lower (Table 3) due to the shorter lifetime and higher AGWP_{CO2} used here. We 1587 1588 have used the lifetime from WMO [2011] of 190 years, which is based on new model 1589 calculations by Prather and Hsu [2008; 2010], and is approximately 40% shorter than the 1590 AR4 estimate of 300 years..

1591

1592 CFC-115 (CClF₂CF₃)

Literature reports of the RE of CFC-115 fall in the range 0.20 W m⁻² ppb⁻¹ to 0.30 W m⁻² ppb⁻¹ 1593 ¹ (mean: 0.24 W m⁻² ppb⁻¹) [Fisher et al., 1990; Jain et al., 2000; Myhre and Stordal, 1997], 1594 while the latest assessments (since *IPCC* [2001]) have used the instantaneous forcing of 0.18 1595 W m⁻² ppb⁻¹ from *Myhre and Stordal* [1997] (note that the value from AR4 falls outside the 1596 range quoted for the range of literature values because they reported the instantaneous RE 1597 1598 while we consider the RE from Myhre and Stordal [1997]). The much higher RE of CFC-115 calculated by Fisher et al. [1990] compared to Myhre and Stordal [1997] and Jain et al. 1599 1600 [2000] is most likely caused by the much higher integrated absorption cross-section in the first study compared to the work of McDaniel et al. [1991] which has been used in the two 1601 latter studies (Table 2). We calculate a RE value of 0.20 W m⁻² ppb⁻¹, which is in agreement 1602 with *Myhre and Stordal* [1997] and close to the RE of 0.21 W m⁻² ppb⁻¹ estimated by *Jain et* 1603 1604 al. [2000]. As for CFC-114, new model calculations [Prather and Hsu, 2008; 2010] suggested a significantly shorter lifetime of 1,020 years for CFC-115 (compared to 1,700 years in AR4). 1605 Nevertheless, the GWP(100) of CFC-115 is still ~4% higher than in AR4 due to the higher 1606 RE of CFC-115 calculated here (Table 3). 1607

1608

1609 4.1.2 Hydrochlorofluorocarbons (HCFCs)

1610 HCFCs are controlled by the Montreal Protocol, but they have been common substitutes for 1611 CFCs due to their lower potential for ozone depletion. As a consequence, atmospheric 1612 concentrations of some HCFCs have grown rapidly over the last decade, as illustrated for 1613 HCFC-22 in Figure 1. The atmospheric lifetimes of HCFCs are generally lower than for 1614 CFCs, but some of these compounds still have sufficiently long lifetimes to yield significant global warming potentials. The absorption cross-section of one of the most well-studied 1615 1616 gases, HCFC-22, is shown in Figure 12. Similarly to the CFCs, most of the absorption from HCFCs occurs in the atmospheric window region $(800 - 1200 \text{ cm}^{-1})$. Previously published 1617 absorption cross-sections are listed in Table 4, while best estimate lifetimes, radiative 1618 1619 efficiencies and GWP(100) values for HCFCs are given in Table 5 and discussed below. 1620 Since the main loss mechanism for HCFCs is through reaction with OH in the troposphere, the S-shaped fit from section 3.3.4 (Equation (2) and dark blue curve in Figure 9) has been 1621 1622 used to account for the non-uniform vertical profile and horizontal distribution of all 1623 compounds presented in this subsection.

1624

1625 HCFC-21 (CHCl₂F)

REs of 0.19 W m⁻² ppb⁻¹ [*Christidis et al.*, 1997] and 0.14 W m⁻² ppb⁻¹ [*Sihra et al.*, 2001] 1626 1627 have been reported for HCFC-21. The difference in the results between the studies reflects different vertical profile assumptions; Christidis et al. [1997] assumed a constant vertical 1628 1629 profile while Sihra et al. [2001] accounted for the fall-off in concentration of this relatively short-lived species (1.7 years atmospheric lifetime) above the troposphere. The RE from Sihra 1630 1631 et al. [2001] is used for the recommended RE in AR4, and the cross-section from that study 1632 has been used in our RE and GWP calculations. Both the HITRAN 2008 and GEISA 2009 databases include the spectrum from Massie et al. [1985], but this spectrum contains only one 1633 of the absorption bands (785-840 cm⁻¹) and has therefore not been employed in our 1634 calculations. Our estimate of 0.15 W m⁻² ppb⁻¹ is in good agreement (3.8% higher prior to 1635 rounding) with the AR4 (see Table 5). 1636

1637

1638 HCFC-22 (CHClF₂)

HCFC-22 is one of the most well-studied compounds with RE estimates in the literature
ranging from 0.18 to 0.23 W m⁻² ppb⁻¹ (mean: 0.21 W m⁻² ppb⁻¹) [*Fisher et al.*, 1990; *Good et al.*, 1998; *Highwood and Shine*, 2000; *Jain et al.*, 2000; *Myhre and Stordal*, 1997; *Naik et al.*,
2000; *Orkin et al.*, 2003; *Pinnock et al.*, 1995; *Sihra et al.*, 2001]. *Papasavva et al.* [1997]
used an *ab initio* spectrum which is approximately 10% more intense than the experimentally

derived spectra (Table 4) and consequently report a RE of 0.23 W m⁻² ppb⁻¹ which is 10% 1644 higher than the average from the experimental studies. AR4 reports a RE of 0.20 W m^{-2} ppb⁻¹ 1645 which is taken from Highwood and Shine [2000]. We have based our calculations on the 1646 1647 spectrum from Ballard et al. [2000b] which is a composite of measurements from five 1648 laboratory groups, and is in good agreement with other reported experimental spectra (see Table 4). Our calculations yield a RE value of 0.20 W m^{-2} ppb⁻¹, which is the same as 1649 1650 recommended by AR4. We note that calculated RE values using absorption cross-sections 1651 available from other studies [Clerbaux et al., 1993; Highwood and Shine, 2000; Orkin et al., 1652 2003; Pinnock et al., 1995; Sihra et al., 2001] (see SI Table 2 for individual results) agree to within 4% of the RE value calculated using the spectrum from Ballard et al. [2000b], 1653 1654 indicating that the uncertainty in the HCFC-22 spectrum is rather small (the spectrum reported by Varanasi et al. [1994] was not included in this comparison because one of the 1655 1656 absorption bands was missing).

1657

1658 HCFC-122 (CHCl₂CF₂Cl)

1659 One study has estimated the instantaneous RE of HCFC-122 with a value 0.23 W m⁻² ppb⁻¹ 1660 [*Orkin et al.*, 2003] (scaled to our recommended CFC-11 RE of 0.26 W m⁻² ppb⁻¹). We have 1661 used their absorption spectrum and calculated a RE value of 0.17 W m⁻² ppb⁻¹. The main 1662 reasons for the lower value calculated here are probably that *Orkin et al.* [2003] used a 1663 simplified approach which were not based on radiative transfer calculations, and that they did 1664 not account for stratospheric temperature adjustment and inhomogeneous distribution in the 1665 troposphere. The lifetime of 1.0 year is taken from *Orkin et al.* [2003].

1666

1667 HCFC-122a (CHFClCFCl₂)

1668 One study has estimated instantaneous RE due to HCFC-122a, with a value 0.24 W m⁻² ppb⁻¹ 1669 [*Orkin et al.*, 2003] (scaled to our recommended CFC-11 RE of 0.26 W m⁻² ppb⁻¹). We 1670 calculate a RE value of 0.21 W m⁻² ppb⁻¹ when using their absorption cross-section and 1671 lifetime estimate of 3.4 years.

1672

1673 HCFC-123 (CHCl₂CF₃)

1674 Literature estimations of the RE of HCFC-123 derived from experimental measurements of the IR spectrum lie in the range 0.14 - 0.22 W m⁻² ppb⁻¹ (mean: 0.18 W m⁻² ppb⁻¹) [Fisher et 1675 al., 1990; Jain et al., 2000; Naik et al., 2000; Orkin et al., 2003; Pinnock et al., 1995; Sihra et 1676 al., 2001]. As seen from Table 4, the infrared spectrum reported in the ab initio study of 1677 1678 Papasavva et al. [1997] is more intense than measured in the experimental studies and consequently the instantaneous RE of 0.22 W m^{-2} ppb⁻¹ is higher than those determined in the 1679 experimental studies. AR4 report a RE of 0.14 W m⁻² ppb⁻¹ which is based on both *Sihra et al.* 1680 [2001] and Jain et al. [2000]. We calculate a slightly higher RE value of 0.15 W m⁻² ppb⁻¹ for 1681 1682 all three sources of absorption spectra [Clerbaux et al., 1993; Orkin et al., 2003; Sihra et al., 2001] (Tables 4-5). It should be noted here that for this compound we have applied a 1683 1684 correction for stratospheric temperature adjustment of 6.5% (the average of the values found by Jain et al. [2000] (5%) and Pinnock et al. [1995] (8%)) rather than the generic 10% 1685 1686 correction used elsewhere in section 4.1.2.

1687

1688 HCFC-123a (CHClFCF₂Cl)

1689 One study has estimated instantaneous RE of HCFC-123a with a value 0.25 W m⁻² ppb⁻¹ 1690 [*Orkin et al.*, 2003] (scaled to our recommended CFC-11 RE of 0.26 W m⁻² ppb⁻¹). We have 1691 used their absorption spectrum and calculated a slightly lower RE value of 0.23 W m⁻² ppb⁻¹.

1692

1693 HCFC-124 (CHClFCF₃)

1694 Previous studies of RE due to HCFC-124 are in relatively good agreement with a range of 0.19 - 0.23 W m⁻² ppb⁻¹ (mean: 0.21 W m⁻² ppb⁻¹) [Fisher et al., 1990; Jain et al., 2000; Naik 1695 et al., 2000; Pinnock et al., 1995; Sihra et al., 2001]. As for HCFC-123, Papasavva et al. 1696 [1997] calculated a higher RE of 0.23 W m⁻² ppb⁻¹ (instantaneous RE) based upon an *ab initio* 1697 absorption cross-section. IPCC AR4 report a RE of 0.22 W m⁻² ppb⁻¹ which is taken from 1698 Fisher et al. [1990] (note that AR4 scaled the RE value from Fisher et al. [1990] to the 1699 previously recommended CFC-11 RE of 0.25 W m^{-2} ppb⁻¹ – see the discussion concerning 1700 CFC-11 in section 4.1.1 - while we refer to the Fisher et al. [1990] value as scaled to our 1701 recommended CFC-11 RE of 0.26 W m⁻² ppb⁻¹). We have used absorption cross-sections 1702 from Sihra et al. [2001] and Clerbaux et al. [1993] to calculate a mean RE value of 0.20 W m⁻ 1703 ² ppb⁻¹ (range: 0.19 - 0.20 W m⁻² ppb⁻¹) (Tables 4-5), which is lower than in *Fisher et al.* 1704

[1990]. However, our calculated RE is in agreement with the newer studies of *Sihra et al.*[2001], *Jain et al.* [2000] and *Naik et al.* [2000], most likely due to the higher integrated
absorption cross-section of *Fisher et al.* [1990] (Table 4).

1708

1709 HCFC-132c (CH₂FCFCl₂)

1710 One study has estimated instantaneous RE due to HCFC-132c, with a value $0.19 \text{ W m}^{-2} \text{ ppb}^{-1}$ 1711 [*Orkin et al.*, 2003] (scaled to our recommended CFC-11 RE of 0.26 W m⁻² ppb⁻¹). We 1712 calculate a RE value of 0.17 W m⁻² ppb⁻¹ when using their absorption cross-section and 1713 lifetime estimate of 4.3 years.

1714

1715 HCFC-141b (CH₃CCl₂F)

1716 Radiative efficiencies for HCFC-141b reported in the published literature are in the range 0.12 - 0.18 W m⁻² ppb⁻¹ (mean: 0.15 W m⁻² ppb⁻¹) [*Fisher et al.*, 1990; *Imasu et al.*, 1995; *Jain* 1717 1718 et al., 2000; Naik et al., 2000; Orkin et al., 2003; Pinnock et al., 1995; Sihra et al., 2001], and the value of 0.14 W m⁻² ppb⁻¹ from *Fisher et al.* [1990] has been used by AR4 (scaled to the 1719 previously recommended CFC-11 RE of 0.25 W m⁻² ppb⁻¹). Papasavva et al. [1997] 1720 calculated a much higher RE (instantaneous RE of 0.21 W m⁻² ppb⁻¹) using an *ab initio* 1721 absorption spectrum. We calculate a slightly higher RE than AR4 with a mean value of 0.16 1722 W m⁻² ppb⁻¹ (range: 0.15 - 0.17 W m⁻² ppb⁻¹) when using absorption cross-sections from 1723 several sources [Clerbaux et al., 1993; Imasu et al., 1995; Orkin et al., 2003; Sihra et al., 1724 2001]. We note that the value of 0.14 W m⁻² ppb⁻¹ from *Fisher et al.* [1990] has been scaled 1725 by AR4 to account for changes in the recommended RE of CFC-11 (from 0.22 W m⁻² ppb⁻¹ in 1726 Fisher et al. [1990] to 0.25 W m⁻² ppb⁻¹ in AR4), and that a scaling to our recommended 1727 CFC-11 forcing of 0.26 W m⁻² ppb⁻¹ results in a RE of 0.15 W m⁻² ppb⁻¹ from *Fisher et al.* 1728 [1990] – in better agreement with our calculations. 1729

1730

1731 HCFC-142b (CH₃CClF₂)

1732 Previous reports of RE of HCFC-142b are in the range 0.16 - 0.21 W m⁻² ppb⁻¹ (mean: 0.18 W

- 1733 m⁻² ppb⁻¹) [Fisher et al., 1990; Jain et al., 2000; Naik et al., 2000; Pinnock et al., 1995; Sihra
- 1734 et al., 2001]. Again, the ab initio study of Papasavva et al. [1997] is at the higher end of the

- 1735 range based on experimental studies as they calculate an instantaneous RE of 0.20 W m⁻² ppb⁻
- ¹. AR4 report a RE of 0.20 W m⁻² ppb⁻¹ which is taken from *Fisher et al.* [1990]. We calculate
- 1737 a mean RE value of 0.19 W m⁻² ppb⁻¹ (range: 0.18 0.20 W m⁻² ppb⁻¹) when using absorption
- 1738 cross-sections from *Sihra et al.* [2001] and *Clerbaux et al.* [1993] (Tables 4-5). Our estimate
- 1739 is lower than Fisher et al. [1990] and Pinnock et al. [1995], but higher than the more recent
- 1740 studies [Jain et al., 2000; Naik et al., 2000; Sihra et al., 2001].
- 1741

1742 HCFC-225ca (CHCl₂CF₂CF₃)

A range of 0.20 - 0.27 W m⁻² ppb⁻¹ (mean: 0.22 W m⁻² ppb⁻¹) for the RE of HCFC-225ca has 1743 1744 been reported in the literature [Jain et al., 2000; Naik et al., 2000; Pinnock et al., 1995; Sihra et al., 2001]. Three of the studies are in good agreement (<3% difference) while Pinnock et al. 1745 [1995] is an outlier with a value of 0.27 W m^{-2} ppb⁻¹, despite the lower integrated absorption 1746 cross-section in their study (Table 4). The reason is that Pinnock et al. [1995] did not take into 1747 1748 account the non-uniform tropospheric distribution, which gives a reduction in the RE of 16% when using our fractional correction method described in section 3.3.4 and a lifetime of 1.9 1749 vears [WMO, 2011]. AR4 has based their RE recommendation of 0.20 W m⁻² ppb⁻¹ on Sihra 1750 et al. [2001] and Jain et al. [2000]. We calculate a mean RE value of 0.22 W m⁻² ppb⁻¹ (range: 1751 0.22 - 0.23 W m⁻² ppb⁻¹) when using absorption cross-sections from Sihra et al. [2001] and 1752 Clerbaux et al. [1993] (Tables 4-5). 1753

1754

1755 HCFC-225cb (CHClFCF₂CClF₂)

1756 The RE of HCFC-225cb has differed considerably in the past literature with a range of 0.25 -0.35 W m⁻² ppb⁻¹ (mean: 0.29 W m⁻² ppb⁻¹) [*Imasu et al.*, 1995; Jain et al., 2000; Naik et al., 1757 2000; Pinnock et al., 1995; Sihra et al., 2001]. A value of 0.32 W m⁻² ppb⁻¹ has been used in 1758 previous assessments and is based on Granier (pers. comm.) [IPCC, 1994]. We calculate a 1759 mean RE value of 0.29 W m⁻² ppb⁻¹ (range: 0.28 - 0.31 W m⁻² ppb⁻¹) when using absorption 1760 1761 cross-sections from Sihra et al. [2001], Clerbaux et al. [1993] and Imasu et al. [1995] (Tables 4-5). Our result differs by almost 10% from the AR4 recommendation. As the AR4 value is 1762 1763 not based on published literature it is difficult to assess the reasons to why our estimate is significantly lower than their value, but we note that our estimate is in agreement with the 1764

mean of published values and close to the most recent published RE estimate of HCFC-225cb 1765 of 0.28 W m⁻² ppb⁻¹ [*Sihra et al.*, 2001]. 1766

1767

1768 (E)-1-Chloro-3,3,3-trifluoroprop-1-ene (CF₃CH=CHCl(E))

1769 The radiative efficiency of (E)-1-chloro-3,3,3-trifluoroprop-1-ene has not been assessed in 1770 AR4, but was estimated by Andersen et al. [2008]. They used the original Pinnock et al. [1995] method and calculated an instantaneous RE of 0.21 W m⁻² ppb⁻¹. Their absorption 1771 cross-section has been used in this study to calculate a lifetime-corrected RE of 0.04 W m⁻² 1772 ppb⁻¹ (Table 5). The short lifetime of 26 days [WMO, 2011] for this compound leads to a 1773 1774 strong effect of the fractional correction factor which has been applied to account for non-1775 uniform mixing (vertical and horizontal). It should be noted here that the uncertainties 1776 associated with this correction factor are very large on a percentage basis for such short-lived 1777 species (see Figure 9 and associated discussion in section 3.3.4), and we further note that our 1778 calculated RE is in good agreement with Andersen et al. [2008] if we assume uniform mixing.

1779

4.1.3 Hydrofluorocarbons (HFCs) 1780

1781 HFCs do not destroy stratospheric ozone [Ravishankara et al., 1994; Wallington et al., 1995] 1782 and have emerged as important replacements for ozone-depleting substances such as the 1783 CFCs. The main removal mechanism for the HFCs is through reaction with OH. The 1784 atmospheric lifetime of HFCs depends on their reactivity towards OH radicals and ranges 1785 from 2.1 days for CH₂=CHF to 242 years for CF₂CH₂CF₃ (HFC-236fa). Compounds with 1786 lifetimes greater than a decade tend to be well mixed in the troposphere. Compounds with 1787 lifetimes less than a year are not well mixed and have an inhomogeneous distribution within the troposphere and needs to be accounted for in RE estimates. HFCs have strong absorption 1788 bands within the atmospheric window region $(800 - 1200 \text{ cm}^{-1})$ and hence have the potential 1789 to be potent greenhouse gases, especially for long-lived gases such as HFC-23 and HFC-1790 1791 236fa which have lifetimes greater than 200 years. At the other extreme, fluorinated alkenes 1792 such as CF₃CF=CH₂ (HFC-1234yf) have very short atmospheric lifetimes (1-2 weeks) and are 1793 not significant greenhouse gases. HFC-134a (CF₃CFH₂) is the most abundant HFC in the 1794 atmosphere and is currently present at a concentration of approximately 60 ppt (Figure 1). 1795 HFC-134a has a lifetime of 13.4 years and its potency as a greenhouse gas lies between those of the long-lived and short lived HFCs. Figure 13 shows the absorption spectrum of HFC-134a which, because of its industrial importance, has been studied extensively and is perhaps the best established of all the HFCs. Published absorption cross-sections for HFCs are listed in Table 6, atmospheric lifetimes, radiative efficiencies, and GWP(100) values for HFCs are presented in Table 7 and discussed below. The *S*-shaped fit from section 3.3.4 (Equation (2) and dark blue curve in Figure 9) has been used to account for a non-uniform vertical profile and geographic distribution for all compounds presented in this subsection.

1803

1804 HFC-23 (CHF₃)

Published estimates of the RE of HFC-23 span the range 0.16 - 0.27 W m⁻² ppb⁻¹ (mean: 0.21 1805 W m⁻² ppb⁻¹) [Gohar et al., 2004; Highwood and Shine, 2000; Jain et al., 2000; Naik et al., 1806 2000; Pinnock et al., 1995; Sihra et al., 2001]. AR4 adopted the value of 0.19 W m⁻² ppb⁻¹ 1807 from Gohar et al. [2004], who used two different radiative transfer methods to estimate 1808 forcings of 0.18 and 0.19 W m⁻² ppb⁻¹. The small differences between results from the two 1809 models used by Gohar et al. [2004] were attributed to slight differences in the treatment of 1810 clouds in the models. The large difference between the results of Gohar et al. [2004] and 1811 those of Jain et al. [2000] (0.248 W m⁻² ppb⁻¹) and Naik et al. [2000] (0.271 W m⁻² ppb⁻¹) is 1812 difficult to explain because all three studies used essentially the same IR spectrum. Two 1813 studies have used *ab initio* methods to estimate HFC-23 RE to be 0.18 W m⁻² ppb⁻¹ [Blowers 1814 and Hollingshead, 2009] and 0.19 W m⁻² ppb⁻¹ [Papasavva et al., 1997], but these are 1815 1816 instantaneous REs and must be increased by approximately 11% [Gohar et al., 2004] to be 1817 comparable with the RE values (including stratospheric temperature adjustment) reported by 1818 Gohar et al. [2004]. We have used absorption cross-sections from Gohar et al. [2004] and Highwood and Shine [2000] to calculate RE values of 0.19 and 0.16 W m⁻² ppb⁻¹, 1819 respectively, which are in excellent agreement with the REs reported in each of the two 1820 individual studies. The mean of our calculated REs (0.18 W m^{-2} ppb⁻¹) is slightly more than 1821 1822 5% lower than the AR4 recommendation. The relatively large range in the integrated 1823 absorption cross-sections for HFC-23 (Table 6), and subsequent large range of REs in our 1824 calculations, indicates that there are uncertainties related to the measurements of the absorption cross-section for this compound (the absorption band below 700 cm⁻¹, which is 1825 1826 only taken into account in Gohar et al. [2004], has only a negligible contribution to the 1827 integrated absorption cross-section).

1828

1829 HFC-32 (CH₂F₂)

1830 Estimates for the RE of HFC-32 based on experimental absorption cross-sections range from $0.09 \text{ to } 0.16 \text{ W m}^{-2} \text{ ppb}^{-1}$ (mean: $0.12 \text{ W m}^{-2} \text{ ppb}^{-1}$) [Gohar et al., 2004; Highwood and Shine, 1831 1832 2000; Jain et al., 2000; Naik et al., 2000; Orkin et al., 2003; Pinnock et al., 1995; Sihra et al., 2001; Zhang et al., 2011b], while estimates based on absorption cross-sections from ab initio 1833 studies are in the range 0.12 - 0.13 W m⁻² ppb⁻¹ (instantaneous RE) [Blowers and 1834 Hollingshead, 2009; Papasavva et al., 1997]. As for HFC-23, the results of Gohar et al. 1835 [2004] were used in AR4 with a value of 0.11 W m^{-2} ppb⁻¹. We have used absorption spectra 1836 from Gohar et al. [2004], Highwood and Shine [2000] and Orkin et al. [2003] and derived a 1837 RE of HFC-32 of 0.11 W m⁻² ppb⁻¹ for all these spectra, in excellent agreement with AR4. It 1838 1839 should be noted that additional absorption cross-sections are available e.g., through the HITRAN and GEISA databases (Table 6), but have not been included to avoid double-1840 1841 counting of absorption cross-sections from the same laboratory groups (e.g., both Highwood 1842 and Shine [2000] and Smith et al. [1996] are based on spectra from the Molecular 1843 Spectroscopy Facility / Rutherford Appleton Laboratory [M.S.F./R.A.L.]). The combination 1844 of a change in the recommended lifetime for this compound (5.2 years in WMO [2011] compared to 4.9 years in AR4) and the higher AGWP_{CO2} used here, result in a GWP(100) 1845 value which is about the same as in AR4 (see Table 7). 1846

1847

1848 HFC-41 (CH₃F)

A radiative efficiency for HFC-41 of 0.02 W m⁻² ppb⁻¹ has been used in previous assessments 1849 and is taken from *Pinnock et al.* [1995] (note that stratospheric decay was accounted for in the 1850 assessments, but not in the original study). A range of 0.02 - 0.03 W m⁻² ppb⁻¹ (mean: 0.03 W 1851 m^{-2} ppb⁻¹) has been reported from studies using measured absorption cross-sections [*Pinnock*] 1852 1853 et al., 1995; Sihra et al., 2001]. The ab initio studies have the same range and mean, but they 1854 have only reported instantaneous RE [Blowers and Hollingshead, 2009; Papasavva et al., 1997]. We used the absorption spectrum from Sihra et al. [2001] and derived a RE value of 1855 0.02 W m⁻² ppb⁻¹, which is in excellent agreement with AR4. It should be noted that 1856 1857 stratospheric temperature adjustment normally leads to a stronger forcing compared to instantaneous RE (recall from section 3.3.2 that we apply a 10% increase for most 1858 1859 compounds), while for HFC-41 it leads to a weakening due to the strong overlap with the absorption spectrum of ozone [*Pinnock et al.*, 1995]. We have carried out explicit LBL model calculations and estimated a 5.0% decrease for the stratospheric temperature adjustment for HFC-41 (see section 3.3.2), and this result has been used (instead of the 10% increase) to calculate the RE of 0.02 W m⁻² ppb⁻¹ above. Due to a change in the recommended lifetime for this compound (2.8 years in *WMO* [2011] compared to 2.4 years in AR4) our recommended GWP value is higher than in AR4 (see Table 7).

1866

1867 HFC-125 (CHF₂CF₃)

Previous studies have reported a fairly wide range of RE values for HFC-125: 0.21 - 0.30 W 1868 m⁻² ppb⁻¹ (mean: 0.25 W m⁻² ppb⁻¹) [Fisher et al., 1990; Highwood and Shine, 2000; Imasu et 1869 al., 1995; Jain et al., 2000; Naik et al., 2000; Orkin et al., 2003; Pinnock et al., 1995; Sihra et 1870 al., 2001; Young et al., 2009b; Zhang et al., 2011b]. Ab initio studies for this compound have 1871 calculated REs that are at the high end of the range of experimental studies with instantaneous 1872 RE of 0.24 W m⁻² ppb⁻¹ [Papasavva et al., 1997] and RE of 0.28 W m⁻² ppb⁻¹ [Good et al., 1873 1998]. The recent study by Zhang et al. [2011b] is an outlier with a value of 0.30 W m⁻² ppb⁻¹, 1874 but they did not identify any clear reason for the large difference between their result and the 1875 1876 results from all other studies. Zhang et al. [2011b] calculate their RE from a combination of forcings from three standard atmospheres; they do not show to what extent this combination is 1877 1878 representative of a true global-mean atmosphere, nor do they show how their outgoing longwave radiation or cloud forcing, using this combination of atmospheres, compare with 1879 1880 satellite observed values, which is an important diagnostic of model behavior [e.g., Forster et al., 2005]. Recent assessments have used the value of 0.23 W m⁻² ppb⁻¹ estimated in 1881 1882 Highwood and Shine [2000]. We have used absorption cross-sections from several sources 1883 [Clerbaux et al., 1993; Highwood and Shine, 2000; Imasu et al., 1995; Orkin et al., 2003; 1884 Young et al., 2009b] (see also Table 6; note that the spectrum from Young et al. [2009b] supersede that of Sihra et al. [2001]) and calculated a mean RE value of 0.23 W m⁻² ppb⁻¹ 1885 (range: 0.21 - 0.24 W m⁻² ppb⁻¹) (Table 7), which is in excellent agreement with AR4 (note 1886 that our use of a lifetime of 28.2 years recommended by [WMO, 2011] is shorter than that of 1887 1888 29 years used in AR4, but this does not affect the GWP(100) value significantly).

1889

1890 HFC-134 (CHF₂CHF₂)

Studies of the radiative efficiency of HFC-134 have reported values in the range 0.18 - 0.271891 $W m^{-2} ppb^{-1}$ (mean: 0.20 $W m^{-2} ppb^{-1}$) [Christidis et al., 1997; Jain et al., 2000; Naik et al., 1892 2000; Sihra et al., 2001; Zhang et al., 2011b]. Again, Zhang et al. [2011b] is an outlier with a 1893 RE value of 0.27 W m⁻² ppb⁻¹, which is more than 30% higher than reported in any of the 1894 1895 other studies (see also the HFC-125 section above for a discussion of Zhang et al. [2011b]). 1896 The *ab initio* studies are in good agreement with the mean of experimental studies for this 1897 compound as both Papasavva et al. [1997] and Good et al. [1998] calculated REs of 0.20 W m^{-2} ppb⁻¹ (the first study calculated instantaneous RE). Previous assessments have used the 1898 value of 0.18 W m⁻² ppb⁻¹ based on *Christidis et al.* [1997] (a scaling factor to account for 1899 decreased concentrations in the stratosphere was applied). We calculate a mean RE value of 1900 $0.19 \text{ W} \text{ m}^{-2} \text{ ppb}^{-1}$ (range: 0.18 - 0.20 W m⁻² ppb⁻¹) when using absorption cross-sections from 1901 two sources [Sihra et al., 2001; Smith et al., 1998]. Our GWP(100) estimate is similar to AR4 1902 1903 due to the combination of a slightly higher RE, a slightly longer lifetime, and a higher 1904 AGWP_{CO2} used here.

1905

1906 HFC-134a (CH₂FCF₃)

Calculations of the RE of HFC-134a are in the range 0.15 - 0.22 W m⁻² ppb⁻¹ (mean: 0.18 W 1907 m⁻² ppb⁻¹) [Fisher et al., 1990; Forster et al., 2005; Gohar et al., 2004; Highwood and Shine, 1908 1909 2000; Imasu et al., 1995; Jain et al., 2000; Naik et al., 2000; Orkin et al., 2003; Pinnock et al., 1995; Sihra et al., 2001; Zhang et al., 2011b], while one ab initio study estimated an 1910 instantaneous RE of 0.14 W m⁻² ppb⁻¹ [Papasavva et al., 1997]. AR4 adopted a value of 0.16 1911 W m⁻² ppb⁻¹ based on the multi-model studies of *Gohar et al.* [2004] and *Forster et al.* [2005]. 1912 1913 Particularly, Forster et al. [2005] derived a "recommended" absorption cross section and applied four radiative transfer models to yield an average RE with relatively low uncertainty 1914 $(0.16\pm0.02 \text{ W m}^{-2} \text{ ppb}^{-1})$, and attributed most of the uncertainty to the radiative forcing 1915 calculation rather than the absorption cross section. In this study we have used the 1916 1917 recommended absorption spectrum from Forster et al. [2005] (Table 6), which is based on measurements from six different laboratory groups, and calculated a radiative forcing of 0.16 1918 W m⁻² ppb⁻¹, the same as used in AR4 (Table 7). The lifetime has been updated to 13.4 years 1919 1920 from WMO [2011] compared to the 14 years used in AR4.

1921

1922 HFC-143 (CH₂FCHF₂)

- 1923 The average RE of HFC-143 reported in the literature based on experimentally measured 1924 absorption spectra is $0.12 \text{ W m}^{-2} \text{ ppb}^{-1}$ (range: $0.11 - 0.14 \text{ W m}^{-2} \text{ ppb}^{-1}$) [*Clerbaux and Colin*, 1925 1994; *Jain et al.*, 2000; *Naik et al.*, 2000; *Pinnock et al.*, 1995; *Sihra et al.*, 2001], while the 1926 *ab initio* study of [*Papasavva et al.*, 1997] estimated an instantaneous RE of 0.14 W m⁻² ppb⁻¹ 1927 ¹. AR4 used 0.13 W m⁻² ppb⁻¹ taken from *Clerbaux and Colin* [1994]. We calculate the same 1928 mean RE value (range: 0.12 - 0.13 W m⁻² ppb⁻¹) using absorption cross-sections from two
- 1929 sources [*M.S.F./R.A.L.*; *Sihra et al.*, 2001].
- 1930

1931 HFC-143a (CH₃CF₃)

The estimated RE of HFC-143a ranges from 0.13 to 0.22 W m⁻² ppb⁻¹ (mean: 0.16 W m⁻² 1932 ppb⁻¹) in previous studies [*Fisher et al.*, 1990; *Highwood and Shine*, 2000; *Jain et al.*, 2000; 1933 1934 Naik et al., 2000; Pinnock et al., 1995; Sihra et al., 2001; Zhang et al., 2011b]. Ab initio studies have calculated RE of 0.15 W m⁻² ppb⁻¹ [Good et al., 1998] and instantaneous RE of 1935 0.16 W m⁻² ppb⁻¹ [*Papasavva et al.*, 1997]. AR4 adopted the value from *Highwood and Shine* 1936 [2000] of 0.13 W m⁻² ppb⁻¹, which is at the lower end of this range. The recent study of Zhang 1937 et al. [2011b] calculated almost 70% higher RE (0.22 W m⁻² ppb⁻¹) than in AR4, but they did 1938 1939 not provide adequate reasons for these discrepancies (see also discussion of HFC-125). By 1940 using absorption cross-sections from three different sources [Di Lonardo and Masciarelli, 2000; Sihra et al., 2001; Smith et al., 1998], we calculate a mean RE value of 0.16 W m⁻² ppb⁻ 1941 ¹ (range: 0.15 - 0.17 W m⁻² ppb⁻¹), which is 22% higher than the AR4 value, but in line with 1942 1943 the mean of estimates from literature measurements. The low value of RE in the AR4 reflects 1944 the use of the infrared spectrum from *Highwood and Shine* [2000] which has an integrated 1945 absorption cross section which is significantly lower than in any of the other studies (Table 6). 1946 We did not include the Highwood and Shine [2000] spectrum here as this was taken from a 1947 lower temperature (253 K) pure gas measurement of Di Lonardo and Masciarelli [2000] who 1948 note that their lower temperature measurements may be more inaccurate if they fail to 1949 properly resolve the sharper spectral features at the lower temperature. Another contribution 1950 to the discrepancy is the use of different factors to correct for a non-uniform vertical profile. 1951 Whereas we use a fractional correction factor of 0.98 based on the method in section 3.3.4 and 1952 a lifetime of 47.1 years, Highwood and Shine [2000] used the crude factor of 0.95 based on 1953 Freckleton et al. [1998].

1954

1955 **HFC-152** (**CH**₂**FCH**₂**F**)

1956 The ab initio study by Papasavva et al. [1997] is the only published investigation of the RE for HFC-152. An instantaneous RE value of 0.09 W m⁻² ppb⁻¹ was reported and this value has 1957 been used in previous IPCC assessments. Using experimentally determined absorption cross-1958 sections from Wallington et al. [1994a] (Tables 6-7) and accounting for the non-uniform 1959 distribution we calculate a much lower RE value of 0.04 W m⁻² ppb⁻¹. The large difference is 1960 mainly due to the short lifetime of 146 days for HFC-152 [WMO, 2011] which leads to a 1961 reduction from 0.08 to 0.04 W m^{-2} ppb⁻¹ when taking into account the non-uniform 1962 1963 distribution (Table 7). Recommended RE and GWP values are updated based on our 1964 calculations.

1965

1966 HFC-152a (CH₃CHF₂)

Literature calculations of the RE of HFC-152a, using measured cross-sections, lie in the range 1967 0.09 - 0.14 W m⁻² ppb⁻¹ (mean: 0.11 W m⁻² ppb⁻¹) [Fisher et al., 1990; Highwood and Shine, 1968 1969 2000; Jain et al., 2000; Naik et al., 2000; Pinnock et al., 1995; Sihra et al., 2001; Zhang et al., 1970 2011b], while the *ab initio* study of *Papasavva et al.* [1997] estimated an instantaneous RE of 0.11 W m⁻² ppb⁻¹. AR4 reports a RE of 0.09 W m⁻² ppb⁻¹ which is taken from *Highwood and* 1971 Shine [2000]. We calculated a slightly higher RE value of 0.10 W m⁻² ppb⁻¹ when using 1972 1973 absorption cross-sections from either of the three different sources [Clerbaux et al., 1993; 1974 Sihra et al., 2001; Vander Auwera, 2000], showing that the uncertainty associated with 1975 measurements of the HFC-152a spectrum is low. The higher GWP value calculated here 1976 reflects the higher RE value, a longer lifetime estimate in the latest review by WMO [2011] (1.5 years) compared to that used in AR4 (1.4 years), and an updated AGWP_{CO2} value used 1977 1978 here.

1979

1980 HFC-161 (CH₃CH₂F)

1981Values of $0.02 - 0.04 \text{ W m}^{-2} \text{ ppb}^{-1}$ have been reported for RE of HFC-161 (mean: 0.03 W m^{-2} 1982ppb⁻¹) [*Christidis et al.*, 1997; *Jain et al.*, 2000; *Naik et al.*, 2000; *Sihra et al.*, 2001]. The *ab*1983*initio* study of *Papasavva et al.* [1997] is at the high end of this range with an instantaneous1984RE of $0.04 \text{ W m}^{-2} \text{ ppb}^{-1}$. A value of $0.03 \text{ W m}^{-2} \text{ ppb}^{-1}$ has been used in previous IPCC1985assessments and is based on *Christidis et al.* [1997] (a scaling factor of 0.8 based on

1986 *Freckleton et al.* [1998] was applied to account for decreased concentrations in the 1987 stratosphere). We calculate a RE value of $0.02 \text{ W m}^{-2} \text{ ppb}^{-1}$ when using the absorption cross-1988 sections from *Sihra et al.* [2001]. The lower RE in our study compared to that in AR4 is 1989 explained by the different lifetime correction factors used as we use a factor of 0.37 to 1990 account for the non-homogeneous mixing while a factor 0.8 was applied to the *Christidis et* 1991 *al.* [1997] result.

1992

1993 HFC-227ca (CF₃CF₂CHF₂)

The radiative efficiency of HFC-227ca has not been assessed in AR4. Values in the range 0.25 - 0.33 W m⁻² ppb⁻¹ (mean: 0.29 W m⁻² ppb⁻¹) are available for this compound [*Christidis et al.*, 1997; *Sihra et al.*, 2001]. We have used the absorption cross-section from *Sihra et al.* [2001] to calculate a RE value of 0.27 W m⁻² ppb⁻¹, which is slightly higher than the RE of 0.25 W m⁻² ppb⁻¹ calculated in their study. The lifetime of 28.2 years is taken from *Christidis et al.* [1997].

2000

2001 HFC-227ea (CF₃CHFCF₃)

Published values of the RE of HFC-227ea lie in the range 0.26 to 0.32 W m⁻² ppb⁻¹ (mean: 0.28 W m⁻² ppb⁻¹) [*Gohar et al.*, 2004; *Jain et al.*, 2000; *Naik et al.*, 2000; *Pinnock et al.*, 1995; *Sihra et al.*, 2001]. AR4 used a RE value of 0.26 W m⁻² ppb⁻¹ which is an average derived from the two models used in *Gohar et al.* [2004]. The absorption cross-section from that study has been used here to calculate a RE value of 0.26 W m⁻² ppb⁻¹, in agreement with that in AR4 (Tables 6-7). Our best estimate GWP value is higher than that in AR4 reflecting the latest information on the atmospheric lifetime of HFC-227ea [*WMO*, 2011].

2009

2010 HFC-236cb (CH₂FCF₂CF₃)

Two studies have been conducted to determine the RE of HFC-236cb. The average of results from the two studies is 0.24 W m⁻² ppb⁻¹ (range: 0.22 - 0.26 W m⁻² ppb⁻¹) [*Christidis et al.*, 1997; *Sihra et al.*, 2001]. Previous assessments have adopted the value of 0.23 W m⁻² ppb⁻¹ based on *Christidis et al.* [1997] (a scaling factor to account for decreased concentrations in 2015 the stratosphere was applied). We calculate the same RE value of 0.23 W m^{-2} ppb⁻¹ when

2016 using the absorption cross-section from *Sihra et al.* [2001] (Tables 6-7).

2017

2018 HFC-236ea (CHF₂CHFCF₃)

2019 Previous IPCC and WMO assessments have used a value of 0.30 W m⁻² ppb⁻¹ based on 2020 *Gierczak et al.* [1996] (a factor 0.8 was applied to yield cloudy-sky adjusted forcing from 2021 their clear-sky instantaneous forcing), which is the only study that have estimated RE due to 2022 HFC-236ea. No new calculations have been carried out here for this compound, thus we 2023 retain the RE from AR4 as our best estimate. The GWP(100) value has been updated, 2024 however, to account for the change in AGWP_{CO2} and the updated lifetime (11.0 years in 2025 *WMO* [2011] compared to 10.7 years in AR4).

2026

2027 HFC-236fa (CF₃CH₂CF₃)

Literature estimates of the RE of HFC-236fa range from 0.23 to 0.29 W m⁻² ppb⁻¹ (mean: 0.26 2028 W m⁻² ppb⁻¹) [*Gierczak et al.*, 1996; *Jain et al.*, 2000; *Naik et al.*, 2000; *Pinnock et al.*, 1995; 2029 Sihra et al., 2001] (note that the upper estimate of 0.29 W m⁻² ppb⁻¹ from Gierczak et al. 2030 [1996] have been scaled by a factor 0.8 to convert from clear-sky instantaneous forcing to 2031 cloudy-sky stratospheric temperature adjusted forcing following WMO [1999]). In previous 2032 assessments, an average of the results from Pinnock et al. [1995] and Gierczak et al. [1996] of 2033 $0.28 \text{ W m}^{-2} \text{ ppb}^{-1}$ has been used. Using the absorption spectrum from Sihra et al. [2001] we 2034 calculate a RE value of 0.24 W m⁻² ppb⁻¹, 13% lower than the AR4 value (Tables 6-7). We 2035 2036 note that the estimate of Gierczak et al. [1996] was crudely scaled to account for clouds and 2037 stratospheric temperature adjustment, and that the resulting RE is at the higher end of the range of REs from the literature. Furthermore, the difference between our RE estimate and the 2038 calculation of *Pinnock et al.* [1995] (0.27 W m⁻² ppb⁻¹) can be partly explained by the higher 2039 2040 integrated absorption cross-section in their study (Table 6).

2041

2042 HFC-245ca (CH₂FCF₂CHF₂)

An RE estimate of 0.23 W m⁻² ppb⁻¹ for HFC-245ca has been used in all IPCC and WMO assessments since *IPCC* [1994] and is based on Fisher (pers. comm.) (original value was 0.20

W m⁻² ppb⁻¹, but it was scaled to 0.23 W m⁻² ppb⁻¹ in WMO [1999] because of a change in the 2045 recommended forcing of CFC-11 – see the discussion of CFC-11 in section 4.1.1), and no 2046 2047 newer estimates were found in the literature. No new calculations have been carried out here 2048 for this compound, thus we retain the RE from AR4 as our best estimate, except that we scale the value by a factor 0.26/0.25=1.04 to account for the update in our recommended RE of 2049 CFC-11. Our recommended RE of HFC-245ca is then 0.24 W m⁻² ppb⁻¹. Also, the GWP(100) 2050 value has been updated to account for the change in $AGWP_{CO2}$ and the updated lifetime (6.5 2051 2052 years in WMO [2011] compared to 6.2 years in AR4).

2053

2054 HFC-245cb (CF₃CF₂CH₃)

The radiative efficiency of HFC-245cb was not assessed in AR4. Published studies give RE in 2055 the range $0.25 - 0.28 \text{ W m}^{-2} \text{ ppb}^{-1}$ (mean: $0.27 \text{ W m}^{-2} \text{ ppb}^{-1}$) [Christidis et al., 1997; Sihra et 2056 al., 2001]. We used the absorption spectrum from two sources [Orkin et al., 2003; Sihra et al., 2057 2001] and calculated a mean RE value of 0.24 W m^{-2} ppb⁻¹ (range: 0.23 - 0.25 W m^{-2} ppb⁻¹) 2058 (Tables 6-7), which is slightly lower than the 0.25 W m⁻² ppb⁻¹ reported by *Sihra et al.* [2001]. 2059 However, they assumed a constant vertical profile for this compound, and we note that our 2060 RE estimate when assuming a constant vertical profile (0.25 W m^{-2} ppb⁻¹) is consistent with 2061 their result. The lifetime of 47.1 years is taken from Christidis et al. [1997] who assumed the 2062 2063 same lifetime as HFC-143a, based on the similar molecular structure of the two compounds.

2064

2065 HFC-245ea (CHF₂CHFCHF₂), HFC-245eb (CH₂FCHFCF₃) and HFC-263fb 2066 (CH₃CH₂CF₃)

The REs of HFC-245ea, HFC-245eb and HFC-263fb have not been assessed in AR4, but 2067 Rajakumar et al. [2006] used a LBL model to calculate REs of 0.18, 0.23 and 0.13 W m⁻² 2068 ppb⁻¹, respectively. Clouds and stratospheric temperature adjustment were included in their 2069 2070 study, but they did not include the effect of a non-homogeneous vertical profile. When using 2071 lifetimes from WMO [2011] and our method described in section 3.3.4, the lifetime-corrected REs from Rajakumar et al. [2006] are 0.16, 0.20 and 0.10 W m⁻² ppb⁻¹ for HFC-245ea, HFC-2072 2073 245eb and HFC-263fb, respectively. Using these REs we derive the recommended GWPs given in Table 7. 2074

2075

2076 HFC-245fa (CHF₂CH₂CF₃)

Published estimates of the RE of HFC-245fa lie in the range 0.24 - 0.29 W m^{-2} ppb⁻¹ (mean: 2077 0.27 W m⁻² ppb⁻¹) [Jain et al., 2000; Ko et al., 1999; Naik et al., 2000; Orkin et al., 2003; 2078 Sihra et al., 2001], and the value of 0.28 W m⁻² ppb⁻¹ from Ko et al. [1999] has been used in 2079 recent assessments. We calculate a lower mean RE value of 0.24 W m⁻² ppb⁻¹ (range: 0.24 -2080 0.25 W m⁻² ppb⁻¹) when using the absorption cross-sections from *Sihra et al.* [2001] and 2081 Orkin et al. [2003] (Tables 6-7). Part of the reason for the weaker RE in this study is the 2082 lower integrated absorption cross-section in Sihra et al. [2001] compared to Ko et al. [1999] 2083 2084 (Table 6), but it could also be related to differences in how the non-homogeneous distribution is accounted for. We note further that the RE estimate of Ko et al. [1999] is at the high end of 2085 the range of literature REs and that our estimate is in agreement with the 0.24 W m^{-2} ppb⁻¹ 2086 calculated by Sihra et al. [2001]. Our RE estimate of 0.24 W m⁻² ppb⁻¹ is approximately 13% 2087 lower than the value of 0.28 W m^{-2} ppb⁻¹ used in AR4 (see Table 7). 2088

2089

2090 HFC-272ca (CH₃CF₂CH₃)

Previous studies of RE due to HFC-272ca are in the range 0.08 - 0.09 W m⁻² ppb⁻¹ (mean: 2091 0.09 W m⁻² ppb⁻¹) [*Pinnock et al.*, 1995; *Sihra et al.*, 2001]. We calculate a RE value of 0.08 2092 W m⁻² ppb⁻¹ using the absorption spectrum from *Sihra et al.* [2001] (Tables 6-7). While there 2093 is no lifetime estimate for CH₃CF₂CH₃ in the literature, using the structure activity 2094 relationship developed by *Calvert et al.* [2008] with $k(-CH_3) = 1.35 \times 10^{-13}$ and $F(-CF_{2-}) =$ 2095 0.045 we estimate $k(OH + CH_3CF_2CH_3) = 1.21 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Combining 2096 this rate coefficient with an average tropospheric OH concentration of 1×10^6 cm⁻³ provides 2097 an estimate for the atmospheric lifetime of 2.6 years. Using this estimated lifetime we derive 2098 the GWP value given in Table 7. 2099

2100

2101 HFC-329p (CHF₂CF₂CF₂CF₃)

The RE of HFC-329p has not been assessed by AR4, but was estimated to 0.31 W m⁻² ppb⁻¹ (instantaneous RE) by *Young et al.* [2009b] who used the original *Pinnock et al.* [1995] method. We have used the absorption cross-section from *Young et al.* [2009b] and calculated the same RE value of 0.31 W m⁻² ppb⁻¹ (Tables 6-7).

2106

2107 HFC-365mfc (CH₃CF₂CH₂CF₃)

A range of 0.21 - 0.23 W m⁻² ppb⁻¹ (mean: 0.22 W m⁻² ppb⁻¹) is available from literature 2108 estimations of the RE of HFC-365mfc [Barry et al., 1997; Inoue et al., 2008; Naik et al., 2109 2000]. AR4 adopted the value of 0.21 W m⁻² ppb⁻¹ from *Barry et al.* [1997], while *WMO* 2110 [2011] used an average of the results from Barry et al. [1997] and the more recent study of 2111 *Inoue et al.* [2008]. The latter study calculated a slightly higher RE of 0.23 W m⁻² ppb⁻¹ 2112 (instantaneous RE) reflecting an approximately 10% more intense infrared absorption 2113 2114 spectrum reported by Inoue et al. [2008]. A precise comparison of the spectra recorded by 2115 Barry et al. [1997] and Inoue et al. [2008] is not possible because Barry et al. [1997] did not 2116 report an integrated absorption cross section. Here we have used the better documented absorption cross-section from *Inoue et al.* [2008] to calculate a radiative forcing of 0.22 W m⁻ 2117 2 ppb⁻¹. Our RE estimate is approximately 6% higher (prior to rounding) than the value used 2118 2119 in AR4 (see Table 7).

2120

2121 HFC-43-10mee (CF₃CHFCHFCF₂CF₃)

AR4 reports a RE of HFC-43-10mee of 0.40 W m⁻² ppb⁻¹ which is based on Fisher (pers. 2122 comm.) [IPCC, 1994] (original value was scaled in WMO [1999] because of a change in the 2123 2124 recommended forcing of CFC-11 - see the discussion of CFC-11 in section 4.1.1). No 2125 published estimates of the RE of this compound exist and no new calculations have been 2126 carried out here, thus we retain the RE from AR4 as our best estimate, except that we scale the value by a factor 0.26/0.25=1.04 to account for the update in our recommended RE of 2127 CFC-11. Our recommended RE of HFC-43-10mee is then 0.42 W m⁻² ppb⁻¹. Also, the 2128 GWP(100) value has been updated to account for the change in AGWP_{CO2} and the updated 2129 lifetime (16.1 years in WMO [2011] compared to 15.9 years in AR4). 2130

2131

2132 HFC-1132a (CH₂=CF₂), HFC-1141 (CH₂=CHF) and (Z)-HFC-1336 (CF₃CH=CHCF₃(Z))

The REs of HFC-1132a, HFC-1141 and (Z)-HFC-1336 were not assessed in AR4. *Baasandorj et al.* [2010] have estimated the radiative efficiencies of HFC-1132a and HFC-1141 to be 0.09 and 0.08 W m⁻² ppb⁻¹, respectively. *Baasandorj et al.* [2011] estimated the radiative efficiency of (Z)-HFC-1336 to be 0.38 W m⁻² ppb⁻¹. The RE values from both studies are instantaneous REs derived using the original *Pinnock et al.* [1995] method for the
forcing calculations. We apply a 10% increase to account for stratospheric temperature adjustment, and an additional correction factor to account for the non-homogeneous mixing (see section 3.3.4) to derive recommended REs of 0.004, 0.002 and 0.074 W m⁻² ppb⁻¹ for HFC-1132a, HFC-1141 and (Z)-HFC-1336, respectively. Lifetimes necessary for the RE lifetime correction and GWP calculation were taken from *WMO* [2011] for HFC-1132a and HFC-1141, and from *Baasandorj et al.* [2011] for (Z)-HFC-1336.

2144

2145 (Z)-HFC-1225ye (CF₃CF=CHF(Z))

Literature values of the RE of (Z)-HFC-1225ye are in close agreement with a range 0.25 -2146 $0.26 \text{ W m}^{-2} \text{ ppb}^{-1}$ (mean: $0.26 \text{ W m}^{-2} \text{ ppb}^{-1}$) [Hurley et al., 2007; Papadimitriou et al., 2008a]. 2147 Our RE calculation using the absorption spectrum from Hurley et al. [2007] and assuming 2148 homogeneous mixing throughout the troposphere is $0.26 \text{ W m}^{-2} \text{ ppb}^{-1}$, in good agreement with 2149 the literature data. However, when we account for the substantially non-homogeneous mixing 2150 of this short-lived species we arrive at the much lower RE value of 0.02 W m⁻² ppb⁻¹ (Tables 2151 6-7). Neither of the two literature studies account for the non-homogeneous mixing of 2152 CF₃CF=CHF in the troposphere. Our recommended RE and GWP values are given in Table 7. 2153

2154

2155 (E)-HFC-1225ye (CF₃CF=CHF(E))

There has been one published study of the RE of (E)-HFC-1225ye which gave a value 0.24 W m^{-2} ppb⁻¹ [*Hurley et al.*, 2007]. We have used the absorption spectrum from *Hurley et al.* [2007] and calculated a RE value of 0.01 W m⁻² ppb⁻¹ (Tables 6-7). As for the (Z)-HFC-1225ye compound discussed above, our RE estimate is in close agreement with the published value when we assume homogeneous mixing of (E)-HFC-1225ye.

2161

2162 (Z)-HFC-1234ze (CF₃CH=CHF(Z))

There has been one published study of the RE of (Z)-HFC-1234ze which gave a value 0.20 W $m^{-2} \text{ ppb}^{-1}$ [*Nilsson et al.*, 2009]. We calculate a RE value of 0.02 W m⁻² ppb⁻¹ using absorption spectrum from *Nilsson et al.* [2009] (Tables 6-7). The RE value estimated here is in good agreement with the published value when homogeneous distribution is assumed. The lifetime of 10 days is taken from *Nilsson et al.* [2009]. 2168

2169 HFC-1234yf (CF₃CF=CH₂)

Literature values for the RE of HFC-1234yf fall in the range 0.22 - 0.24 W m⁻² ppb⁻¹ (mean: 0.23 W m⁻² ppb⁻¹) [*Nielsen et al.*, 2007; *Orkin et al.*, 2010; *Papadimitriou et al.*, 2008a]. We calculate a mean RE value of 0.02 W m⁻² ppb⁻¹ both when using the absorption cross-section from *Orkin et al.* [2010] and from *Nielsen et al.* [2007] (Tables 6-7). Neither of the previous studies accounted for the non-homogeneous mixing of this short-lived compound and we note that our estimate is in excellent agreement with the mean of published RE values when we assume uniform mixing of HFC-1234yf.

2177

2178 (E)-HFC-1234ze (trans-CF₃CH=CHF)

Results from the published studies of the RE of (E)-HFC-1234ze lie in the range 0.24 - 0.27W m⁻² ppb⁻¹ (mean: 0.26 W m⁻² ppb⁻¹) [*Orkin et al.*, 2010; *Søndergaard et al.*, 2007]. We calculate a RE value of 0.04 W m⁻² ppb⁻¹ when using absorption cross-sections from both of these studies (Tables 6-7). The non-homogeneous mixing of this short-lived compound was not accounted for in the two studies; our estimate of RE is consistent with the published values if we assume uniform mixing.

2185

2186HFC-1243zf,HFC-1345zfc,3,3,4,4,5,5,6,6,6-nonafluorohex-1-ene,21873,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-eneand3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-2188heptadecafluorodec-1-ene ($C_xF_{2x+1}CH=CH_2$ (x=1, 2, 4, 6 and 8))

2189 In the recent study by Andersen et al. [2012a], REs were calculated for five compounds that 2190 have not been included in previous assessments. They used the original *Pinnock et al.* [1995] method to calculate instantaneous REs of 0.16, 0.18, 0.34, 0.38 and 0.42 W m⁻² ppb⁻¹ for 2191 2192 HFC-1243zf, HFC-1345zfc, 3,3,4,4,5,5,6,6,6-nonafluorohex-1-ene, 3,3,4,4,5,5,6,6,7,7,8,8,8-2193 tridecafluorooct-1-ene and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodec-1-ene, 2194 respectively, assuming uniform mixing of these gases. As can be seen in Table 7, the corresponding REs calculated in this study are in close agreement to Andersen et al. [2012a], 2195 while they are substantially lower – in the range 0.01 - 0.03 W m^{-2} ppb⁻¹ – when accounting 2196 for non-homogeneous mixing. It should be noted here that the uncertainties associated with 2197 2198 the lifetime correction factor are very large on a percentage basis for such short-lived species (see Figure 9 and associated discussion in section 3.3.4). The absorption cross-sections used
here are from *Andersen et al.* [2012a] (Table 6), and the lifetimes necessary for the fractional
correction and GWP calculation have been taken from *Andersen et al.* [2005].

2202

2203 4.1.4 Chlorocarbons and Hydrochlorocarbons

2204 Chlorocarbons and hydrochlorocarbons are ozone-depleting substances and are therefore controlled under the Montreal Protocol. Lifetimes for the chlorocarbons 2205 and hydrochlorocarbons considered here range from less than a year for CH₂ClCH₂Cl to 26 years 2206 2207 for CCl₄ (carbon tetrachloride). Figure 1 shows the contrasting time-histories of the atmospheric concentrations of the most abundant chlorocarbon (CCl₄) and hydrochlorocarbon 2208 2209 (CH₃CCl₃, methyl chloroform). Methyl chloroform concentrations fell rapidly after implementation of the Montreal Protocol, due to a combination of rapidly-decreasing 2210 2211 emissions and its short (5 year) lifetime. By contrast, due to continued emissions of carbon tetrachloride it remains the fourth most abundant of the compounds considered here (about 90 2212 2213 ppt), with concentrations decreasing only rather slowly (at a rate of about 1.2 ppt year⁻¹ 2214 [WMO, 2011]). Figure 14 shows the absorption spectrum of carbon tetrachloride – the 2215 symmetry of this molecule results in a quite simple spectrum, with most of the absorption concentrated in the $750 - 800 \text{ cm}^{-1}$ spectral region. Previously published absorption cross-2216 2217 sections are listed in Table 8, while updated atmospheric lifetimes, radiative efficiencies, and 2218 100-year GWP values for chlorocarbons and hydrochlorocarbons are presented in Table 9 and 2219 discussed below. With the exception of carbon tetrachloride, which is mainly lost by 2220 photolysis [WMO, 2011], the S-shaped fit from section 3.3.4 (Equation (2) and dark blue 2221 curve in Figure 9) has been used to account for a non-uniform vertical profile and geographic 2222 distribution for all compounds presented in this subsection.

2223

2224 Methyl chloroform (CH₃CCl₃)

The studies that have calculated RE of methyl chloroform present values in the range 0.06 -0.10 W m⁻² ppb⁻¹ (mean: 0.07 W m⁻² ppb⁻¹) [*Fisher et al.*, 1990; *Imasu et al.*, 1995; *Jain et al.*, 2000; *Orkin et al.*, 2003]. Both *Fisher et al.* [1990] and *Jain et al.* [2000] used the same absorption cross-section [*Fisher et al.*, 1990]. *Orkin et al.* [2003] presented a 9% larger absorption cross-section and, based on the measured spectrum of the Earth's outgoing

- radiation obtained by NIMBUS 4 [*Kunde et al.*, 1974], a relative RE to CFC-11 of 0.38. AR4 adopted the RE value of 0.06 W m⁻² ppb⁻¹ from *Fisher et al.* [1990]. We have used the absorption cross-sections from two sources [*Imasu et al.*, 1995; *Orkin et al.*, 2003] and calculated a slightly higher RE value of 0.07 W m⁻² ppb⁻¹ for both spectra.
- 2234

2235 Carbon tetrachloride (CCl₄)

Previous studies of carbon tetrachloride RE present values in the range 0.09 - 0.13 W m⁻² ppb⁻ 2236 ¹ (mean: 0.11 W m⁻² ppb⁻¹) [*Fisher et al.*, 1990; *Jain et al.*, 2000; *Myhre and Stordal*, 1997]; 2237 Fisher et al. [1990] and Jain et al. [2000] based their calculations on the absorption cross 2238 2239 section presented by Fisher et al. [1990], while Myhre and Stordal [1997] employed the absorption cross section of Massie et al. [1985]. AR4 adopted the RE of 0.13 W m⁻² ppb⁻¹ 2240 from Jain et al. [2000]. We have used the more recent absorption cross-section from the study 2241 2242 of Nemtchinov and Varanasi [2003], which includes temperature and pressure dependency and an inter-comparison of all previous data, and derive a RE value of 0.17 W m⁻² ppb⁻¹. This 2243 is significantly higher (35% higher) than the AR4 value (Table 9) and entirely due to the 2244 higher absorption cross-section of the newer data (Table 8) than that was used in the RE 2245 2246 calculation of Jain et al. [2000]. In contrast to the other compounds listed in this section, carbon tetrachloride is mainly lost by photolysis rather than reaction with OH [WMO, 2011]. 2247 2248 Hence, we have used the exponential fit from section 3.3.4 (Equation (1) and red curve in Figure 9) instead of the S-shaped fit to account for a non-uniform vertical profile, although 2249 2250 this has only a small impact on the RE because this compound is relatively well-mixed in the 2251 atmosphere (lifetime of 26.0 years).

2252

2253 Methyl chloride (CH₃Cl)

Only one study has estimated the methyl chloride RE presenting a value of 0.01 W m⁻² ppb⁻¹ [*Grossman et al.*, 1997], which is also the value that has been used in the AR4 assessment. Grossman and co-workers employed a combination of absorption cross-sections from *Brown et al.* [1987] and HITRAN. No new calculations have been carried out here for this compound, thus we retain the RE from AR4 as our best estimate. The GWP(100) value has, however, been updated to account for the change in AGWP_{CO2}.

2260

2261 Methylene chloride (CH₂Cl₂)

No estimate of the methylene chloride RE has been found in the published literature. AR4 reports a RE of 0.03 W m⁻² ppb⁻¹ that has been used in all assessments since *IPCC* [1994] and is based on Fisher (pers. comm.) (scaled to the previously recommended CFC-11 RE of 0.25 W m⁻² ppb⁻¹). No new calculations have been carried out here for this compound, thus we retain the RE and GWP(100) from AR4 as our best estimate (the GWP(100) for this compound rounds to 9 after updating the AGWP_{CO2} value).

2268

2269 Chloroform (CHCl₃)

The two previous reports on chloroform RE are in the range 0.09 - 0.11 W $m^{-2} ppb^{-1}$ (mean: 2270 0.10 W m⁻² ppb⁻¹) [Highwood and Shine, 2000; Sihra et al., 2001] and are both based on the 2271 spectroscopic data from McPheat and Duxbury [2000]. AR4 has adopted the RE of 0.11 W m⁻ 2272 2 ppb⁻¹ from *Highwood and Shine* [2000]. We have employed the absorption cross-section 2273 from McPheat and Duxbury [2000], but we derive a substantially lower RE value of 0.08 W 2274 2275 m^{-2} ppb⁻¹ (Tables 8-9). The reason for the ~30% lower value in the present study is linked to 2276 the different methods correcting for the non-homogeneous mixing of this short-lived species. 2277 Highwood and Shine [2000] used a factor of 0.8 from Freckleton et al. [1998] while we use a 2278 fractional correction factor of 0.55 based on the method described in section 3.3.4 and a 2279 lifetime of 0.4 years [WMO, 2011]. Recommended RE and GWP values, based on our calculations, are presented in Table 9. 2280

2281

2282 **1,2-Dichloroethane (CH₂ClCH₂Cl)**

1,2-dichloroethane has a relatively low RE with estimates of 0.02 W m⁻² ppb⁻¹ in the literature [*Highwood and Shine*, 2000; *Sihra et al.*, 2001]; both studies use the absorption cross-section of *Vander Auwera* [2000]. The present calculations, employing the same spectroscopic data, yield a RE about half the magnitude, 0.01 W m⁻² ppb⁻¹ (Tables 8-9). As for chloroform, the calculated RE value is consistent with the previous studies when a homogeneous distribution is assumed.

2289

4.1.5 Bromocarbons, Hydrobromocarbons, and Halons

2291 The bromocarbons, hydrobromocarbons, and halons are ozone-depleting substances on 2292 account of both presences of bromine, and in some compounds, also chlorine. They are 2293 controlled under the Montreal Protocol. Lifetimes for the compounds considered here range 2294 from less than a year in the case of methylene bromide (CH_2Br_2) to 65 years in the case of Halon-1301 (CBrF₃). The most abundant hydrobromocarbon in the atmosphere is methyl 2295 bromide (about 7.5 ppt, decreasing at 0.2 ppt year⁻¹ [WMO, 2011]) and the most abundant 2296 halon is Halon-1211 (about 4.2 ppt, decreasing at 0.05 ppt year⁻¹ [WMO, 2011]). Figure 15 2297 2298 shows the absorption spectrum of Halon-1301 ($CBrF_3$) – the relatively simple structure of this molecule is reflected in an absorption spectrum where most of the intensity is concentrated in 2299 2300 two narrow bands between 1,000 and $1,200 \text{ cm}^{-1}$.

2301 Previously published absorption cross-sections are listed in Table 10, while updated atmospheric lifetimes, radiative efficiencies, and GWP(100) values for bromocarbons, 2302 hydrobromocarbons, and halons are presented in Table 11 and discussed below. Three of the 2303 2304 compounds are mainly lost by photolysis in the stratosphere (Halon-1211, Halon-1301 and 2305 Halon-2402 [WMO, 2011]), and we have therefore used the exponential fit from section 3.3.4 2306 (Equation (1) and red curve in Figure 9) to account for a non-uniform vertical profile for these 2307 compounds. The remaining compounds are mainly lost through reaction with OH and we 2308 have therefore used the S-shaped fit from section 3.3.4 (Equation (2) and dark blue curve in 2309 Figure 9) to account for a non-uniform vertical profile and geographic distribution for these 2310 compounds.

2311

2312 Methyl bromide (CH₃Br)

2313 The RE of methyl bromide is low with a mean of 0.006 W m^{-2} ppb⁻¹ (range: 0.005 - 0.007 W

2314 m⁻² ppb⁻¹) from published estimates [*Christidis et al.*, 1997; *Grossman et al.*, 1997; *Jain et al.*,

2315 2000; Sihra et al., 2001]. AR4 has adopted a RE of 0.01 W m⁻² ppb⁻¹ based on the results of

2316 Grossman et al. [1997] and Christidis et al. [1997] (rounded to two decimals). Grossman et

al. [1997] used the molecular parameters of Anttila et al. [1983] and Graner and Blass [1975]

- 2318 to model the CH₃Br spectrum. We have used the absorption cross-section from *Sihra et al.*
- 2319 [2001] and derive $RE = 0.004 \text{ W m}^{-2} \text{ ppb}^{-1}$ (Tables 10-11), which is lower than the AR4 value
- 2320 $(0.006 \text{ W m}^{-2} \text{ ppb}^{-1})$. The reason is that the previous studies assumed a constant vertical

profile, while we applied a lifetime correction factor of 0.70 using the method described in section 3.3.4 and a lifetime of 0.8 years [*WMO*, 2011]. The present calculations are in excellent agreement with the 0.007 W m⁻² ppb⁻¹ calculated by *Christidis et al.* [1997] when a constant vertical profile of methyl bromide is assumed. The best estimate RE and GWP are shown in Table 11.

2326

2327 Methylene bromide (CH₂Br₂)

Previous studies of RE due to methylene bromide are in the range $0.011 - 0.021 \text{ W m}^{-2} \text{ ppb}^{-1}$ (mean: $0.017 \text{ W m}^{-2} \text{ ppb}^{-1}$) [*Christidis et al.*, 1997; *Jain et al.*, 2000; *Sihra et al.*, 2001]; AR4 recommends RE of $0.01 \text{ W m}^{-2} \text{ ppb}^{-1}$ (rounded to two decimals) from *Christidis et al.* [1997] (note that AR4 accounted for stratospheric decay [*WMO*, 1999]). When using the absorption cross-section from *Sihra et al.* [2001], we calculate a RE value of $0.008 \text{ W m}^{-2} \text{ ppb}^{-1}$, which leads to a new recommended GWP(100) value of 1 (Tables 10-11).

2334

2335 Halon-1201 (CHBrF₂)

Literature reports of Halon-1201 RE are in the range 0.15 - 0.18 W m⁻² ppb⁻¹ (mean: 0.17 W 2336 m⁻² ppb⁻¹) [*Christidis et al.*, 1997; *Jain et al.*, 2000; *Orkin et al.*, 2003; *Sihra et al.*, 2001]; 2337 AR4 adopted a RE of 0.14 W m⁻² ppb⁻¹ which is taken from *Christidis et al.* [1997] (note that 2338 AR4 accounted for stratospheric decay [WMO, 1999]). We derive a mean RE of 0.15 W m⁻² 2339 ppb⁻¹ (range: 0.15 - 0.16 W m⁻² ppb⁻¹) when using the absorption cross-sections from *Sihra et* 2340 al. [2001], Orkin et al. [2003] and the recent study by Charmet et al. [2010] (Tables 10-11). 2341 2342 Our RE estimate is in agreement with the value from Sihra et al. [2001], but it is more than 5% higher than the AR4 estimate (Table 11). Despite the higher RE, our recommended 2343 GWP(100) value is lower than in AR4 due to the shorter lifetime recommended by WMO 2344 [2011] (5.2 years compared to 5.8 years in AR4) and the higher $AGWP_{CO2}$ used here. 2345

2346

2347 Halon-1202 (CBr₂F₂)

One study has estimated RE due to Halon-1202 with a value 0.29 W m⁻² ppb⁻¹ [*Orkin et al.*, 2349 2003] (when scaled to our recommended CFC-11 RE of 0.26 W m⁻² ppb⁻¹). We have used the 2350 absorption cross-section from the same study and calculated a slightly lower RE of 0.27 W m⁻² ² ppb⁻¹. It should be noted that the recent study by *Papanastasiou et al.* [2013] suggests a lifetime of 2.52 years, which is shorter than the 2.9 years [*WMO*, 2011] used here.

2353

2354 Halon-1211 (CBrClF₂)

Previous reports of the RE of Halon-1211 are in the range 0.25 - 0.33 W m⁻² ppb⁻¹ (mean: 2355 0.28 W m⁻² ppb⁻¹) [Christidis et al., 1997; Jain et al., 2000; Sihra et al., 2001]. AR4 reports a 2356 RE of 0.30 W m⁻² ppb⁻¹, which is based on the results of *Christidis et al.* [1997] (note that 2357 AR4 accounted for stratospheric decay [WMO, 1999]). We have used the absorption cross-2358 section from Sihra et al. [2001] and calculated a RE value of 0.29 W m⁻² ppb⁻¹, which is 2359 consistent (within 5% difference) with the AR4 value (Tables 10-11). For Halon-1211 we 2360 2361 have carried out explicit simulations using the Oslo LBL model and derived a factor of 0.937 to account for the non-uniform vertical profile induced by loss through photolysis in the 2362 stratosphere (see section 3.3.4 for details), and this factor has been used to derive the RE of 2363 0.29 W m⁻² ppb⁻¹. It should be noted that *Papanastasiou et al.* [2013] have recently suggested 2364 2365 a slightly longer lifetime of 16.4 years compared to the 16.0 years [WMO, 2011] which have been used here. 2366

2367

2368 Halon-1301 (CBrF₃)

Estimates of the RE of Halon-1301 in the literatures range from 0.27 to 0.33 W m⁻² ppb⁻¹ (mean: 0.30 W m⁻² ppb⁻¹) [*Charmet et al.*, 2008; *Drage et al.*, 2006; *Jain et al.*, 2000; *Orkin et al.*, 2003; *Ramanathan et al.*, 1985; *Sihra et al.*, 2001]. AR4 used a RE of 0.32 W m⁻² ppb⁻¹ taken from *Ramanathan et al.* [1985]. We have used absorption cross-sections from three sources [*Charmet et al.*, 2008; *Orkin et al.*, 2003; *Sihra et al.*, 2001] and calculated a mean RE value of 0.30 W m⁻² ppb⁻¹ (range: 0.29 - 0.31 W m⁻² ppb⁻¹), about 6% lower than AR4.

2375

2376 Halon-2301 (CH₂BrCF₃)

One study has estimated RE due to Halon-2301 with a value 0.17 W m⁻² ppb⁻¹ [*Orkin et al.*, 2378 2003] (scaled to our recommended CFC-11 RE of 0.26 W m⁻² ppb⁻¹). We have used their 2379 absorption cross-section and calculated a lower RE value of 0.14 W m⁻² ppb⁻¹. Our value 2380 includes corrections for stratospheric temperature adjustment and non-homogeneous mixing, which were not accounted for in the published estimate. The lifetime of 3.4 years is takenfrom *Orkin et al.* [2003].

2383

2384 Halon-2311 / Halothane (CHBrClCF₃)

2385 The RE of Halon-2311 has not been assessed in AR4, but was estimated to be in the range $0.17 - 0.21 \text{ W m}^{-2} \text{ ppb}^{-1}$ (mean: 0.19 W m⁻² ppb⁻¹) in previous studies [Andersen et al., 2012b; 2386 Orkin et al., 2003]. Both these studies assumed homogeneous mixing throughout the 2387 troposphere and used the original *Pinnock et al.* [1995] method to calculate the instantaneous 2388 RE. We calculate a lower RE with a mean value of 0.13 W m^{-2} ppb⁻¹ (range: 0.13 - 0.14 W m⁻²) 2389 2 ppb⁻¹) when using the absorption cross-sections from Andersen et al. [2012b] and Orkin et 2390 al. [2003] (Tables 10-11). The lower value calculated here primarily reflects the correction 2391 2392 factor we have applied to account for non-homogeneous mixing, but it is also a result of the 2393 difference between the original Pinnock curve and the new curve presented in section 3.3.1, 2394 whereas the latter curve generally yields lower REs (in this case ~5% lower).

2395

2396 Halon-2401 (CHFBrCF₃)

Orkin et al. [2003] have estimated the RE due to Halon-2401 with a value 0.23 W m⁻² ppb⁻¹ (when scaled to our recommended CFC-11 RE of 0.26 W m⁻² ppb⁻¹). We have used their absorption cross-section and calculated a RE value of 0.19 W m⁻² ppb⁻¹. Again, the lower value results mainly from the lifetime correction factor applied here to account for nonhomogeneous mixing. The lifetime of 2.9 years is taken from *Orkin et al.* [2003].

2402

2403 Halon-2402 (CBrF₂CBrF₂)

Sihra et al. [2001] estimated the RE of Halon-2402 presenting a value of 0.33 W m⁻² ppb⁻¹, which is also the RE adopted by AR4. We have used the absorption cross-section from *Sihra* et al. [2001] and calculated a RE value of 0.31 W m⁻² ppb⁻¹, about 6% lower than that used in AR4. We have used a lifetime of 20.0 years [*WMO*, 2011], but we note that the recent study by *Papanastasiou et al.* [2013] has estimated a significantly longer lifetime of 28.3 years, and consequently higher GWP values for this compound.

2410

2411 4.1.6 Fully Fluorinated Species

2412 Fully fluorinated compounds are generally long-lived compounds removed by photolysis in 2413 the stratosphere, although unsaturated compounds may be very short-lived because of their reactivity towards OH radicals. Perfluorocarbons (PFCs) usually have strong absorption in the 2414 1200-1300 cm⁻¹ region of the spectrum (as illustrated for CF₄ in Figure 16) and so are 2415 radiatively active in the atmosphere. As a result – and combined with their long lifetimes – 2416 2417 saturated PFCs have some of the largest GWPs of any compounds detected in the atmosphere. 2418 These compounds are identified within the Kyoto Protocol as gases whose presence in the 2419 atmosphere must be controlled, as has sulphur hexafluoride. As noted in section 1, nitrogen 2420 trifluoride was added to the basket of greenhouse gases in the second commitment period of 2421 the Kyoto Protocol. Published absorption cross-sections are listed in Table 12, while updated 2422 atmospheric lifetimes, radiative efficiencies, and GWP(100) values for fully fluorinated 2423 species are presented in Table 13 and discussed below. For sulfuryl fluoride and six short-2424 lived compounds we have used the S-shaped fit from section 3.3.4 (Equation (2) and dark 2425 blue curve in Figure 9) to account for a non-uniform vertical profile and geographic 2426 distribution due to their reactivity towards OH. The remaining compounds have very long lifetimes (>500 years) and are lost by photolysis in the stratosphere, hence we have used the 2427 2428 exponential fit from section 3.3.4 (Equation (1) and red curve in Figure 9) to account for a 2429 non-uniform vertical profile for these compounds.

2430

2431 Nitrogen trifluoride (NF₃)

2432 There is one study of the RE for nitrogen trifluoride in the literature. Robson et al. [2006] calculated a cloudy-sky adjusted radiative forcing of 0.21 W m⁻² ppb⁻¹ by using a combination 2433 of line-by-line and narrow band radiative transfer models, and this value has been used in 2434 IPCC and WMO assessments (since WMO [2007]). Earlier assessments reported a much 2435 lower value of 0.13 W m⁻² ppb⁻¹ (instantaneous RE), but these calculations were based on 2436 incomplete cross-section data. We have used the spectrum from Robson et al. [2006] and 2437 calculated a RE value of 0.20 W m⁻² ppb⁻¹ (Table 12-13), which is consistent (within 5% 2438 difference) with AR4. Since AR4, the lifetime of NF₃ has been studied by Prather and Hsu 2439 2440 [2008] who suggest a much shorter lifetime of 550 years, partly due to inclusion of the $O(^{1}D)$ + NF₃ reaction, compared to the 740 years recommended in AR4. WMO [2011] used an 2441 updated rate constant for the O(¹D) reaction to obtain a lifetime of 500 years, which is the 2442

value we have used here. It should be noted that a very recent study by *Papadimitriou et al.* [2013] included temperature dependence of the NF₃ UV absorption spectrum and suggested a longer lifetime for NF₃ of 585 years ($\pm 20\%$).

2446

2447 Sulphur hexafluoride (SF₆)

Previous studies of the RE for sulphur hexafluoride are in the range $0.49 - 0.68 \text{ W m}^{-2} \text{ ppb}^{-1}$ (mean: 0.56 W m⁻² ppb⁻¹) [*Jain et al.*, 2000; *Myhre and Stordal*, 1997; *Zhang et al.*, 2011a]. *Zhang et al.* [2011a] estimated a much higher RE than the other studies, and this was also the case for several of the HFCs calculated by *Zhang et al.* [2011b] (see discussion of HFC-125 in section 4.1.3). AR4 adopted a RE of 0.52 W m⁻² ppb⁻¹ from *Myhre and Stordal* [1997], while we calculate a 10% higher RE value of 0.57 W m⁻² ppb⁻¹ (range: 0.54 - 0.59 W m⁻² ppb⁻¹) using absorption cross-sections from the GEISA and HITRAN databases (Tables 12-13).

2455

2456 (Trifluoromethyl)sulfur pentafluoride (SF₅CF₃)

2457 Previous reports of RE of (trifluoromethyl)sulfur pentafluoride are in the range 0.57 - 0.59 W m⁻² ppb⁻¹ (mean: 0.58 W m⁻² ppb⁻¹) [Nielsen et al., 2002; Sihra et al., 2001; Sturges et al., 2458 2000], and AR4 adopted the RE of 0.57 W m⁻² ppb⁻¹ from Sturges et al. [2000]. We calculate 2459 a mean RE value of 0.59 W m⁻² ppb⁻¹ (range: 0.58 - 0.61 W m⁻² ppb⁻¹), consistent (within 5% 2460 difference) with the AR4, using absorption cross-sections from two sources [Nielsen et al., 2461 2002; Rinsland et al., 2003] (Tables 12-13). Both of these spectra include an absorption 2462 feature at 612.5 cm⁻¹ which was not included in the measurements of *Sturges et al.* [2000], 2463 and this explains the slightly higher RE calculated here. 2464

2465

2466 Sulphuryl fluoride (SO₂F₂)

Previous reports of RE of sulphuryl fluoride are in the range 0.20 - 0.22 W m⁻² ppb⁻¹ (mean: 0.21 W m⁻² ppb⁻¹) [*Andersen et al.*, 2009; *Papadimitriou et al.*, 2008b]. We calculate a RE value of 0.20 W m⁻² ppb⁻¹ using the absorption spectrum from *Andersen et al.* [2009] (Tables 12-13) – in good agreement with the previous literature.

2471

2472 **PFC-14 (CF₄)**

Previous reports of the RE of PFC-14 are in the range 0.08 - 0.12 W m⁻² ppb⁻¹ (mean: 0.10 W 2473 m⁻² ppb⁻¹) [Bravo et al., 2010b; Hurley et al., 2005; Jain et al., 2000; Myhre and Stordal, 2474 1997; Roehl et al., 1995; Sihra et al., 2001; Zhang et al., 2011a]. Bravo et al. [2010b] report a 2475 relatively low RE value of 0.08 W m⁻² ppb⁻¹ (instantaneous RE) from their B3LYP/6-31G** 2476 2477 calculations, but it should be noted that CF₄ was part of the training set used to determine corrections to band positions. AR4 adopted a RE of 0.10 W m⁻² ppb⁻¹ from *Hurley et al.* 2478 [2005], and we calculate a similar mean RE of 0.09 W m^{-2} ppb⁻¹ (range: 0.09 - 0.10 W m^{-2} 2479 ppb⁻¹) when using absorption data from *Hurley et al.* [2005] (only the Ford data, and not the 2480 2481 M.S.F./R.A.L. data) and from the HITRAN database (Tables 12-13). Interestingly, as PFC-14 has a very strong and narrow absorption band centered near 1280 cm⁻¹, which is close to the 2482 edge of the atmospheric window region, the spectral resolution is more important for PFC-14 2483 than for other compounds. When using a 10 cm^{-1} resolution instead of 1 cm^{-1} in our 2484 calculations, the RE of PFC-14 is underestimated by ~8%, as shown in Figure 6 and briefly 2485 2486 discussed in section 3.3.1. For PFC-14 we have carried out explicit simulations using the Oslo 2487 LBL model and derived a 10.5% increase to account for stratospheric temperature adjustment (see section 3.3.3 for details), and this value has been used (rather than the generic 10% 2488 increase) in the calculation of the RE value of 0.09 W m^{-2} ppb⁻¹. 2489

2490

2491 **PFC-116** (C₂F₆)

Previous reports of RE of PFC-116 are in the range 0.25 - 0.35 W m⁻² ppb⁻¹ (mean: 0.27 W m⁻² 2492 ² ppb⁻¹) [Bravo et al., 2010b; Highwood and Shine, 2000; Myhre and Stordal, 1997; Roehl et 2493 al., 1995; Sihra et al., 2001; Zhang et al., 2011a]. Bravo et al. [2010b] report a value for RE 2494 of 0.23 W m⁻² ppb⁻¹ (instantaneous RE) from their B3LYP/6-31G** calculations, but it should 2495 be noted that C_2F_6 was part the training set used to determine corrections to band positions. 2496 Papasavva et al. [1997] obtained an *ab initio* RE value of 0.33 W m⁻² ppb⁻¹ using the MP2 2497 with a wavenumber scaling factor of 0.9427. In AR4 a RE value of 0.26 W m⁻² ppb⁻¹ was 2498 used and is taken from *Highwood and Shine* [2000]. We calculate a mean RE value of 0.25 W 2499 m^{-2} ppb⁻¹ (range: 0.24 - 0.26 W m⁻² ppb⁻¹), which is in good agreement with AR4, and we 2500 2501 have used absorption cross-sections from three sources [Bravo et al., 2010b; Sihra et al., 2502 2001; Zou et al., 2004] (Tables 12-13). It should be noted here that as both Bravo et al. 2503 [2010b] and Highwood and Shine [2000] present absorption data from M.S.F./R.A.L., we 2504 here choose the most recent spectrum measurement from Bravo et al. [2010b]. Also note that 2505 the *Zou et al.* [2004] spectrum does not include the absorption band located at 715 cm⁻¹ but 2506 this had negligible impact on the RE, thus we keep this spectrum in our calculation.

2507

2508 **PFC-c216** (c-C₃F₆)

Assessments since *WMO* [1999] have used a RE for PFC-c216 of 0.42 W m⁻² ppb⁻¹ which is reported to have been taken from *Papasavva et al.* [1997]. However, *Papasavva et al.* [1997] did not report a RE for this compound and so the origin of the value used in AR4 is unclear. The only estimate of the RE for c-C₃F₆ that we are aware of is from a calculation (B3LYP/6-31G**), which gives an instantaneous RE of 0.21 W m⁻² ppb⁻¹ [*Bravo et al.*, 2010b]. An updated RE (assuming a 10% increase to account for stratospheric temperature adjustment) and GWP values for PFC-c216 are given in Table 13.

2516

2517 **PFC-218** (C₃F₈)

Previous reports of RE of PFC-218 are in the range 0.26 - 0.28 W m⁻² ppb⁻¹ (mean: 0.27 W m⁻² 2518 ² ppb⁻¹) [*Bravo et al.*, 2010b; *Roehl et al.*, 1995; *Sihra et al.*, 2001]. *Bravo et al.* [2010b] also 2519 report an instantaneous RE value of 0.27 W m⁻² ppb⁻¹ from their B3LYP/6-31G** 2520 calculations - consistent with their instantaneous RE derived from experimental cross-2521 sections. AR4 reports a RE of 0.26 W m⁻² ppb⁻¹ which is taken from *Roehl et al.* [1995]. We 2522 calculate a slightly higher mean RE value of 0.28 W m⁻² ppb⁻¹ (range: 0.27 - 0.28 W m⁻² ppb⁻ 2523 ¹) using experimental absorption cross-sections from two sources [*Bravo et al.*, 2010b; *Sihra* 2524 2525 et al., 2001] (Tables 12-13). The higher RE calculated here can be explained by the much 2526 lower integrated absorption cross-section in the PFC-218 spectrum of Roehl et al. [1995] 2527 compared to other studies (see Table 12).

2528

2529 **PFC-318 (c-C₄F₈)**

Previous reports of RE of PFC-318 based on experimentally measured absorption spectra are in the range $0.31 - 0.32 \text{ W m}^{-2} \text{ ppb}^{-1}$ (mean: $0.31 \text{ W m}^{-2} \text{ ppb}^{-1}$) [*Highwood and Shine*, 2000; *Sihra et al.*, 2001; *Vasekova et al.*, 2006] while *Bravo et al.* [2010b] report a value for RE of $0.30 \text{ W m}^{-2} \text{ ppb}^{-1}$ from their B3LYP/6-31G** calculations, in good agreement with the values derived from the experimentally measured spectra. AR4 reports a RE of $0.32 \text{ W m}^{-2} \text{ ppb}^{-1}$ taken from *Highwood and Shine* [2000]. We have used the absorption spectrum from the same study and our calculations give a RE value of $0.32 \text{ W m}^{-2} \text{ ppb}^{-1}$ which is in agreement with AR4 (Tables 12-13).

2538

2539 **PFC-31-10** (C₄F₁₀)

2540 Previous estimates of the RE for PFC-31-10 based on experimentally measured absorption spectra are in the range 0.33 - 0.37 W m⁻² ppb⁻¹ (mean: 0.36 W m⁻² ppb⁻¹) [*Bravo et al.*, 2541 2010b; Roehl et al., 1995; Sihra et al., 2001]. Bravo et al. [2010b] also report an 2542 instantaneous RE of 0.34 W m⁻² ppb⁻¹ from their B3LYP/6-31G** calculations - consistent 2543 with their instantaneous RE derived from experimental cross-sections. AR4 report a RE of 2544 0.33 W m⁻² ppb⁻¹ which is taken from *Roehl et al.* [1995]. We calculate a higher RE value of 2545 0.36 W m⁻² ppb⁻¹ when using the experimental absorption cross-section from *Bravo et al.* 2546 [2010b] (Tables 12-13). As for PFC-218, the higher RE calculated here can be explained by 2547 the lower integrated absorption cross-section in Roehl et al. [1995] compared to Bravo et al. 2548 [2010b]. Updated values of recommended RE and GWP for PFC-31-10 are given in Table 13. 2549

2550

2551 Perfluorocyclopentene (c-C₅F₈)

Previous reports of RE of perfluorocyclopentene are in the range 0.22 - 0.32 W m⁻² ppb⁻¹ 2552 (mean: 0.27 W m⁻² ppb⁻¹) [Bravo et al., 2010b; Vasekova et al., 2006]. Part of the reason for 2553 the large difference between these two studies is that Vasekova et al. [2006] applied a factor 2554 2555 of 0.8 to account for non-homogeneous vertical profile, while *Bravo et al.* [2010b] assumed a 2556 constant vertical profile. No new calculations have been carried out here for this compound and to provide recommended RE we therefore use the average of the instantaneous REs 2557 reported in the literature $(0.30 \text{ W m}^{-2} \text{ ppb}^{-1})$ and account for stratospheric temperature 2558 adjustment as well as non-homogeneous mixing (see sections 3.3.2 and 3.3.4) and end up with 2559 a RE value of 0.08 W m⁻² ppb⁻¹. The only lifetime reported in the literature for this compound 2560 2561 is 1.0 year from Vasekova et al. [2006] who refer to a non-traceable source. Considering that *Cometto et al.* [2010] estimated a lifetime of only 31 days for CF₃CF=CFCF₃, we think that 2562 2563 the lifetime from Vasekova et al. [2006] may be too long and instead use a value of 31 days when applying the lifetime correction and calculating the GWP value. 2564

2565

2566 **PFC-41-12** (*n*-C₅F₁₂)

Previous reports of RE of PFC-41-12 are in the range 0.40 - 0.41 W m⁻² ppb⁻¹ (mean: 0.41 W 2567 m⁻² ppb⁻¹) [Bravo et al., 2010b; Roehl et al., 1995]. Bravo et al. [2010b] also report an 2568 instantaneous RE of 0.40 W m⁻² ppb⁻¹ from their B3LYP/6-31G** calculations – in agreement 2569 with their instantaneous RE estimate based on experimental absorption cross-sections (it 2570 2571 should be noted that C₅F₁₂ was part the training set used to determine corrections to band positions). AR4 has used a value of 0.41 W m⁻² ppb⁻¹ which is taken from *Roehl et al.* [1995], 2572 2573 and we calculate the exact same RE value when using the experimental absorption cross-2574 section from Bravo et al. [2010b] (Tables 12-13).

2575

2576 **PFC-51-14** (*n*-C₆F₁₄)

Previous reports of RE of PFC-51-14 are in the range 0.43 - 0.49 W m⁻² ppb⁻¹ (mean: 0.46 W 2577 m⁻² ppb⁻¹) [Bravo et al., 2010b; Roehl et al., 1995]. Bravo et al. [2010b] also report an 2578 instantaneous RE of 0.42 W m⁻² ppb⁻¹ from their B3LYP/6-31G** calculations, but it should 2579 2580 be noted that C₆F₁₄ was part of the training set used to determine corrections to band positions. AR4 report a RE of 0.49 W m⁻² ppb⁻¹ which is taken from *Roehl et al.* [1995]. We 2581 calculate a RE value of 0.44 W m⁻² ppb⁻¹ when using the experimental absorption cross-2582 2583 section from Bravo et al. [2010b] (Tables 12-13). The lower RE value calculated here is presumably due to the lower integrated absorption cross-section in Bravo et al. [2010b] than 2584 in Roehl et al. [1995] (Table 12). 2585

2586

2587 **PFC-61-16** (*n*-C₇F₁₆)

Ivy et al. [2012] calculated the RE of PFC-61-16 using experimental absorption data and derived a value of 0.48 W m⁻² ppb⁻¹. *Bravo et al.* [2010b] reported a value of 0.45 W m⁻² ppb⁻¹ using absorption data from B3LYP/6-31G** calculations, in reasonable agreement with the result obtained using experimental absorption data. We have used the absorption spectrum from *Ivy et al.* [2012] and calculated a RE value of 0.50 W m⁻² ppb⁻¹ (Tables 12-13).

2593

2594 **PFC-71-18** (C₈F₁₈)

Previous experimental results for RE of PFC-71-18 are in the range 0.50 - 0.57 W m⁻² ppb⁻¹ 2595 (mean: 0.53 W m⁻² ppb⁻¹) [*Bravo et al.*, 2010b; *Ivy et al.*, 2012]. We calculate a mean RE 2596 value of 0.55 W m⁻² ppb⁻¹ (range: 0.51 - 0.59 W m⁻² ppb⁻¹) when using absorption cross-2597 sections from both of these studies (Tables 12-13). The large range in our calculations is 2598 2599 caused by the large difference in the integrated absorption cross-sections of Bravo et al. [2010b] and Ivy et al. [2012] (Table 12). The lifetime of 3,000 years is taken from Bravo et al. 2600 [2010b], who also report a value for RE of 0.50 W m⁻² ppb⁻¹ from their B3LYP/6-31G** 2601 calculations, but it should be noted that PFC-71-18 was part of the training set used to 2602 2603 determine corrections to band positions.

2604

2605 **Perfluorodecalin** (mixed C₁₀F₁₈, Z-C₁₀F₁₈, *E*-C₁₀F₁₈)

The RE of perfluorodecalin has been reported to be 0.56 W m^{-2} ppb⁻¹ [*Shine et al.*, 2005b] and 2606 this value was adopted by AR4. We calculate a RE value of 0.55 W m⁻² ppb⁻¹ using the 2607 absorption cross-section from Shine et al. [2005b] (Tables 12-13), which was derived 2608 experimentally in the wavenumber range $600 - 1500 \text{ cm}^{-1}$ while the absorption bands were 2609 calculated in the lower wavenumber range $0 - 600 \text{ cm}^{-1}$. Our calculations for the isomers Z-2610 $C_{10}F_{18}$ and $E-C_{10}F_{18}$ yield REs (in the wavenumber range 600 - 1500 cm⁻¹) of 0.56 and 0.48 2611 W m⁻² ppb⁻¹, respectively. Bravo et al. [2010b] report instantaneous RE values of 0.58, 0.60 2612 and 0.56 W m⁻² ppb⁻¹ for $C_{10}F_{18}$ (mixed), Z- $C_{10}F_{18}$, E- $C_{10}F_{18}$, respectively, from their 2613 B3LYP/6-31G** calculations. 2614

2615

2616 **PFC-1114** (**CF**₂=**CF**₂)

Previous results for RE of PFC-1114 are in the range $0.01 - 0.11 \text{ W m}^{-2} \text{ ppb}^{-1}$ (mean: 0.06 W m⁻² ppb⁻¹) [*Acerboni et al.*, 2001; *Drage et al.*, 2006]. (*Acerboni et al.* [2001] used vertical profiles from a CTM distribution while *Drage et al.* [2006] assumed a constant profile.) Due to the short lifetime of 1.1 days, we calculate a RE value which rounds to 0.00 W m⁻² ppb⁻¹ when using the absorption cross-section from *Acerboni et al.* [2001] (Tables 12-13) and the correction factor for non-uniform mixing discussed in section 3.3.4.

2623

2624 **PFC-1216** (**CF**₃**CF**=**CF**₂)

2625 Only one study has estimated RE due to PFC-1216, with a value 0.04 W m⁻² ppb⁻¹ [*Acerboni* 2626 *et al.*, 2001] (vertical profiles from a CTM distribution were used). We have used their 2627 spectrum and calculated a RE value of 0.01 W m⁻² ppb⁻¹ when accounting for the non-2628 homogeneous vertical profile (Tables 12-13).

2629

2630 **Perfluorobuta-1,3-diene** (CF₂=CFCF=CF₂)

Previous reports of RE of Perfluorobuta-1,3-diene are in the range $0.01 - 0.20 \text{ W m}^{-2} \text{ ppb}^{-1}$ (mean: $0.11 \text{ W m}^{-2} \text{ ppb}^{-1}$) [*Acerboni et al.*, 2001; *Bravo et al.*, 2010b]. (*Acerboni et al.* [2001] used vertical profiles from a CTM distribution while *Bravo et al.* [2010b] assumed a constant profile.) We calculate a RE value which rounds to $0.00 \text{ W m}^{-2} \text{ ppb}^{-1}$ when using the absorption cross-section from *Acerboni et al.* [2001] (Tables 12-13).

2636

2637 **Perfluorobut-1-ene** (CF₃CF₂CF=CF₂)

2638 Only one study has estimated RE due to perfluorobut-1-ene, with a value 0.29 W m⁻² ppb⁻¹ 2639 *Young et al.* [2009a]. We calculate a RE value of 0.02 W m⁻² ppb⁻¹ when using their 2640 absorption cross-section, and account for stratospheric temperature adjustment and non-2641 homogeneous distribution. A lifetime of 6 days has been used in the RE and GWP calculation 2642 for this compound, assuming that its lifetime is comparable to the lifetime of PFC-1216.

2643

2644 **Perfluorobut-2-ene** (CF₃CF=CFCF₃)

Previous reports of RE of perfluorobut-2-ene are in the range 0.30 - 0.32 W m⁻² ppb⁻¹ (mean: 0.31 W m⁻² ppb⁻¹) [*Cometto et al.*, 2010; *Young et al.*, 2009a]. We calculate a RE value of 0.07 W m⁻² ppb⁻¹ when using the absorption spectra and lifetime estimate (31 days) from *Cometto et al.* [2010], and accounting for stratospheric temperature adjustment and nonhomogeneous distribution.

2650

2651 Other PFCs

In the sections above, recommended values of RE have been presented for the range of fully fluorinated compounds considered in AR4, along with a small number of others, where 2654 experimental data are available. In addition, *Bravo et al.* [2010b] report estimates of RE for a
2655 range of other PFCs, based on theoretical calculations.

2656

2657 4.1.7 Halogenated Alcohols and Ethers

This is a very broad range of compounds with lifetimes stretching from days to centuries. The generally complex structure, compared to other compounds considered here, leads to a rich infrared absorption spectrum – Figure 17 shows the spectrum of isoflurane (CHF₂OCHClCF) a molecule used as an inhalation anesthetic, which has absorption bands stretching across much of the infrared.

2663 Previously published absorption cross-sections are listed in Table 14, while updated atmospheric lifetimes, radiative efficiencies, and 100-year GWP values for halogenated 2664 2665 alcohols and ethers are presented in Table 15 and discussed below. In contrast to sections 4.1.1 - 4.1.6, not all compounds have their own individual piece of text in this section. For the 2666 purpose of presentation quality and brevity, some compounds are grouped together where we 2667 2668 found it appropriate. However, all the information about previously published estimates (both based on experimental and *ab initio* absorption spectra) and results from our calculations can 2669 2670 be found in Tables 14-15, and in Table S7 in the supplementary material. With the exception of PFPMIE, which is lost by photolysis in the upper atmosphere [Young et al., 2006], the S-2671 2672 shaped fit from section 3.3.4 (Equation (2) and dark blue curve in Figure 9) has been used to account for a non-uniform vertical profile and geographic distribution for all compounds 2673 2674 presented in this subsection.

2675 In what follows, we focus particularly on the experimental studies. There have been *ab* initio studies from three groups [Blowers et al., 2007; 2008b; Bravo et al., 2011a; Good et al., 2676 2677 1998]. We can make the following general observations about these studies. The work from the group of Blowers tends to calculate REs that are significantly higher than those obtained 2678 2679 from experimentally determined values. Differences are around 25%, but can be as high as 40%. This group does not adjust for atmospheric lifetimes, so the differences can appear 2680 2681 greater. The calculations from Bravo et al. [2011a] tend to agree with experimental values within about 10-15%, although the more sophisticated lifetime adjustment applied here can 2682 make the differences appear larger. However, REs calculated for the HG' HFPEs are some 2683 35% higher than experimental values, although it should be noted that only one group has 2684

studied these compounds experimentally [*Stevenson et al.*, 2004]. *Good et al.* [1998] examined only three compounds using a narrow band model; they obtain values that are somewhat higher than those using experimentally determined cross-sections. In the text below, we do not discuss the *ab initio* calculations except where they provide the only RE values, or are of special note. Whenever RE values based on *ab initio* calculations are presented, this has been clearly marked in the text.

2691 A large number of the compounds in this section were examined by Imasu et al. 2692 [1995], who reported both laboratory spectroscopy measurements and REs, calculated for a 2693 clear-sky mid-latitude atmosphere. In WMO [1999] (which became a source for REs used in 2694 many subsequent IPCC and WMO Ozone assessments), these were approximately converted to global-mean all-sky adjusted RE by taking their RE relative to Imasu et al's [1995] own 2695 CFC-11 calculation and then multiplying by the CFC-11 RE (0.25 W m⁻² ppb⁻¹) used in WMO 2696 [1999] (see footnote i of Table 10-6 of WMO [1999]). Henceforth in this section, we refer to 2697 these forcings as "Imasu et al. [1995] as modified by WMO [1999]". When referring to the 2698 2699 Imasu et al. [1995] REs we renormalize the WMO [1999] forcings to account for our recommended 4% increase in the CFC-11 RE (see section 4.1.1). 2700

2701

2702 HFE-125 (CHF₂OCF₃)

2703 Previous reports of RE due to HFE-125 are in the range $0.41 - 0.44 \text{ W m}^{-2} \text{ ppb}^{-1}$ (mean: $0.42 \text{ W m}^{-2} \text{ ppb}^{-1}$) [*Christidis et al.*, 1997; *Heathfield et al.*, 1998; *Sihra et al.*, 2001]. IPCC AR4 2705 uses a RE of $0.44 \text{ W m}^{-2} \text{ ppb}^{-1}$ taken from *Christidis et al.* [1997], *Good et al.* [1998] and 2706 *Heathfield et al.* [1998] (the latter two after rescaling as reported in *WMO* [1999]). We have 2707 used the absorption cross-sections from *Sihra et al.* [2001] and calculated a RE of 0.41 W m⁻² 2708 ppb⁻¹ – 8% lower than that in AR4.

2709

2710 HFE-134 (HG-00) (CHF₂OCHF₂)

2711 Previous reports of RE of HFE-134 (HG-00) are in the range $0.40 - 0.44 \text{ W m}^{-2} \text{ ppb}^{-1}$ (mean: 2712 $0.43 \text{ W m}^{-2} \text{ ppb}^{-1}$) [*Andersen et al.*, 2010a; *Heathfield et al.*, 1998; *Imasu et al.*, 1995; *Myhre* 2713 *et al.*, 1999]. IPCC AR4 used a RE value of $0.45 \text{ W m}^{-2} \text{ ppb}^{-1}$ which is taken from *Good et al.* 2714 [1998] and *Heathfield et al.* [1998] after rescaling in *WMO* [1999]. Here we have used the 2715 absorption cross-section from *Imasu et al.* [1995] and calculated a RE value of 0.44 W m^{-2} 2716 ppb⁻¹, which is in good agreement with AR4. Due to an update in the lifetime for this 2717 compound (24.4 years in *WMO* [2011] compared to 26 years in AR4), and a higher AGWP_{CO2} 2718 value, the GWP(100) value is significantly lower than that in AR4 (see Table 15).

2719

2720 HFE-143a (CH₃OCF₃)

2721 Previous reports of RE of HFE-143a are in the range $0.17 - 0.19 \text{ Wm}^{-2} \text{ ppb}^{-1}$ (mean: 0.18 W 2722 $\text{m}^{-2} \text{ ppb}^{-1}$) [*Christensen et al.*, 1999; *Sihra et al.*, 2001]. IPCC AR4 reports a RE of 0.27 W m⁻ 2723 $^2 \text{ ppb}^{-1}$ which is taken from the *ab initio* study of *Good et al.* [1998] after rescaling assuming 2724 CFC-11 RE = 0.25 W m⁻² ppb⁻¹ in *WMO* [1999]. We calculate a RE value of 0.18 W m⁻² ppb⁻¹ 2725 using absorption cross-section from *Sihra et al.* [2001]. Our estimate is much lower (34% 2726 lower) than the AR4 value, which is based on an *ab initio* study, but in good agreement with 2727 experimental studies.

2728

2729 HFE-227ea (CF₃CHFOCF₃)

2730 Previous reports of RE of HFE-227ea are in the range 0.31 - 0.42 W m⁻² ppb⁻¹ (mean: 0.37 W m⁻² ppb⁻¹) [*Imasu et al.*, 1995; *Jain et al.*, 2001; *Oyaro et al.*, 2005; *Takahashi et al.*, 2002]. 2732 IPCC AR4 reports a RE of 0.40 W m⁻² ppb⁻¹ which is taken from *Imasu et al.* [1995] as 2733 modified by *WMO* [1999]. We calculate a RE value of 0.44 W m⁻² ppb⁻¹ both when using 2734 absorption cross-sections from *Oyaro et al.* [2005] and *Imasu et al.* [1995]. Our estimate is 2735 10% higher than in AR4.

2736

2737 HCFE-235ca2 (enflurane) (CHF₂OCF₂CHFCl)

2738 Previous studies of RE due to HCFE-235ca2 (enflurane) are in the range 0.42 - 0.45 W m⁻² 2739 ppb⁻¹ (mean: 0.43 W m⁻² ppb⁻¹) [*Andersen et al.*, 2012b; *Dalmasso et al.*, 2006]. We have 2740 used the absorption cross-sections from these two studies and calculated a mean RE value of 2741 0.41 W m⁻² ppb⁻¹ (range: 0.39 - 0.42 W m⁻² ppb⁻¹).

2742

2743 HCFE-235da2 (isoflurane) (CHF₂OCHClCF₃)

Previous reports of RE due to HCFE-235da2 (isoflurane) are in the range 0.37 - 0.48 W m⁻²
ppb⁻¹ (mean: 0.44 W m⁻² ppb⁻¹) [*Andersen et al.*, 2010b; *Christidis et al.*, 1997; *Ryan and*

- Nielsen, 2010; Sihra et al., 2001]. IPCC AR4 accounted for stratospheric decay and reports a
 RE of 0.38 W m⁻² ppb⁻¹ which is taken from *Christidis et al.* [1997]. We calculate a RE value
 of 0.42 W m⁻² ppb⁻¹ both when using absorption cross-sections from *Andersen et al.* [2010c]
 and from *Ryan and Nielsen* [2010]. Our estimate is about 10% higher than in AR4.
- 2750

2751 HFEs studied theoretically by *Blowers et al.* [2007] and *Blowers et al.* [2008a]

For some HFE compounds, no RE estimates based on experimental absorption cross-sections exist, and the *ab initio* studies of *Blowers et al.* [2007] and *Blowers et al.* [2008a] provide the

- 2754 only RE estimates of these HFEs. These compounds are:
- 2755 HFE-236ca (CHF₂OCF₂CHF₂)
- 2756 Fluoro(methoxy)methane (CH₃OCH₂F)
- 2757 Difluoro(methoxy)methane (CH₃OCHF₂)
- 2758 Fluoro(fluoromethoxy)methane (CH₂FOCH₂F)
- 2759 Difluoro(fluoromethoxy)methane (CH₂FOCHF₂)
- 2760 Trifluoro(fluoromethoxy)methane (CH₂FOCF₃)
- 2761 Trifluoro(trifluoromethoxy)methane (CF₃OCF₃)
- 2762

2763 Note that Blowers et al. [2007] estimated REs for some hydrofluoroethers not listed in 2764 this section. Blowers et al. [2007] and Blowers et al. [2008a] calculated instantaneous REs by 2765 using the theoretical procedure described by Papasavva et al. [1997] combined with the Pinnock et al. [1995] method (their RE estimates are listed in Table S7 in the supplementary 2766 2767 material). Since absorption spectra were unavailable for the seven compounds listed above, no new calculations have been carried out here. Thus, we use the REs from *Blowers et al.* [2007] 2768 2769 and Blowers et al. [2008a], accounting for stratospheric temperature adjustment and lifetime 2770 correction (see sections 3.3.2 and 3.3.4, respectively), and present new best estimate RE and 2771 GWP values in Table 15. The lifetime of HFE-236ca is from WMO [2011], the lifetime of fluoro(methoxy)methane is from Urata et al. [2003], while a lifetime estimate could not be 2772 2773 found for trifluoro(trifluoromethoxy)methane and thus we only present RE assuming a 2774 uniform distribution for this compound. The lifetimes of the remaining compounds are taken 2775 from Blowers et al. [2008a]. The resulting REs are 0.56, 0.07, 0.17, 0.19, 0.30, 0.33 and 0.53 W m⁻² ppb⁻¹ for HFE-236ca, fluoro(methoxy)methane, difluoro(methoxy)methane, 2776 2777 fluoro(fluoromethoxy)methane, difluoro(fluoromethoxy)methane, 2778 trifluoro(fluoromethoxy)methane and trifluoro(trifluoromethoxy)methane, respectively. 2779 However, it should be stressed that these REs are based on ab initio studies, and the uncertainties are therefore larger than for REs based on experimental absorption spectra, as 2780 2781 discussed in section 3.6.1.

2782

2783 HFE-236ea2 (desflurane) (CHF₂OCHFCF₃)

Previous studies of RE of HFE-236ea2 (desflurane) are in the range 0.45 - 0.47 W m⁻² ppb⁻¹ 2784 (mean: 0.46 W m⁻² ppb⁻¹) [Andersen et al., 2010b; Imasu et al., 1995; Oyaro et al., 2005]. 2785 IPCC AR4 used a RE of 0.44 W m⁻² ppb⁻¹ which is taken from *Imasu et al.* [1995] as 2786 modified by WMO [1999]. We calculate a mean RE value of 0.45 W m⁻² ppb⁻¹ (range: 0.45 -2787 0.46 W m⁻² ppb⁻¹) using absorption cross-sections from three sources [Andersen et al., 2010c; 2788 Imasu et al., 1995; Oyaro et al., 2005]. Our RE estimate is in good agreement with AR4, but 2789 due to an updated lifetime estimate (10.8 years in WMO [2011] compared to 5.8 years in 2790 AR4), our GWP(100) value is much higher, despite the higher $AGWP_{CO2}$ value used here. 2791

2792

2793 HFEs studied by Imasu et al. [1995]

For a number of HFE compounds, *Imasu et al.* [1995] is the only study providing REs based on experimental absorption cross-sections:

- 2796 HFE-236fa (CF₃CH₂OCF₃)
- 2797 HFE-245cb2 ($CF_3CF_2OCH_3$)
- 2798 HFE-245fa1 (CHF₂CH₂OCF₃)
- 2799 HFE-329mcc2 (CHF₂CF₂OCF₂CF₃)
- 2800 HFE-338mmz1 ((CF₃)₂CHOCHF₂)
- 2801 HFE-338mcf2 (CF₃CH₂OCF₂CF₃)
- 2802 HFE-347mcf2 ($CHF_2CH_2OCF_2CF_3$)

- 2803 HFE-347mmy1 ((CF₃)₂CFOCH₃)
- 2804 HFE-356mec3 (CH₃OCF₂CHFCF₃)
- 2805 HFE-356pcf2 (CHF₂CH₂OCF₂CHF₂)
- 2806 HFE-356pcf3 ($CHF_2OCH_2CF_2CHF_2$)
- 2807 HFE-356pcc3 (CH₃OCF₂CF₂CHF₂)
- 2808 1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)-2-propanol ((CF₃)₃COH)
- 2809 2,2,3,3,4,4,5,5-Octafluorocyclopentanol (-(CF₂)₄CH(OH)-)
- 2810 1,1,1,3,3,3-Hexafluoropropan-2-ol ((CF₃)₂CHOH)
- 2811

2812 Many of the compounds listed above have also been studied using *ab initio* methods in 2813 Blowers et al. [2007] and Bravo et al. [2011a] (see Table 14). As previously mentioned, the 2814 uncertainties are larger for theoretical studies and we choose to focus on the experimental 2815 studies when these are available. With the exception of 1,1,1,3,3,3-hexafluoro-2-2816 (trifluoromethyl)-2-propanol, for which no lifetime estimate is available in the literature, all 2817 the 15 compounds listed above, and their REs, have been reported in AR4 based on Imasu et al. [1995] as modified by WMO [1999]. We have used the Imasu et al. [1995] cross-sections 2818 2819 to calculate new estimates of RE, taking into account both stratospheric temperature 2820 adjustment (by increasing the instantaneous RE by 10% as described in section 3.3.2) and 2821 fractional correction (by using the method described in section 3.3.4). Table 15 presents the 2822 results of our calculations and highlights the best estimate RE and GWP(100) values for each 2823 compound. For 5 of the 14 compounds which are listed above and included in AR4, our 2824 calculation of RE differed by more than 5% compared to AR4. The differences in RE between 2825 our calculation and AR4 were larger for compounds which were not well-mixed in the 2826 atmosphere (with lifetimes typically less than a few years), because lifetime corrections were not considered in AR4 (recall from the introduction to section 4.1.7 that the Imasu et al. 2827 [1995] results were scaled to a CFC-11 value of 0.25 W m⁻² ppb⁻¹ as explained in WMO 2828 2829 [1999]). In many of the cases the REs in our calculation were in good agreement with AR4, 2830 but the updated lifetimes, which we take from WMO [2011], led to a change in the GWP(100) 2831 compared to AR4 (note also that the updated AGWP_{CO2} lead to ~5% lower GWP(100) for all compounds compared to AR4). 2832

2833

2834 HFE-245fa2 (CHF₂OCH₂CF₃)

Previous calculations of RE of HFE-245fa2 are in the range 0.33 - 0.39 W m⁻² ppb⁻¹ (mean: 2835 0.37 W m⁻² ppb⁻¹) [Christidis et al., 1997; Imasu et al., 1995; Oyaro et al., 2005; Sihra et al., 2836 2001]. IPCC AR4 reports a RE of 0.31 W m⁻² ppb⁻¹ which is taken from *Christidis et al.* 2837 [1997], but modified to approximately account for stratospheric decay as described in WMO 2838 [1999]. We have used absorption cross-sections from *Oyaro et al.* [2005], *Sihra et al.* [2001] 2839 and *Imasu et al.* [1995] and calculated a RE value of 0.36 W m⁻² ppb⁻¹ for all three absorption 2840 spectra. The reason for the 16% higher RE value calculated here compared to AR4 is related 2841 2842 to the different factors to account for the non-uniform distribution in the atmosphere. AR4 used a crude factor of 0.8 from *Freckleton et al.* [1998] while our method (see section 3.3.4) 2843 yields a factor of 0.93 for a lifetime of 5.5 years. 2844

2845

2846 **2,2,3,3,3-Pentafluoropropan-1-ol** (CF₃CF₂CH₂OH)

2847 Previous studies of RE due to 2,2,3,3,3-pentafluoropropan-1-ol are in the range 0.25 - 0.26 W $m^{-2} ppb^{-1}$ (mean: 0.25 W $m^{-2} ppb^{-1}$) [Antiñolo et al., 2012b; Imasu et al., 1995; Sellevåg et al., 2848 2007]. IPCC AR4 reports a RE of 0.24 W m⁻² ppb⁻¹ which is taken from *Imasu et al.* [1995] as 2849 modified by WMO [1999]. We calculate a mean RE value of 0.14 W m⁻² ppb⁻¹ (range: 0.13 -2850 0.15 W m⁻² ppb⁻¹) using absorption cross-sections from three sources [Antiñolo et al., 2012b; 2851 Imasu et al., 1995; Sellevåg et al., 2007]. Our estimate is much lower (42% different) than 2852 2853 that in AR4. The short lifetime of 0.3 years [Antiñolo et al., 2012b] for this compound leads 2854 to a strong effect of the fractional correction factor which has been applied to account for nonuniform mixing (vertical and horizontal). It should be noted here that the uncertainties 2855 2856 associated with this correction factor are very large on a percentage basis for such short-lived species (see Figure 9 and associated discussion in section 3.3.4), and we further note that our 2857 2858 calculated instantaneous RE (i.e., without applying corrections for stratospheric temperature 2859 adjustment and lifetime correction) is in good agreement with the published instantaneous RE 2860 estimates (Table 7 in supplementary material).

2861

2862 HFE-254cb1 (CH₃OCF₂CHF₂)

Previous calculations of RE of HFE-254cb1 are in the range $0.29 - 0.30 \text{ W m}^{-2} \text{ ppb}^{-1}$ (mean: 0.29 W m⁻² ppb⁻¹) [*Heathfield et al.*, 1998; *Imasu et al.*, 1995]. IPCC AR4 used a RE of 0.28 W m⁻² ppb⁻¹ which is taken from *Imasu et al.* [1995] as modified by *WMO* [1999]. We calculate an 8% lower RE value of 0.26 W m⁻² ppb⁻¹ using absorption cross-section from *Imasu et al.* [1995].

2868

2869 HFE-263fb1 (CF₃CH₂OCH₃)

Previous reports of RE of HFE-263fb2 are in the range 0.19 - 0.21 W m⁻² ppb⁻¹ (mean: 0.20 2870 W m⁻² ppb⁻¹) [Imasu et al., 1995; Osterstrom et al., 2012; Oyaro et al., 2005]. IPCC AR4 2871 gives a RE of 0.20 W m⁻² ppb⁻¹ which is taken from *Imasu et al.* [1995] as modified by *WMO* 2872 [1999]. Using absorption cross-sections from three studies [Imasu et al., 1995; Osterstrom et 2873 al., 2012; Oyaro et al., 2005] that give the same results we calculate a much lower (81%) 2874 mean RE value of 0.04 W m⁻² ppb⁻¹. The reason for the large differences between our estimate 2875 2876 and the AR4 is the lifetime correction factor of 0.18 (for a lifetime of 23 days [WMO, 2011]) 2877 which has been applied here to account for non-uniform distribution (vertical and horizontal). It should be noted here that the uncertainties associated with this correction factor are very 2878 2879 large on a percentage basis for such short-lived species (see Figure 9 and associated 2880 discussion in section 3.3.4). Our calculated RE is, however, in good agreement with the 2881 results from Imasu et al. [1995], and hence AR4, if we compare instantaneous RE (i.e., 2882 without applying corrections for stratospheric temperature adjustment and lifetime correction) (Table 7 in supplementary material). 2883

2884

2885 HFEs studied by Oyaro et al. [2005]

For the following HFE compounds, *Oyaro et al.* [2005] is the only study providing REs basedon experimental absorption cross-sections:

- 2888 HFE-263m1 (CF₃OCH₂CH₃)
- 2889 1,1,2-Trifluoro-2-(trifluoromethoxy)-ethane (CHF₂CHFOCF₃)
- $2890 \qquad 1-E thoxy-1, 1, 2, 3, 3, 3-hexa fluoropropane (CF_3CHFCF_2OCH_2CH_3)$
- $2891 \qquad 1, 1, 1, 2, 2, 3, 3 Heptafluoro-3 (1, 2, 2, 2 tetrafluoroethoxy) propane (CF_3 CF_2 CF_2 OCHFCF_3)$

2892

2893 Ab initio studies are available for these compounds [Blowers et al., 2007; Bravo et al., 2894 2011a] (Table 14), but we focus here on the experimental data from *Oyaro et al.* [2005]. They used the Pinnock et al. [1995] method to estimate instantaneous REs of 0.21, 0.35, 0.33 and 2895 0.56 W m⁻² ppb⁻¹ for HFE-263m1, 1,1,2-Trifluoro-2-(trifluoromethoxy)-ethane, 1-Ethoxy-2896 2897 1,1,2,3,3,3-hexafluoropropane, and1,1,1,2,2,3,3-Heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)-2898 propane, respectively. The corresponding RE estimates from our calculations (now taking 2899 into account stratospheric temperature adjustment and inhomogeneous distribution in the troposphere) are 0.13, 0.35, 0.33 and 0.58 W m⁻² ppb⁻¹, respectively, when using absorption 2900 cross-sections from Oyaro et al. [2005] and lifetime estimates of 0.4 [Bravo et al., 2011a], 2901 2902 9.8, 0.4 and 67.0 years [Oyaro et al., 2005], respectively. None of these compounds are 2903 included in AR4, thus we provide new best estimates of RE and GWP for all these 2904 compounds.

2905

2906 **3,3,3-Trifluoropropan-1-ol** (CF₃CH₂CH₂OH)

2907 Previous experimental studies of 3,3,3-trifluoropropan-1-ol have reported values for RE in the range 0.17 - 0.20 W m⁻² ppb⁻¹ (mean: 0.19 W m⁻² ppb⁻¹) [*Jimenez et al.*, 2010; *Sellevåg et al.*, 2908 2007]. We have used absorption cross-sections from *Jimenez et al.* [2010]. Sellevåg et al. 2909 [2007] and Waterland et al. [2005] and calculated the same RE of 0.02 W m⁻² ppb⁻¹ for all 2910 three spectra. Our calculated instantaneous REs of 0.21 W m⁻² ppb⁻¹ and 0.17 W m⁻² ppb⁻¹ 2911 using spectra from Jimenez et al. [2010] and Sellevåg et al. [2007], respectively, compare 2912 2913 well with the previously published REs (which did not account for stratospheric temperature 2914 adjustment and lifetime correction). The lifetime of 12.0 days is taken from Jimenez et al. 2915 [2010].

2916

2917 Sevoflurane, HFE-347mmz1 ((CF₃)₂CHOCH₂F)

Experimental studies have reported RE values for sevoflurane in the range 0.35 - 0.37 W m⁻² ppb⁻¹ (mean: 0.36 W m⁻² ppb⁻¹) [*Andersen et al.*, 2010c; *Ryan and Nielsen*, 2010]. We have used the absorption cross-sections from these two studies and calculated a RE value of 0.32W m⁻² ppb⁻¹ for both spectra. It should be noted here that *Andersen et al.* [2010c] and *Ryan and Nielsen* [2010] calculated the instantaneous RE using the *Pinnock et al.* [1995] method 2923 while we have accounted for stratospheric temperature adjustment and non-uniform 2924 distribution in the troposphere.

2925

2926 HFE-347mcc3 (HFE-7000) (CH₃OCF₂CF₂CF₃)

Previous experimental studies of HFE-347mcc3 (HFE-7000) have reported values for RE in the range 0.32 - 0.35 W m⁻² ppb⁻¹ (mean: 0.34 W m⁻² ppb⁻¹) [*Bravo et al.*, 2010a; *Imasu et al.*, 1995; *Ninomiya et al.*, 2000]. We have used the absorption cross-sections from all these three studies and calculated a mean RE value of 0.35 W m⁻² ppb⁻¹ (range: 0.33 - 0.36 W m⁻² ppb⁻¹). Our estimate is in reasonable agreement with the RE of 0.34 W m⁻² ppb⁻¹ in AR4 (which originated from *Imasu et al.* [1995] as modified by *WMO* [1999]).

2933

2934 HFE-347pcf2 (CHF₂CF₂OCH₂CF₃)

2935 One experimental study has reported a value of RE for this HFE-347pcf2 [Heathfield et al., 1998]. The original value (0.47 W m⁻² ppb⁻¹) was determined using the *Pinnock et al.* [1995] 2936 method. There is some confusion regarding the RE of this molecule. WMO [1999] (where it is 2937 referred to as HFE-347mfc2) use the Heathfield et al. [1998] value - this molecule then does 2938 not seem to appear in IPCC or WMO/UNEP ozone assessments tabulations until IPCC [2007] 2939 which recommends a value of 0.25 W m^{-2} ppb⁻¹ – this is perhaps a lifetime-corrected version 2940 of the earlier value, although no reference is given. We recommend instead, using the original 2941 Heathfield et al. [1998] value, applying our generic correction of a 10% increase to account 2942 2943 for stratospheric temperature adjustment and applying the lifetime correction (assuming a 2944 lifetime of 6 years) from section 3.3.4 of 0.93. This yields our recommended value of 0.48 W $m^{-2} ppbv^{-1}$. 2945

2946

2947 HFE-356mff2 (CF₃CH₂OCH₂CF₃)

Previous experimental studies of HFE-356mff2 have reported values for RE in the range 0.33 - 0.35 W m⁻² ppb⁻¹ (mean: 0.35 W m⁻² ppb⁻¹) [*Oyaro et al.*, 2004; *Sihra et al.*, 2001; *Wallington et al.*, 1998]. We calculate a mean RE value of 0.17 W m⁻² ppb⁻¹ (range: 0.17 -0.18 W m⁻² ppb⁻¹) using absorption cross-sections from two sources [*Oyaro et al.*, 2004; *Sihra et al.*, 2001]. The non-homogeneous mixing of this short-lived compound was not accounted for in the three previous studies; our estimate of RE is consistent with the published values if we assume uniform mixing.

2955

2956 HFE-356mmz1 ((CF₃)₂CHOCH₃)

2957 Previous experimental studies of HFE-356mmz1 have both reported values for RE of 0.31 W m⁻² ppb⁻¹ [*Imasu et al.*, 1995; Ovaro et al., 2004] (note that the *Imasu et al.* [1995] value is 2958 here scaled to our recommended CFC-11 RE of 0.26 W m⁻² ppb⁻¹). The Imasu et al. [1995] 2959 value (as modified by WMO [1999]) of 0.30 W m⁻² ppb⁻¹ was used by IPCC AR4. We have 2960 used the absorption cross-sections from Imasu et al. [1995] and Oyaro et al. [2004] and 2961 calculated a RE value of 0.15 W m⁻² ppb⁻¹ for both of these spectra. Our estimate is 50% 2962 lower than AR4, and this is almost entirely due to the factor applied here to account for non-2963 2964 homogeneous mixing for this short-lived species (lifetime of 97.1 days [Oyaro et al., 2004]). 2965 The best estimate RE and GWP values are shown in Table 15.

2966

2967 HFE-365mcf3 (CF₃CF₂CH₂OCH₃)

Previous experimental studies of HFE-365mcf3 have reported values for RE in the range 0.28 2968 - 0.33 W m⁻² ppb⁻¹ (mean: 0.30 W m⁻² ppb⁻¹) [Imasu et al., 1995; Oyaro et al., 2004; Thomsen 2969 et al., 2011] (note that the Imasu et al. [1995] value is here scaled to our recommended CFC-2970 11 RE of 0.26 W m⁻² ppb⁻¹). The Imasu et al. [1995] value (as modified by WMO [1999]) of 2971 0.27 W m⁻² ppb⁻¹ was used by IPCC AR4. In contrast to the published values we have 2972 accounted for stratospheric temperature adjustment and non-homogeneous mixing in the 2973 troposphere (assuming a lifetime of 19.3 days [Ovaro et al., 2004]), and calculated a RE value 2974 of 0.05 W m⁻² ppb⁻¹ when using absorption cross-sections from both Ovaro et al. [2004] and 2975 Imasu et al. [1995]. Our estimate is ~80% lower than that in AR4, but it should be noted here 2976 2977 that the uncertainties associated with the lifetime correction factors are very large on a percentage basis for such short-lived species (see Figure 9 and associated discussion in 2978 2979 section 3.3.4), and we further note that our calculated instantaneous RE is consistent with the 2980 published estimates.

2981

2982 HFEs studied theoretically by Bravo et al. [2011a]

- 2983 For a number of HFE compounds, no RE estimates based on experimental absorption cross-
- 2984 sections exist and the *ab initio* study of *Bravo et al.* [2011a] provides the only RE estimate of
- these HFEs. These compounds are:
- 2986 HFE-365mcf2 (CF₃CF₂OCH₂CH₃)
- 2987 HG-02 (HF₂C–(OCF₂CF₂)₂–OCF₂H)
- 2988 HG-03 (HF₂C–(OCF₂CF₂)₃–OCF₂H)
- 2989 HG-20 ($HF_2C-(OCF_2)_2-OCF_2H$)
- 2990 HG-21 (HF₂C–OCF₂CF₂OCF₂OCF₂O–CF₂H)
- 2991 HG-30 (HF₂C–(OCF₂)₃–OCF₂H)
- 2992 1-Ethoxy-1,1,2,2,3,3,3-heptafluoropropane (CF₃CF₂CF₂OCH₂CH₃)
- 2993 Fluoroxene (CF₃CH₂OCH=CH₂)
- 2994 1,1,2,2-Tetrafluoro-1-(fluoromethoxy)ethane (CH₂FOCF₂CF₂H)
- 2995 HG'-10 (CH₃OCF₂OCH₃)
- 2996 $HG'-20 (CH_3O(CF_2O)_2CH_3)$
- 2997 HG'-30 (CH₃O(CF₂O)₃CH₃)
- 2998

2999 For all of the compounds listed above we have used the theoretical absorption cross-3000 sections from Bravo et al. [2011a] to calculate estimates of RE, taking into account both 3001 stratospheric temperature adjustment (by increasing the instantaneous RE by 10% as 3002 described in section 3.3.2) and fractional correction (by using the method described in section 3.3.4). For three of these compounds (HG'-10, HG'-20, HG'-30), no lifetime estimates were 3003 3004 found in the literature, and hence the RE estimates for these compounds assumes a uniform 3005 vertical and horizontal distribution in the atmosphere. Lifetimes for the remaining nine 3006 compounds were taken from Bravo et al. [2011a]. The study of Bravo et al. [2011a] used the 3007 Pinnock et al. [1995] method to estimate instantaneous REs, and accounted for nonhomogeneous mixing by applying the exponential function from Sihra et al. [2001] (see 3008 3009 section 3.3.4) for compounds where lifetime estimates were known. The RE estimates of 3010 Bravo et al. [2011a] are listed in Table S7 in the supplementary material, while our results are 3011 presented in Table 15. In general, differences are small but reflect the use of an updated

- *Pinnock et al.* [1995] curve in this study, and that the stratospheric temperature adjustment was not taken into account in *Bravo et al.* [2011a]. None of the compounds listed above are included in AR4, thus we provide new best estimates of RE and GWP for all these compounds. It should, however, be kept in mind that RE estimates based on *ab initio* calculations are associated with larger uncertainties than estimates based on experimental cross-sections, as discussed in section 3.6.1 (see also Table 1).
- 3018

3019 HFE-374pc2 (CHF₂CF₂OCH₂CH₃)

Previous experimental studies of HFE-374pc2 have reported values for RE in the range 0.31 -3020 0.32 W m⁻² ppb⁻¹ (mean: 0.31 W m⁻² ppb⁻¹) [Heathfield et al., 1998; Imasu et al., 1995]. AR4 3021 uses a RE of 0.25 W m⁻² ppb⁻¹ taken from *Heathfield et al.* [1998], but modified in WMO 3022 [1999] to crudely account for non-homogeneous mixing by applying a factor of 0.8 based on 3023 *Freckleton et al.* [1998]. We calculate a RE value of 0.30 W m⁻² ppb⁻¹ using absorption cross-3024 sections from Imasu et al. [1995]. Due to the different methods used to account for non-3025 3026 homogeneous mixing, our estimate is 19% higher than in AR4. The lifetime of 5.0 years is 3027 taken from AR4.

3028

3029 **4,4,4-Trifluorobutan-1-ol** (CF₃(CH₂)₂CH₂OH)

Jimenez et al. [2010] used the *Pinnock et al.* [1995] method and report an instantaneous RE value for 4,4,4-trifluorobutan-1-ol of 0.11 W m⁻² ppb⁻¹. We have used their absorption crosssection and calculated the same instantaneous RE. When taking into account stratospheric temperature adjustment and non-homogeneous mixing in the troposphere (assuming a lifetime of 4.0 days [*Jimenez et al.*, 2010]), our calculation yield a RE value of 0.01 W m⁻² ppb⁻¹.

3035

3036 HFE-43-10pccc124 (H-Galden 1040x, HG-11) (CHF₂OCF₂OC₂F₄OCHF₂)

3037 Previous experimental studies of HFE-43-10pccc124 (H-Galden 1040x, HG-11) have 3038 reported values for RE in the range 0.99 - 1.37 W m⁻² ppb⁻¹ (mean: 1.12 W m⁻² ppb⁻¹) 3039 [*Christidis et al.*, 1997; *Myhre et al.*, 1999; *Sihra et al.*, 2001; *Wallington et al.*, 2009]. IPCC 3040 AR4 use a RE of 1.37 W m⁻² ppb⁻¹ taken from *Myhre et al.* [1999]. We have used the 3041 absorption cross-section from *Wallington et al.* [2009] and calculated a 26% lower RE value of 1.02 W m⁻² ppb⁻¹, which is the same as the estimate in *Wallington et al.* [2009]. It should be noted here that the spectrum from *Wallington et al.* [2009] supersedes previous Ford measurements of HG-11 [*Christidis et al.*, 1997; *Sihra et al.*, 2001] and that the cross-section from *Cavalli et al.* [1998], which has been used in *Myhre et al.* [1999], is an overestimate [*Wallington et al.*, 2009].

3047

3048 HFE-449s1 (HFE-7100) (C₄F₉OCH₃)

Previous studies of RE due to HFE-449s1 (HFE-7100) are in the range 0.31 - 0.37 W m⁻² ppb⁻¹ (mean: 0.34 W m⁻² ppb⁻¹) [*Bravo et al.*, 2010a; *Sihra et al.*, 2001; *Wallington et al.*, 1997]. IPCC AR4 report a RE of 0.31 W m⁻² ppb⁻¹ which is taken from *Wallington et al.* [1997] as modified by *WMO* [1999]. We estimate a 17% higher RE of 0.36 W m⁻² ppb⁻¹ using the absorption cross-sections from two sources [*Bravo et al.*, 2010a; *Sihra et al.*, 2001] and applying our lifetime correction. The main reason for the higher estimate is due to lower lifetime correction with a factor of 0.92 instead of 0.8 applied in *WMO* [1999].

3056

3057 HFEs studied by Sihra et al. [2001]

For the following HFE compounds, *Sihra et al.* [2001] is the only study providing REs based
on experimental absorption cross-sections:

3060 *n*-HFE-7100 (*n*-C₄F₉OCH₃)

3061 *i*-HFE-7100 (*i*-C₄F₉OCH₃)

3062 *i*-HFE-7200 (*i*-C₄F₉OC₂H₅)

3063

Ab initio studies are available for these compounds [Blowers et al., 2007; Bravo et al., 3064 2011a] (Table 14), but we focus here on the experimental data from Sihra et al. [2001]. They 3065 3066 assumed homogeneous distribution in the atmosphere and estimated REs of 0.47, 0.37 and 0.34 W m⁻² ppb⁻¹ for *n*-HFE-7100, *i*-HFE-7100 and *i*-HFE-7200, respectively. Our 3067 calculations are consistent with the Sihra et al. [2001] results if we make the same assumption 3068 and use their absorption cross-sections. When accounting for non-homogeneous vertical and 3069 3070 horizontal distribution, our calculations yield lower REs with values of 0.42, 0.35 and 0.24 W m^{-2} ppb⁻¹ for *n*-HFE-7100, *i*-HFE-7100 and *i*-HFE-7200, respectively. We have then assumed 3071

- that the lifetime of *n*-HFE-7100 and *i*-HFE-7100 are the same as for HFE-7100 (4.7 years [*WMO*, 2011]), and that *i*-HFE-7200 has the same lifetime as HFE-7200 (0.8 years [*WMO*, 2011]). None of these compounds are included in AR4, thus we provide new best estimates of RE and GWP for all these compounds.
- 3076

3077 HFE-569sf2 (HFE-7200) (C₄F₉OC₂H₅)

Previous studies of RE due to HFE-569sf2 (HFE-7200) are in the range $0.30 - 0.39 \text{ W m}^{-2}$ ppb⁻¹ (mean: $0.33 \text{ W m}^{-2} \text{ ppb}^{-1}$) [*Bravo et al.*, 2010a; *Christensen et al.*, 1998; *Sihra et al.*, 2001]. IPCC AR4 report a RE of $0.30 \text{ W m}^{-2} \text{ ppb}^{-1}$ which is taken from *Christensen et al.* [1998] as modified by *WMO* [1999]. We have used absorption cross-sections from two sources [*Bravo et al.*, 2010a; *Sihra et al.*, 2001] and calculated a mean RE value of 0.30 W m⁻² $^{2} \text{ ppb}^{-1}$ (range: 0.29 - 0.32 W m⁻² ppb⁻¹) – in agreement with AR4.

3084

3085 *n*-HFE-7200 (*n*-C₄F₉OC₂H₅)

3086 The only estimates of the RE of *n*-HFE-7200 are from the *ab initio* studies of *Bravo et al.* [2011a] and Blowers et al. [2007] who both used the Pinnock et al. [1995] method to 3087 calculate instantaneous REs of 0.47 and 0.55 W m⁻² ppb⁻¹, respectively. We have used the 3088 theoretical absorption spectrum from Bravo et al. [2011a] and calculated a similar 3089 instantaneous RE (0.45 W m⁻² ppb⁻¹). When accounting for stratospheric temperature 3090 adjustment and non-homogeneous tropospheric distribution, our RE estimate is 0.35 W m⁻² 3091 ppb⁻¹. We have then assumed that *n*-HFE-7200 has the same lifetime as HFE-7200 (0.8 years 3092 3093 [*WMO*, 2011]).

3094

3095 HFE-236ca12 (HG-10) (CHF₂OCF₂OCHF₂)

The RE of HFE-236ca12 (HG-10) has been estimated to be 0.66 W m⁻² ppb⁻¹ in *Myhre et al.* [1999], and this value was used in the AR4 report. We have used the absorption cross-section from the same study and calculated a RE value of 0.65 W m⁻² ppb⁻¹ – in good agreement with AR4. Due to an updated lifetime for this compound, from 12.1 years in AR4 to 25.0 years in *WMO* [2011], our calculated GWP(100) value is considerably higher than in AR4, despite the higher AGWP_{CO2} value used here. 3102

3103 HFE-338pcc13 (HG-01) (CHF₂OCF₂CF₂OCHF₂)

3104 *Myhre et al.* [1999] have estimated a RE due to HFE-338pcc13 (HG-01) of 0.87 W m⁻² ppb⁻¹,

which is the value adopted by AR4. We have used the *Myhre et al.* [1999] absorption cross-

3106 section and calculated a similar RE value of $0.86 \text{ W m}^{-2} \text{ ppb}^{-1}$. We use an updated lifetime of

3107 12.9 years [WMO, 2011], compared to 6.2 years in AR4, and this leads to a GWP(100) value

- 3108 which is about a factor 2 higher than in AR4.
- 3109

3110 **2-Ethoxy-3,3,4,4,5-pentafluorotetrahydro-2,5-bis[1,2,2,2-tetrafluoro-1-**

3111 (trifluoromethyl)ethyl]-furan (C₁₂H₅F₁₉O₂)

3112 Javadi et al. [2007] used the Pinnock et al. [1995] method to estimate an instantaneous RE 3113 due to 2-ethoxy-3,3,4,4,5-pentafluorotetrahydro-2,5-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-furan of 0.60 W m⁻² ppb⁻¹. Since no new calculations have been 3114 carried out here for this compound, we apply our generic correction of a 10% increase to 3115 account for stratospheric temperature adjustment, and our lifetime correction factor (assuming 3116 3117 a lifetime of 1.0 year [Javadi et al., 2007]) from section 3.3.4 of 0.74, and recommend a RE value of 0.49 W m^{-2} ppbv⁻¹. 3118

3119

3120 HFEs studied by Andersen et al. [2004]

For the following HFE compounds, *Andersen et al.* [2004] is the only study providing REsbased on experimental absorption cross-sections:

3123 HG'-01 (CH₃OCF₂CF₂OCH₃)

3124 HG'-02 (CH₃O(CF₂CF₂O)₂CH₃)

3125 HG'-03 (CH₃O(CF₂CF₂O)₃CH₃)

3126

3127 RE estimates using *ab initio* calculations are available for these compounds [*Bravo et* 3128 *al.*, 2011a] (Table S7 in the supplementary material), but we focus here on the experimental 3129 data from *Andersen et al.* [2004]. They used the *Pinnock et al.* [1995] method to estimate 3130 instantaneous REs of 0.32, 0.61 and 0.83 W m⁻² ppb⁻¹ for HG'-01, HG'-02 and HG'-03, 3131 respectively. The corresponding RE estimates from our calculations (now taking into account 3132 stratospheric temperature adjustment and inhomogeneous distribution in the troposphere) are 3133 0.29, 0.56 and 0.76 W m⁻² ppb⁻¹, respectively, when using absorption cross-sections and 3134 lifetimes from *Andersen et al.* [2004]. None of these compounds are included in AR4, thus we 3135 provide new best estimates of RE and GWP for all these compounds.

3136

3137 HFE-329me3 (CF₃CFHCF₂OCF₃)

3138 *Wallington et al.* [2004] have calculated an instantaneous RE value of HFE-329me3 of 0.48 3139 W m⁻² ppb⁻¹ by using experimental absorption cross-section and the *Pinnock et al.* [1995] 3140 method. We have used the absorption spectrum from the same study and calculated the same 3141 RE value when accounting for stratospheric temperature adjustment. Due to the relatively 3142 long lifetime of 40 years [*Wallington et al.*, 2004], the compound is well-mixed in the 3143 troposphere and the lifetime correction factor does not impact the RE value.

3144

3145 HFE-338mec3 (CF₃CFHCF₂OCF₂H)

Previous experimental studies of RE due to HFE-338mec3 are in the range 0.49 - 0.51 W m⁻² ppb⁻¹ (mean: 0.50 W m⁻² ppb⁻¹) [*Oyaro et al.*, 2005; *Wallington et al.*, 2004]. We have used the absorption cross-sections from both these studies and calculated a mean RE value of 0.51 W m⁻² ppb⁻¹ (range: 0.51 - 0.52 W m⁻² ppb⁻¹) when assuming a uniform distribution in the atmosphere. This is probably an upper estimate as no fractional correction factor has been applied because of the large disagreement found in the literature of the lifetime for this compound [*Oyaro et al.*, 2005; *Wallington et al.*, 2004].

3153

3154 HFEs studied by Waterland et al. [2005]

3155 For the following HFE compounds, *Waterland et al.* [2005] is the only study providing 3156 experimental absorption cross-sections:

- 3157 3,3,4,4,5,5,6,6,7,7,7-Undecafluoroheptan-1-ol (CF₃(CF₂)₄CH₂CH₂OH)
- 3158 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluorononan-1-ol (CF₃(CF₂)₆CH₂CH₂OH)

3159 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Nonadecafluoroundecan-1-ol

3160 $(CF_3(CF_2)_8CH_2CH_2OH)$

3161

3162 Waterland et al. [2005] did not estimate REs of the compounds listed above, but we 3163 have used their absorption cross-sections to calculate REs of 0.06, 0.07 and 0.05 W m^{-2} ppb⁻¹ 3,3,4,4,5,5,6,6,7,7,7-undecafluoroheptan-1-ol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-3164 for 3165 pentadecafluorononan-1-ol and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11nonadecafluoroundecan-1-ol, respectively. The lifetimes for all three compounds were 3166 3167 assumed to be 20 days based on Ellis et al. [2003].

3168

3169 **2-Chloro-1,1,2-trifluoro-1-methoxyethane** (CH₃OCF₂CHFCl)

3170 One experimental study has used the *Pinnock et al.* [1995] method to estimate an 3171 instantaneous RE due to 2-chloro-1,1,2-trifluoro-1-methoxyethane of 0.26 W m⁻² ppb⁻¹ 3172 [*Dalmasso et al.*, 2006]. We have used their absorption cross-section to calculate a slightly 3173 lower RE value of 0.21 W m⁻² ppb⁻¹ (now taking into account stratospheric temperature 3174 adjustment and inhomogeneous distribution in the troposphere). The lifetime of 1.4 years is 3175 taken from *Dalmasso et al.* [2006].

3176

3177 **PFPMIE** (perfluoropolymethylisopropyl) (CF₃OCF(CF₃)CF₂OCF₂OCF₃)

3178 One experimental study has estimated RE due to PFPMIE (perfluoropolymethylisopropyl), with a value 0.65 W m⁻² ppb⁻¹ [Young et al., 2006] which is used in IPCC AR4. We have used 3179 the same absorption cross-section and calculated the same RE value. In contrast to the other 3180 3181 compounds listed in this section, PFPMIE is lost by photolysis in the upper atmosphere and this results in a long lifetime of approximately 800 years [Young et al., 2006]. Hence, we have 3182 used the exponential fit from section 3.3.4 (Equation (1) and red curve in Figure 9) rather than 3183 3184 the S-shaped fit to account for a non-uniform vertical profile, although this has almost a 3185 negligible impact on the RE because such long-lived compounds are relatively well-mixed 3186 throughout the atmosphere.

3187

3188 HFE-216 (CF₃OCF=CF₂)

3189 Mashino et al. [2000] have estimated the instantaneous RE of HFE-216 by using the Pinnock et al. [1995] method and report a value of 0.28 W m⁻² ppb⁻¹. We have used their absorption 3190 cross-section, accounted for stratospheric temperature adjustment and lifetime correction, and 3191 calculated a much lower RE value of 0.02 W m⁻² ppb⁻¹. The reason for the large difference is 3192 3193 the short lifetime of 8.4 days [Mashino et al., 2000] which leads to a strong correction when 3194 accounting for non-homogeneous horizontal and vertical distribution in the troposphere. It 3195 should be noted here that the uncertainties associated with the lifetime correction factors are 3196 very large on a percentage basis for such short-lived species (see Figure 9 and associated 3197 discussion in section 3.3.4).

3198

3199 HFEs studied theoretically by Bravo et al. [2011b]

3200 For a number of HFE compounds, no RE estimates based on experimental absorption cross-

3201 sections exist and the *ab initio* study of *Bravo et al.* [2011b] provides the only RE estimate of

- 3202 these HFEs. These compounds are:
- 3203 Trifluoromethyl formate (HCOOCF₃)
- 3204 Perfluoroethyl formate (HCOOCF₂CF₃)
- 3205 Perfluoropropyl formate (HCOOCF₂CF₂CF₃)
- 3206 Perfluorobutyl formate (HCOOCF₂CF₂CF₂CF₃)
- 3207 2,2,2-Trifluoroethyl formate (HCOOCH₂CF₃)
- 3208 3,3,3-Trifluoropropyl formate (HCOOCH₂CH₂CF₃)
- 3209 1,2,2,2-Tetrafluoroethyl formate (HCOOCHFCF₃)
- 3210 1,1,1,3,3,3-Hexafluoropropan-2-yl formate (HCOOCH(CF₃)₂)
- 3211 Perfluorobutyl acetate (CH₃COOCF₂CF₂CF₂CF₃)
- 3212 Perfluoropropyl acetate (CH₃COOCF₂CF₂CF₃)
- 3213 Perfluoroethyl acetate (CH₃COOCF₂CF₃)
- 3214 Trifluoromethyl acetate (CH₃COOCF₃)
- 3215 Methyl carbonofluoridate (FCOOCH₃)
- 3216 Fluoromethyl carbonofluoridate (FCOOCFH₂)
- 3217 Difluoromethyl carbonofluoridate (FCOOCF₂H)
- 3218 Trifluoromethyl carbonofluoridate (FCOOCF₃)
- 3219 Perfluoroethyl carbonofluoridate (FCOOCF₂CF₃)
- 3220 2,2,2-Trifluoroethyl carbonofluoridate (FCOOCH₂CF₃)
- 3221 1,1-Difluoroethyl carbonofluoridate (FCOOCF₂CH₃)
- 3222 Perfluoropropyl carbonofluoridate (FCOOCF₂CF₂CF₃)
- 3223 Trifluoromethyl 2,2,2-trifluoroacetate (CF₃COOCF₃)
- 3224 Perfluoroethyl 2,2,2-trifluoroacetate (CF₃COOCF₂CF₃)
- 3225 1,1-Difluoroethyl 2,2,2-trifluoroacetate (CF₃COOCF₂CH₃)
- 3226 1,1,1,3,3,3-Hexafluoropropan-2-yl 2,2,2-trifluoroacetate (CF₃COOCH(CF₃)₂)
- 3227 Vinyl 2,2,2-trifluoroacetate (CF₃COOCH=CH₂)
- 3228 Ethyl 2,2,2-trifluoroacetate (CF₃COOCH₂CH₃)
- 3229 2,2,2-Trifluoroethyl 2,2,2-trifluoroacetate (CF₃COOCH₂CF₃)
- 3230 Allyl 2,2,2-trifluoroacetate (CF₃COOCH₂CHCH₂)
- 3231 Methyl 2,2,2-trifluoroacetate (CF₃COOCH₃)
- 3232 Phenyl 2,2,2-trifluoroacetate (CF₃COOPh)
- 3233 Methyl 2-fluoroacetate (H₂CFCOOCH₃)
- 3234 Difluoromethyl 2,2-difluoroacetate (HCF₂COOCHF₂)
- 3235 Methyl 2,2-difluoroacetate (HCF₂COOCH₃)
- 3236 Difluoromethyl 2,2,2-trifluoroacetate (CF₃COOCHF₂)
- 3237

For all of the compounds listed above we have used the theoretical absorption crosssections from *Bravo et al.* [2011b] to calculate estimates of RE, taking into account both stratospheric temperature adjustment (by increasing the instantaneous RE by 10% as described in section 3.3.2) and the fractional correction (by using the method described in section 3.3.4). For 14 of the 34 compounds listed above, no lifetime estimates were found in the literature, hence the RE estimates for these compounds assume a uniform vertical and

3244 horizontal distribution in the atmosphere. Lifetimes for the remaining 20 compounds were 3245 taken from various sources [Blanco and Teruel, 2007; Bravo et al., 2011b; Chen et al., 2006; Christensen et al., 1998; Oyaro et al., 2004; Wallington et al., 1988; Wallington et al., 1997; 3246 3247 WMO, 2011] (see Table S7 in the supplementary material for details). The Bravo et al. 3248 [2011b] study used the *Pinnock et al.* [1995] method to estimate instantaneous REs, but they 3249 did not account for non-homogeneous mixing. The RE estimates of Bravo et al. [2011b] are 3250 listed in Table S7 in the supplementary material, while our results are presented in Table 15. 3251 In general, differences reflect the use of an updated Pinnock et al. [1995] curve in this study, 3252 and that stratospheric temperature adjustment and lifetime correction were not taken into 3253 account in Bravo et al. [2011b]. None of the compounds listed above are included in AR4, 3254 thus we provide new best estimates of RE and GWP for all these compounds. It should, 3255 however, be kept in mind that RE estimates based on *ab initio* calculations are associated with 3256 larger uncertainties than estimates based on experimental cross-sections, as discussed in 3257 section 3.6.1 (see also Table 1).

3258

3259 **2,2,3,3,4,4,4-Heptafluorobutan-1-ol** (C₃**F**₇**CH**₂**OH**)

One experimental study has estimated the instantaneous lifetime-corrected RE due to 2,2,3,3,4,4,4-heptafluorobutan-1-ol with a value 0.20 W m⁻² ppb⁻¹ [*Bravo et al.*, 2010a]. We have used their absorption cross-section and calculated the same RE value when also taking into account stratospheric temperature adjustment and when using our own lifetime correction method (*Bravo et al.* [2010a] used the exponential function of *Sihra et al.* [2001]). The lifetime of 0.6 years is taken from *Bravo et al.* [2010a].

3266

3267 **2,2,3,3-Tetrafluoro-1-propanol** (CHF₂CF₂CH₂OH)

Previous experimental studies of RE due to 2,2,3,3-tetrafluoro-1-propanol are in the range 0.20 - 0.23 W m⁻² ppb⁻¹ (mean: 0.22 W m⁻² ppb⁻¹) [*Antiñolo et al.*, 2012b; *Sellevåg et al.*, 2007]. We have used the absorption cross-sections from these two studies and calculated a RE value of 0.11 W m⁻² ppb⁻¹ for both sources. The lifetime correction applied here is the main reason for the lower value compared to earlier work where the instantaneous RE assuming constant distribution was estimated. The lifetime of 91.2 days is taken from *Antiñolo et al.* [2012b].

3276 2,2,3,4,4,4-Hexafluoro-1-butanol (CF₃CHFCF₂CH₂OH)

The experimental study of *Sellevåg et al.* [2007] has used the *Pinnock et al.* [1995] method to estimate an instantaneous RE due to 2,2,3,4,4,4-hexafluoro-1-butanol of 0.37 W m⁻² ppb⁻¹. We have used their absorption cross-section and calculated a RE value of 0.19 W m⁻² ppb⁻¹ when taking into account stratospheric temperature adjustment and lifetime correction. The lifetime of 94.9 days is taken from *Sellevåg et al.* [2007].

3282

3283 2,2,3,3,4,4,4-Heptafluoro-1-butanol (CF₃CF₂CF₂CH₂OH)

One experimental study has estimated the instantaneous RE due to 2,2,3,3,4,4,4-heptafluoro-1-butanol, with a value 0.30 W m⁻² ppb⁻¹ [*Sellevåg et al.*, 2007]. We calculate a RE value of 0.16 W m⁻² ppb⁻¹ using the absorption cross-section from the same study. Our RE estimate accounts for stratospheric temperature adjustment and lifetime correction; the latter factor explains the lower RE calculated here. The lifetime of 0.3 years is taken from *Sellevåg et al.* [2007].

3290

3291 **1,1,2,2-Tetrafluoro-3-methoxy-propane** (CHF₂CF₂CH₂OCH₃)

One experimental study has estimated the instantaneous RE due to 1,1,2,2-tetrafluoro-3-3292 methoxy-propane with a value 0.24 W m⁻² ppb⁻¹ [Oyaro et al., 2004]. We have used their 3293 absorption cross-section and calculated a much lower RE value of 0.04 W m⁻² ppb⁻¹ when 3294 3295 taking into account stratospheric temperature adjustment and non-homogeneous distribution 3296 in the troposphere (these factors were not taken into account in the published RE estimate). 3297 The lifetime of 14.2 days is taken from Oyaro et al. [2004], and it should be noted here that the uncertainties associated with the lifetime correction factor are very large on a percentage 3298 3299 basis for such short-lived species (see Figure 9 and associated discussion in section 3.3.4),

3300

$3301 \quad Perfluoro-2-methyl-3-pentanone (CF_3CF_2C(O)CF(CF_3)_2)$

No RE estimates of perfluoro-2-methyl-3-pentanone exist in the literature. Here we have used the absorption cross-section from *D'Anna et al.* [2005] and calculate a RE value of 0.03 W m⁻ 2 ppb⁻¹ assuming a lifetime of 7.0 days [*D'Anna et al.*, 2005].

3306 3,3,3-Trifluoro-propanal (CF₃CH₂CHO)

3307 No RE estimates of 3,3,3-trifluoro-propanal can be found in the literature, but here we have 3308 calculated its RE by using the absorption cross-sections of Antiñolo et al. [2011] and Sellevag 3309 et al. [2004a]. Due to the very short lifetime of only 2.0 days for this compound [Antiñolo et al., 2011], our calculated RE rounds to 0.00 W m⁻² ppb⁻¹ when applying the lifetime 3310 correction (section 3.3.4). Uncertainties related to the fractional correction are large for 3311 3312 compounds with such short lifetimes. The mean RE calculated here when assuming a uniform horizontal and vertical distribution is 0.16 W m⁻² ppb⁻¹, and should be considered an upper 3313 3314 estimate.

3315

3316 4,4,4-Trifluorobutanal (CF₃(CH₂)₂CHO)

3317 No RE or lifetime estimates of 4,4,4-trifluorobutanal can be found in the literature. Here we 3318 have used the absorption cross-section from *Antiñolo et al.* [2012a] and calculated a RE value 3319 of 0.16 W m⁻² ppb⁻¹ assuming a constant horizontal and vertical distribution in the 3320 troposphere. Hence, this RE value should be considered an upper estimate.

3321

3322 **2-Fluoroethanol** (CH₂FCH₂OH)

In the experimental study of *Sellevag et al.* [2004b] a broadband model and a CTM were used to estimate the RE due to 2-fluoroethanol with a value $0.02 \text{ W m}^{-2} \text{ ppb}^{-1}$. We have used their absorption cross-section and calculated the same RE value. The lifetime of 20.4 days is taken from *Sellevag et al.* [2004b].

3327

3328 **2,2-Difluoroethanol** (CHF₂CH₂OH)

One experimental study has estimated RE due to 2,2-difluoroethanol, with a value 0.02 W m⁻² ppb⁻¹ [*Sellevag et al.*, 2004b]. We used their absorption cross-section and calculated a higher RE value of 0.04 W m⁻² ppb⁻¹. As discussed in section 3.3.4 and illustrated in Figure 9, the uncertainties when applying lifetime corrections are large for such short-lived compounds (lifetime of 40.0 days [*Sellevag et al.*, 2004b]).

3335 2,2,2-Trifluoroethanol (CF₃CH₂OH)

3336 Previous experimental studies of RE due to 2,2,2-trifluoroethanol are in the range 0.09 - 0.19 W m⁻² ppb⁻¹ (mean: 0.14 W m⁻² ppb⁻¹) and stem from the work of Sellevag et al. [2004b] and 3337 Imasu et al. [1995] (note that the RE from the latter study has been scaled to our 3338 recommended CFC-11 RE of 0.26 W m⁻² ppb⁻¹). We calculate a RE value of 0.10 W m⁻² ppb⁻¹ 3339 when using the absorption cross-sections from both these sources. Our value is close to the 3340 RE of 0.09 W m⁻² ppb⁻¹ from *Sellevag et al.* [2004b] who used a CTM to account for the non-3341 homogeneous tropospheric distribution. The lifetime of 0.3 years is taken from *Sellevag et al.* 3342 3343 [2004b].

3344

3345 HFEs studied by Andersen et al. [2010b]

For the following HFE compounds, *Andersen et al.* [2010b] is the only study providing REsbased on experimental absorption cross-sections:

3348 1,1'-Oxybis[2-(difluoromethoxy)-1,1,2,2-tetrafluoroethane (HCF₂O(CF₂CF₂O)₂CF₂H)

3349 1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12-hexadecafluoro-2,5,8,11-Tetraoxadodecane

 $3350 \quad (HCF_2O(CF_2CF_2O)_3CF_2H)$

3351 1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12,13,13,15,15-eicosafluoro-2,5,8,11,14-

3352 Pentaoxapentadecane ($HCF_2O(CF_2CF_2O)_4CF_2H$)

3353

3354 Andersen et al. [2010b] used the Pinnock et al. [1995] method to estimate 3355 instantaneous REs of these compounds. Since absorption spectra were unavailable for the 3356 three compounds listed above, no new calculations have been carried out here. Thus, we use the REs from Andersen et al. [2010b], accounting for stratospheric temperature adjustment 3357 3358 and lifetime correction (see sections 3.3.2 and 3.3.4, respectively), and present new best estimate REs of 1.15, 1.43 and 1.46 W m⁻² ppb⁻¹ for 1,1'-oxybis[2-(difluoromethoxy)-1,1,2,2-3359 3360 tetrafluoroethane, 1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12-hexadecafluoro-2,5,8,11-3361 tetraoxadodecane and 1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12,13,13,15,15-eicosafluoro-2,5,8,11,14-pentaoxapentadecane, respectively. We have used the same assumption as in 3362 3363 Andersen et al. [2010b] of a lifetime for all three compounds of 26 years.

Additional metrics for most important gases: GTPs and GWPs for other time horizons

3367 While we have used a time horizon of 100 years in the main tables we also show GWP values for 20 and 500 years for a selection of gases together with GTP values for the same gases in 3368 Table 16. The GTP values vary with time horizon in a way that depends on adjustment time 3369 3370 and how this compares with the time scale for the response of CO₂. For gases with short and 3371 medium lifetimes (e.g., HFC-152a and HCFC-22), the GTP falls rapidly with time horizon 3372 from 20 to 100 years. By contrast, the longer-lived gases, such as HFC-23 and CFC-12, show 3373 GTPs that increase from time horizons of 20 to 50 years, before decreasing, while for the very 3374 long-lived gases (SF₆ and PFC-14), the GTP values continue to increase out to 100 years. The 3375 contrast between the GWP and GTP values in Table 16 is particularly noticeable for gases 3376 with short and medium lifetimes - for example, for HCFC-22, the GWP drops by an about a 3377 factor of 3 between time horizons of 20 and 100 years, whereas the GTP drops by more than 3378 an order of magnitude. This reflects the fact that the integral nature of the GWP means that it 3379 keeps the memory of the strong short-lived forcing, while the GTP, being an end-point metric, 3380 retains less of a memory, and the impact of the forcing pulse on temperature has largely disappeared after 100 years. 3381

Compared to *Fuglestvedt et al.* [2010], the GWP and GTPs for CCl_4 are higher due to the higher RE calculated in this study compared to the recommended RE in AR4 (see discussion of CCl_4 in section 4.1.4 for details). The metric values for SF₆ have also increased (except for GWP 500-yr) due to the increase of the best estimate RE for this compound (see section 4.1.6).

3387 It should be noted that while the impulse response function for CO_2 includes climate-3388 carbon cycle feedbacks, no feedbacks are included for the non- CO_2 gases. The magnitude of 3389 this bias has not been assessed for the gases addressed here. However, *Gillett and Matthews* 3390 [2010] found that for N₂O and CH₄ the GWP-100 values increased by 20% when climate-3391 carbon feedbacks were included; which gives some indication of the bias in the GWP values 3392 presented here.

3394 **5** Summary and conclusions

3395 We present a comprehensive assessment of the radiative efficiencies (REs) for a large number 3396 of halocarbons and related radiatively-active compounds including CFCs, HCFCs, bromofluorocarbons and bromochlorofluorocarbons (halons), HFCs, PFCs, SF₆, NF₃, and 3397 related halogen containing compounds. A consistent method for calculating RE has been used 3398 3399 for all compounds ruling out any differences related to the radiative transfer method. Further, 3400 our results have been compared with previously published literature and new best estimates 3401 have been presented for lifetimes, REs, and GWPs. A total of 223 compounds were included 3402 in this study. Here we summarize our main findings:

- 34031. Absorption cross-sections have been collected from various sources including freely-
available databases and requests to authors of individual studies. The absorption cross-
section data used include experimental data and *ab initio* calculations. For most of the
important halocarbons, several independent sources are available for absorption cross
sections. However, we find insufficient data available (and hence encourage further
studies) for HFC-23, HFC-236ea, HFC-245ca, CCl₄, and several HFEs.
- 3409 2. An updated version of the simplified method presented in *Pinnock et al.* [1995] to calculate REs was developed and is presented. In the updated version an improved 3410 3411 representation of clouds and the spatial distribution of temperature and water vapor 3412 leads to changes in the estimated REs of up to 10% from those estimated using the 3413 values given by *Pinnock et al.* [1995]. For most compounds we apply a generic correction to account for the effect of stratospheric temperature adjustment. The 3414 3415 simulations by the simplified method are performed with a LBL model and results are presented on a 1 cm⁻¹ resolution. There was very little (1-2%) difference between REs 3416 calculated using 1 cm^{-1} or 10 cm^{-1} resolution, but it is greater for some compounds, 3417 most notably CF_4 where the difference is 8%. 3418
- 3419
 3. Simulations using a chemical transport model and results from the existing literature
 3420 were used to develop simple lifetime-dependent correction factors to account for
 3421 inhomogeneous mixing in the atmosphere. Application of these correction factors is
 3422 shown to be particularly important for very short-lived compounds and leads to
 3423 substantially lower REs than generally reported in the literature.
- 3424 4. We estimate that the uncertainty (5-95% confidence range) in RE of compounds for 3425 which we have experimental absorption cross-sections is approximately 13% for gases 3426 with atmospheric lifetimes greater than 5 years, and approximately 23% for gases with 3427 lifetimes less than 5 years. For compounds for which only *ab initio* cross-sections are 3428 available, the estimated uncertainties are 16% and 25% for compounds with lifetimes 3429 greater and less than 5 years, respectively. These estimates assume that empirical 3430 corrections based on knowledge of the spectra of related compounds have been 3431 applied to the *ab initio* cross-sections to account for systematic errors in the

3432 3433 3434 3435 3436 3437	calculation of the wavenumbers of the vibrational modes. Where more generic corrections have been made, the errors can be somewhat larger. Our estimated uncertainties are larger than the value of 10% given in IPCC AR4 for the RE of the long-lived greenhouse gases. The uncertainty in GWP _{HFC-134a} is estimated to 24%, 34% and 37% for a 20, 100, and 500 year time horizon. For CFC-11 the GWP uncertainties are 23%, 38% and 47% for a 20, 100, and 500 year time horizon.
3438 3439 3440 3441 3442 3443 3444 3445	5. Compared to AR4, the REs presented here differed significantly (by more than 5%) for 49 compounds, while 42 compounds had similar (<5% difference) RE as in AR4. For 7 of the compounds included in AR4 we have not carried out calculations because spectrally-resolved absorption cross-section data were not available, but for 2 of these compounds we have updated the recommended RE based on values from the literature. Best estimate REs and GWPs have also been presented for 112 compounds which were not included in AR4. For 20 additional compounds we have only presented new REs and not GWPs due to missing lifetime estimates.
3446 3447	6. Substantial updates in REs are made for several important gases: CFC-11, CFC-115, HCFC-124, HCFC-225cb, HFC-143a, HFC-245fa, CCl ₄ , CHCl ₃ , and SF ₆ .
3448 3449 3450 3451 3452	7. As shown in Figure 18, where there are substantial differences between the REs evaluated in the present work and those given in AR4, the values evaluated here tend to be lower than those given in AR4. This trend largely reflects an improvement in the methodology used to correct for the inhomogeneous mixing of shorter lived species (see section 3.3.4).
3453 3454 3455 3456 3457 3458 3459	8. SF ₆ has the highest GWP(100) with a value of 23,500 (relative to CO ₂) as a result of its high RE and very long lifetime. A majority of the compounds considered here have a GWP(100) below 1,000 and almost half of the compounds have a GWP(100) below 100. (See Figure 19 showing GWP(100) values in ordered ranking for all the compounds investigated in this study.) The AGWPs for CO ₂ have been updated and this leads to a lowering of the GWP(100) values of approximately 6% compared to AR4.
3460 3461 3462 3463 3464 3465	9. We have calculated GWPs for 20, 100, and 500 year time horizons and Global Temperature change Potentials (GTP) for 20, 50 and 100 years. The contrast between the GWP and GTP values is particularly noticeable for gases with short and medium lifetimes and reflects the integral nature of the GWP which retains memory of the strong short-lived forcing, while the GTP, being an end-point metric, has less of a memory.
3466	The GWP and GTP values are expected to change in the future, reflecting changes related to
3467	the reference gas CO_2 (i.e., $AGWP_{CO2}$ and $AGTP_{CO2}$ will be updated as background
3468	conditions change and models improve) and as our understanding of the RE and lifetimes of
3469	the compounds improve. In future reviews it will be important to distinguish between changes

in GWP and GTP values that are due to changes in RE and/or lifetime of the non-CO₂ gas and those that are due to the changes related to the reference gas CO_2 (i.e., AGWP_{CO2} and AGTP_{CO2}). Updated GWPs and GTPs can be obtained by multiplying old values with the ratio between old and new AGWP_{CO2} and AGTP_{CO2} values, respectively.

3474 Our main focus has been on providing a comprehensive and self-consistent set of new 3475 calculations of REs. A follow up study could be a detailed assessment of lifetimes with 3476 calculations of how uncertainties in lifetimes together with uncertainties in RE propagate to 3477 GWPs and GTPs.

3478 There are several important impacts of our new results. First of all, the large number 3479 of compounds included in the review, and the high degree of consistency in the method of 3480 calculating REs of each compound, make it a lot easier for researchers, industry and others to 3481 compare the potential climate impacts (i.e., the GWPs and GTPs) of molecules, and this may be helpful in choosing compounds that are more climate-friendly. Such a consistent set of RE 3482 3483 values may also be relevant for future assessment reports and could in turn have policy 3484 implications. Second, the contribution from halocarbons to the present-day total radiative 3485 forcing of anthropogenic greenhouse gases is also expected to change slightly as a result of 3486 our updated RE numbers. In particular, carbon tetrachloride (CCl₄) has a high atmospheric concentration and the RE for this compound is much higher in our study (0.17 W m^{-2} ppb⁻¹) 3487 than in AR4 (0.13 W m^{-2} ppb⁻¹). Finally, we provide the research community with an 3488 improved tool for calculating the RE, GWP and GTP of a compound in a relatively simple 3489 3490 manner.

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3492 Supplementary Material

3493 Supplementary Material is available and includes additional tables, the updated Pinnock et al.
3494 curve, and a large number of absorption cross-sections (see SM_Readme.txt for more
3495 information).

3496

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Source of uncertainty	Estimated contribution to total RF uncertainty	References used as basis for uncertainty estimates
Absorption cross-sections	~5% for experimentally determined spectra,	[Ballard et al., 2000b; Bravo et al., 2010b; Forster et al., 2005]
	~10% for ab initio spectra	
Radiation scheme	~5%	[Collins et al., 2006; Forster et al., 2005; Oreopoulos et al., 2012]
Clouds	~5%	[Forster et al., 2005; Gohar et al., 2004]
Spectral overlap and water vapor distribution	~3%	[Forster et al., 2005; Jain et al., 2000; Pinnock et al., 1995]
Surface temperature and atmospheric temperature	~3%	[Forster et al., 2005]
Tropopause level	~5%	[Forster et al., 2005; Freckleton et al., 1998; Myhre and Stordal, 1997]
Temporal and spatial averaging	~1%	[Freckleton et al., 1998; Myhre and Stordal, 1997]
Stratospheric temperature adjustment	~4%	[Forster et al., 2005; Gohar et al., 2004]
Non-uniform vertical profile	~5% for lifetimes > ~5 years,	[Sihra et al., 2001] + this study
	~20% for lifetimes < ~5 years	
Total (RSS) (experimental)	~13% for lifetimes > ~5 years	
	~23% for lifetimes < ~5 years	
Total (RSS) (ab initio)	~15% for lifetimes > ~5 years	

Table 1. Estimated contributions to the total radiative forcing uncertainty.

4329	Table 2. Integrated absorption cross-sections (S) for chlorofluorocarbons (CFCs) from the literature. Spectra used in RE calculations in the present study are indicated in
4330	bold.

Name	CAS#	Acronym	Formula	Data ¹	T/K	Wn. range /cm ⁻¹	S^2	Reference	Database ³
Trichlorofluoromethane	75-69-4	CFC-11	CCl ₃ F	E	295	820 - 1120	9.3	[Orkin et al., 2003]	
				E	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$				
				E				[Naik et al., 2000]	
				E				[Ninomiya et al., 2000]	
				E	296	810 - 1120	9.5	[Varanasi-priv.com., 2000]	Н
				А				[Good et al., 1998]	
				E	298	800 - 1120	9.4	[Heathfield et al., 1998]	G
				E	296	810 - 1120	9.0	[Christidis et al., 1997]	G
				E	296	700 - 1500	9.8	[Imasu et al., 1995]	
				E	296	810 - 1120	9.5	[Li and Varanasi, 1994]	G
				E	293	800 - 1120	9.2	[McDaniel et al., 1991]	
				E		810 - 1120	8.9	[Fisher et al., 1990]	
				E		800 - 1120	9.8	[<i>Varanasi and Chudamani</i> , 1988a]	
				Е		800 - 1120	8.4	[<i>Massie et al.</i> , 1985]	
				Е		800 - 1120	10.3	[Kagann et al., 1983]	
				Е		800 - 1120	8.9	[Nanes et al., 1980]	
				Е		800 - 1120	8.9	[Varanasi and Ko, 1977]	
Dichlorodifluoromethane	75-71-8	CFC-12	CCl_2F_2	Е	295	850 - 1190	13.5	[<i>Myhre et al.</i> , 2006]	
				Е	296	640 - 1200	12.2	[Hurley-priv.com., 2003]	G
				Е	295	850 - 1190	12.9	[Orkin et al., 2003]	
				Е	296	500 - 1500	12.2	[Sihra et al., 2001]	
				Е	296	850 - 1200	13.6	[Varanasi-priv.com., 2000]	Н
				А				[Good et al., 1998]	
				Е	296	850 - 1200	13.6	[Varanasi and Nemtchinov, 1994]	G
				Е	287	850 - 1190	13.5	[Clerbaux et al., 1993]	G
				Е	293	850 - 1190	12.6	[<i>McDaniel et al.</i> , 1991]	-
				Ē	296	850 - 1190	12.1	[<i>Fisher et al.</i> , 1990]	
				E	300	850 - 1190	13.4	[Varanasi and Chudamani, 1988a]	
				Е	298	800 - 1200	12.7	[Vanthanh et al., 1986]	

				E	296	850 - 1190	13.3	[<i>Massie et al.</i> , 1985]	
				E	296	850 - 1190	13.6	[Kagann et al., 1983]	
				E	300	850 - 1190	12.9	[Varanasi and Ko, 1977]	
				E				[Morcillo et al., 1966]	
Chlorotrifluoromethane	75-72-9	CFC-13	CClF ₃	E	293	765 - 1235	14.8	[McDaniel et al., 1991]	Η
				Е		1050 - 1291	16.3	[Varanasi and Chudamani, 1988b]	
				E		755 - 1291	16.1	[Golden et al., 1978]	
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	CFC-113	CCl_2FCClF_2	E	283	600 - 1250	13.7	[Le Bris et al., 2011]	
				E	293	780 - 1232	12.7	[McDaniel et al., 1991]	Н
				Е		618 - 1397	12.7	[Fisher et al., 1990]	
				E		780 - 1235	19.4	[Rogers and Stephens, 1988]	
				Е		780 - 1235	14.1	[Varanasi and Chudamani, 1988b]	
1,2-Dichloro-1,1,2,2- tetrafluoroethane	76-14-2	CFC-114	$CClF_2CClF_2$	Е	293	815 - 1285	15.2	[McDaniel et al., 1991]	Н
				Е		555 - 1397	15.4	[Fisher et al., 1990]	
				E		820 - 1310	23.9	[Rogers and Stephens, 1988]	
				E		820 - 1310	15.8	[Varanasi and Chudamani, 1988b]	
				E		1025 - 1310	12.0	[<i>Massie et al.</i> , 1985]	
1-Chloro-1,1,2,2,2-pentafluoroethane	76-15-3	CFC-115	$CClF_2CF_3$	Е	293	955 - 1260	12.1	[McDaniel et al., 1991]	Η
				Е		618 - 1397	17.4	[Fisher et al., 1990]	

4331 ¹ Type of data: E, Experimental; A, Ab initio.

4332 ² Integrated absorption cross-section in units of 10^{-17} cm² molecule⁻¹ cm⁻¹ for the wavenumber interval specified.

4333 ³ Database: H, HITRAN 2008; G, GEISA 2009

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4337	Table 3. Lifetimes, radiative efficiencies and direct GWPs (relative to CO ₂) for chlorofluorocarbons (CFCs).
4338	Compounds in bold either have significant current atmospheric concentrations or a clear potential for future
4339	emissions. Recommended RE and GWP(100) values are indicated in bold. Lifetimes are from WMO [2011].

			Radiat	ive Efficiency (W	$V m^{-2} ppb^{-1}$)	GV	VP(100)
Acronym	Formula	Lifetime (yr)	AR4	This study – const. profile	This study – lifetime corr.	AR4	This study – lifetime corr.
CFC-11	CCl ₃ F	45.0	0.25	0.28	0.26	4,750	4,660
CFC-12	CCl_2F_2	100.0	0.32	0.33	0.32	10,900	10,200
CFC-13	CClF ₃	640.0	0.25	0.26	0.25	14,400	13,900
CFC-113	CCl ₂ FCClF ₂	85.0	0.30	0.31	0.30	6,130	5,820
CFC-114	CClF ₂ CClF ₂	190.0	0.31	0.32	0.31	10,000	8,590
CFC-115	CClF ₂ CF ₃	1,020.0	0.18	0.21	0.20	7,370	7,670

Name	CAS#	Acronym	Formula	Data ¹	T/K	Wn. range /cm ⁻¹	S^2	Reference	Database ³
Dichlorofluoromethane	75-43-4	HCFC-21	CHCl ₂ F	Е	296	600 - 1500	7.4	[Sihra et al., 2001]	
			-	Е	296	450 - 2000	6.8	[Christidis et al., 1997]	
				Е	296	785 - 840	2.7	[Massie et al., 1985]	Н
Chlorodifluoromethane	75-45-6	HCFC-22	CHClF ₂	Е	295	750 - 1380	10.0	[<i>Orkin et al.</i> , 2003]	
			_	Е	296	700 - 1400	10.1	[Sihra et al., 2001]	
				Е	293	775 - 1375	10.1	[Ballard et al., 2000b]	G
				E	273	750 - 1400	10.2	[<i>Highwood and Shine</i> , 2000]	
				Е				[Naik et al., 2000]	
				А		600 - 1500	11.6	[Papasavva et al., 1997]	
				Е	296	765 - 1390	10.2	[Pinnock et al., 1995]	G
				Е	296	735 - 1380	9.7	[Anastasi et al., 1994]	
				Е	296	1070 - 1195	6.9	[Varanasi et al., 1994]	G
				Е	287	765 - 1380	10.3	[Clerbaux et al., 1993]	Н
				E	293	755 - 1390	10.3	[Cappellani and Restelli, 1992]	
				Е	293	775 - 1375	9.0	[<i>McDaniel et al.</i> , 1991]	
				Е		775 - 1397	9.5	[Fisher et al., 1990]	
				Е		775 - 1170	9.4	[Varanasi and Chudamani, 1988b]	
1,1,2-Trichloro-2,2- difluoroethane	354-21-2	HCFC-122	CHCl ₂ CF ₂ Cl	Е	295	560 - 1360	10.4	[Orkin et al., 2003]	
1,1,2-Trichloro-1,2- difluoroethane	354-15-4	HCFC-122a	CHFClCFCl ₂	Е	295	590 - 1380	9.9	[Orkin et al., 2003]	
2,2-Dichloro-1,1,1- trifluoroethane	306-83-2	HCFC-123	CHCl ₂ CF ₃	Е	295	480 - 1430	13.1	[Orkin et al., 2003]	
				E	296	700 - 1500	11.9	[Sihra et al., 2001]	
						600 1500	1/1	$\begin{bmatrix} Papasawa at al 1007 \end{bmatrix}$	
				F	206	700 1/00	12.0	[Pinnock at al 1995]	G
				E	290	700 - 1400 480 - 1420	12.0	[1 innock et al., 1775] [Olliff and Fischer 1004]	U
				E		400 - 1430	12.7	[Ouijj and Fischer, 1994]	

4342	Table 4. Integrated absorption cross-sections (S) for hydrochlorofluorocarbons (HCFCs) from the literature. Spectra used in RE calculations in the present study are
4343	indicated in bold.

				E	287	740 - 1450	12.9	[Clerbaux et al., 1993]	Η	
				Ε	293	648 - 1440	12.7	[<i>Cappellani and Restelli</i> , 1992]		
				E		649 - 1307	10.6	[Fisher et al., 1990]		
1,2-Dichloro-1,1,2- trifluoroethane	354-23-4	HCFC-123a	CHClFCF ₂ Cl	Ε	295	450 - 1400	12.3	[Orkin et al., 2003]		
2-Chloro-1,1,1,2- tetrafluoroethane	2837-89- 0	HCFC-124	CHClFCF ₃	Е	296	700 - 1500	13.4	[Sihra et al., 2001]		
				E				[Naik et al., 2000]		
				А		600 - 1500	15.7	[Papasavva et al., 1997]		
				E	296	670 - 1435	13.8	[Pinnock et al., 1995]	G	
				E	287	675 - 1430	14.4	[Clerbaux et al., 1993]	Η	
				E		440 - 1420	15.0	[Fisher et al., 1990]		
1,1-Dichloro-1,2- difluoroethane	1842-05- 3	HCFC-132c	CH ₂ FCFCl ₂	Е	295	425 - 1490	8.4	[Orkin et al., 2003]		
1,1-Dichloro-1- fluoroethane	1717-00- 6	HCFC-141b	CH ₃ CCl ₂ F	Е	283	570 - 3100	8.1	[Le Bris et al., 2012]		
				Е	295	540 - 1540	8.0	[Orkin et al., 2003]		
				Е	296	700 - 1500	7.1	[Sihra et al., 2001]		
				Е				[Naik et al., 2000]		
				А		600 - 1500	9.1	[Papasavva et al., 1997]		
				Е	296	700 - 1500	8.3	[Imasu et al., 1995]		
				Е	296	700 - 1470	7.2	[Pinnock et al., 1995]	G	
				E		540 - 1480	7.6	[Olliff and Fischer, 1994]		
				E	287	710 - 1470	7.8	[Clerbaux et al., 1993]	Η	
				Е		555 - 1420	7.1	[Fisher et al., 1990]		
1-Chloro-1,1- difluoroethane	75-68-3	HCFC-142b	CH ₃ CClF ₂	Е	283	650 - 3500	10.8	[Le Bris and Strong, 2010]		
				Е	296	700 - 1500	9.6	[Sihra et al., 2001]		
				E				[<i>Naik et al.</i> , 2000]		
				А		600 - 1500	11.8	[Papasavva et al., 1997]		
				Е	296	650 - 1425	10.1	[Pinnock et al., 1995]	G	
				Е	287	650 - 1469	11.1	[Clerbaux et al., 1993]	Η	
				Е	293	647 - 1485	10.7	[Cappellani and Restelli, 1992]		
				Е		649 - 1397	9.6	[Fisher et al., 1990]		
3,3-Dichloro-1,1,1,2,2-	422-56-0	HCFC-	CHCl ₂ CF ₂ CF ₃	Е	296	700 - 1400	18.0	[Sihra et al., 2001]		
pent	afluoropropane		225ca							
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					E				[Naik et al., 2000]	
					E	296	700 - 1400	14.6	[Pinnock et al., 1995]	
					Е	287	695 - 1420	17.7	[Clerbaux et al., 1993]	Н
1,3- pent	Dichloro-1,1,2,2,3- afluoropropane	507-55-1	HCFC- 225cb	CHClFCF ₂ CClF ₂	Е	296	700 - 1400	15.2	[Sihra et al., 2001]	
1					Е				[Naik et al., 2000]	
					E	296	700 - 1500	16.6	[Imasu et al., 1995]	
					E	296	700 - 1400	15.1	[Pinnock et al., 1995]	
					E	287	715 - 1375	15.6	[Clerbaux et al., 1993]	Н
(E)- triflu	1-Chloro-3,3,3- loroprop-1-ene	102687- 65-0		trans-CF ₃ CH=CHCl	Е	295	600 - 1800	17.4	[Andersen et al., 2008]	

4345 ² Integrated absorption cross-section in units of 10^{-17} cm² molecule⁻¹ cm⁻¹ for the wavenumber interval specified.

4346 ³ Database: H, HITRAN 2008; G, GEISA 2009.

- **Table 5.** Lifetimes, radiative efficiencies (RE) and direct GWPs (relative to CO₂) for hydrochlorofluorocarbons
- 4350 (HCFCs). Compounds in **bold** either have significant current atmospheric concentrations or a clear potential for
- 4351 future emissions. Recommended RE and GWP 100-yr values are indicated in bold. Lifetimes are from WMO

4352 [2011] except those in italic (see text for details).

			Radiat	ive Efficiency (V	$W \text{ m}^{-2} \text{ ppb}^{-1}$)	GW	P 100-yr
Acronym /	Formula	Lifetime	AR4	This study –	This study	AR4	This study
name		(yr)		const.	– lifetime		– lifetime
				profile	corr.		corr.
HCFC-21	CHCl ₂ F	1.7	0.14	0.18	0.15	151	148
HCFC-22	CHClF ₂	11.9	0.20	0.22	0.21	1,810	1,760
HCFC-122	CHCl ₂ CF ₂ Cl	1.0		0.23	0.17		59
HCFC-122a	CHFClCFCl ₂	3.4		0.23	0.21		258
HCFC-123	CHCl ₂ CF ₃	1.3	0.14	0.19	0.15	77	79
HCFC-123a	CHClFCF ₂ Cl	4.0		0.25	0.23		370
HCFC-124	CHClFCF ₃	5.9	0.22	0.21	0.20	609	527
HCFC-132c	CH ₂ FCFCl ₂	4.3		0.19	0.17		338
HCFC-141b	CH ₃ CCl ₂ F	9.2	0.14	0.17	0.16	725	782
HCFC-142b	CH ₃ CClF ₂	17.2	0.20	0.19	0.19	2,310	1,980
HCFC-225ca	CHCl ₂ CF ₂ CF ₃	1.9	0.20	0.26	0.22	122	127
HCFC-225cb	CHClFCF ₂ CClF ₂	5.9	0.32	0.32	0.29	595	525
(E)-1-Chloro-							
3,3,3-	trans-	260 days		0.22	0.04		1
trifluoroprop-	CF ₃ CH=CHCl	20.0 days		0.22	0.04		1
1-ene							

4355	Table 6. Integrated absorption cross-sections (S) for hydrofluorocarbons (HFCs) from the literature. Spectra used in RE calculations in the present study are indicated in
4356	bold.

Name	CAS#	Acronym	Formula	Data ¹	T/K	Wn. range /cm ⁻¹	S^2	Reference	Database ³
Trifluoromethane	75-46-7	HFC-23	CHF ₂	А	298			[Blowers and	
Timuoromounane	10 10 1	III C 25	cin 3		220			Hollingshead, 2009]	
				E	296	400 - 1500	11.8	[Gohar et al., 2004]	
				E	296	700 - 1500	11.7	[Sihra et al., 2001]	
				Е	253	655 - 1415	10.1	[<i>Highwood and Shine</i> , 2000]	
				E				[Naik et al., 2000]	
				А		600 - 1500	12.9	[Papasavva et al., 1997]	
				Е	296	700 - 1400	12.7	[Pinnock et al., 1995]	
D:floor and the sec	75 10 5		CULE	•	200			[Blowers and	
Diffuorometnane	/5-10-5	HFC-32	CH_2F_2	А	298			Hollingshead, 2009]	
				Е	296	400 - 1550	5.8	[Gohar et al., 2004]	
				Е	295	450 - 1480	5.9	[Orkin et al., 2003]	
				Е	296	700 - 1500	5.7	[Sihra et al., 2001]	
				Е	253	450 - 1475	5.6	[Highwood and Shine, 2000]	
				Е				[<i>Naik et al.</i> , 2000]	
				А		600 - 1500	6.1	[Papasavva et al., 1997]	
				Е	297	995 - 1475	5.2	[<i>Smith et al.</i> , 1996]	Н
				Е	296	700 - 1400	6.3	[Pinnock et al., 1995]	G
				Е	297	995 - 1475	5.2	[M.S.F./R.A.L.]	G
	500 50 0				200			Blowers and	
Fluoromethane	593-53-3	HFC-41	CH ₃ F	A	298			Hollingshead, 2009]	
				Е	296	700 - 1400	1.5	[Sihra et al., 2001]	
				А		600 - 1500	1.7	[Papasavva et al., 1997]	
				Е	296	700 - 1400	1.8	[Pinnock et al., 1995]	
1,1,1,2,2-Pentafluoroethane	354-33-6	HFC-125	CHF ₂ CF ₃	Е	296	700 - 1480	15.5	[Young et al., 2009b]	
	-	-	2 5	Е	295	460 - 1480	16.6	[Orkin et al., 2003]	
				Е	296	700 - 1500	16.5	[<i>Sihra et al.</i> , 2001]	
				E	293	550 - 1480	17.2	[Di Lonardo and Masciarelli, 2000]	G

			Е	253	550 - 1480	16.6	[Highwood and Shine, 2000]	
			Е				[<i>Naik et al.</i> , 2000]	
			А				[<i>Good et al.</i> , 1998]	
			А		600 - 1500	16.8	[Papasavva et al., 1997]	
			Е	296	700 - 1500	17.0	[Imasu et al., 1995]	
			Е	296	700 - 1400	16.1	[Pinnock et al., 1995]	G
			Е		460 - 1480	16.0	[Olliff and Fischer, 1994]	_
			Е	287	700 - 1465	16.1	[Clerbaux et al., 1993]	G
			Е		500 - 1307	14.5	[<i>Fisher et al.</i> , 1990]	_
1.1.2.2-Tetrafluoroethane 359-35-3	HFC-134	CHF ₂ CHF ₂	Е	296	450 - 1550	10.5	[Sihra et al., 2001]	
,,,		- 2 - 2	Е				[<i>Naik et al.</i> , 2000]	
			Ā				[Good et al., 1998]	
			E	296	450 - 2000	9.7	[Christidis et al., 1997]	
			Ā	_, ,	600 - 1500	10.6	[Papasavva et al., 1997]	
			E	297	600 - 1700	11.4	[<i>Smith et al.</i> , 1998]	Н
			Ē	296	450 - 1420	10.5	[Hurley-priv.com., 2003]	G
			Е	297	600 - 1700	11.4	[M.S.F./R.A.L.]	G
1.1.1.2-Tetrafluoroethane 811-97-2	HFC-134a	CH ₂ FCF ₂	Е	296	250 - 2000	13.2	[Forster et al., 2005]	_
-,-,-,		2 5	Ē	296	300 - 1550	13.1	[<i>Gohar et al.</i> , 2004]	
			Е	296	1035 - 1340	11.4	[Nemtchinov and Varanasi, 2004]	Н
			Е	296	700 - 1500	12.4	[Hurley-priv.com., 2003]	G
			Е	295	490 - 1550	13.6	[Orkin et al., 2003]	
			Е	296	700 - 1550	12.4	[<i>Sihra et al.</i> , 2001]	
			E	253	75 - 1540	13.6	[<i>Highwood and Shine</i> , 2000]	
			Е				[Naik et al., 2000]	
			А		600 - 1500	13.6	[Papasavva et al., 1997]	
			E		600 - 1448	13.5	[Newnham et al., 1996]	
			Е	296	700 - 1500	13.5	[Imasu et al., 1995]	
			E	296	700 - 1400	13.1	[Pinnock et al., 1995]	
			E		490 - 1510	13.4	[Olliff and Fischer, 1994]	
			E	287	815 - 1485	12.6	[Clerbaux et al., 1993]	Н
			E	293	610 - 1490	13.2	[Cappellani and Restelli, 1992]	
			E		618 - 1420	12.2	[Fisher et al., 1990]	

				Е	296	600 - 1600	12.5	[M.S.F./R.A.L.]	G
1,1,2-Trifluoroethane	430-66-0	HFC-143	CH_2FCHF_2	Е	296	700 - 1550	7.1	[Sihra et al., 2001]	
				Е				[<i>Naik et al.</i> , 2000]	
				А		600 - 1500	7.2	[Papasavva et al., 1997]	
				E	296	700 - 1400	6.9	[Pinnock et al., 1995]	
				Е	287	700 - 1500	6.9	[Clerbaux and Colin,	
				F	206	400 1500	76	1994] [MSE/DAL]	G
1 1 1-Trifluoroethane	420-46-2	HFC-143a	CH ₂ CF ₂	F	296	700 - 1500	12.7	[M.S.F./K.A.L.] [Sibra et al 2001]	0
	420 40 2	III C 1450		L	270	700 1500	12.7	[Di Lonardo and	
				E	293	797 - 1460	12.8	[Di Lonardo ana Masciarelli, 2000]	G
				Е	253	800 - 1470	12.0	[<i>Highwood and Shine</i> , 2000]	
				F				[Naik at al 2000]	
								$\begin{bmatrix} Cood at al & 1998 \end{bmatrix}$	
				F	207	700 1500	13.6	[0000 et al., 1996] [Smith et al. 1998]	НG
					291	600 - 1500	13.0	$\begin{bmatrix} Smun \ et \ ut., 1990 \end{bmatrix}$	11, 0
				F	296	500 - 1500	12.7	[Pinnock et al 1995]	G
				F	293	796 - 1 <i>474</i>	12.5	[Olliff and Fischer 1994]	0
				F	275	555 - 1535	12.0	[Fisher et al 1990]	
1 2-Difluoroethane	624-72-6	HFC-152	CHAECHAE			600 - 1500	4.2	[Panasawa et al 1997]	
1,2 Diffuorocularie	024 72 0	III C 152		11		000 1500	7.2	[Wallington et al	
				E		810 - 1510	3.7	[// <i>annyton</i> cr an, 1994a]	
1,1-Difluoroethane	75-37-6	HFC-152a	CH ₃ CHF ₂	E	296	700 - 1500	6.8	[Sihra et al., 2001]	
				Е	253	830 - 1500	6.7	[<i>Highwood and Shine</i> , 2000]	
				Е				[Naik et al., 2000]	
				Е	293	840 - 1490	6.9	[Vander Auwera, 2000]	G
				А		600 - 1500	7.1	[Papasavva et al., 1997]	
				E	296	700 - 1400	7.4	[Pinnock et al., 1995]	G
				E	287	840 - 1490	6.9	[Clerbaux et al., 1993]	Н
				Е	293	830 - 1485	6.9	[<i>Cappellani and Restelli</i> , 1992]	
				Е		775 - 1420	6.1	[<i>Fisher et al.</i> , 1990]	
Fluoroethane	353-36-6	HFC-161	CH ₃ CH ₂ F	Е	296	450 - 1600	2.4	[Sihra et al., 2001]	
			5 - 4	Е	'			[<i>Naik et al.</i> , 2000]	
				E	296	450 - 2000	2.2	[Christidis et al., 1997]	

				A		600 - 1500	2.4	[Papasavva et al., 1997]
,1,1,2,2,3,3-Heptafluoropropane	2252-84-8	HFC-227ca	$CF_3CF_2CHF_2$	E	296	450 - 1550	19.9	[Sihra et al., 2001]
				E	296	450 - 2000	20.9	[Christidis et al., 1997]
1,1,1,2,3,3,3-Heptafluoropropane	431-89-0	HFC-227ea	CF ₃ CHFCF ₃	E	296	400 - 1550	23.3	[Gohar et al., 2004]
				E	296	700 - 1500	22.3	[Sihra et al., 2001]
				E				[<i>Naik et al.</i> , 2000]
				E	296	700 - 1400	23.0	[Pinnock et al., 1995]
,1,1,2,2,3-Hexafluoropropane	677-56-5	HFC- 236cb	CH ₂ FCF ₂ CF ₃	Е	296	450 - 1550	17.0	[Sihra et al., 2001]
				E	296	450 - 2000	16.5	[Christidis et al., 1997]
,1,1,2,3,3-Hexafluoropropane	431-63-0	HFC-236ea	CHF ₂ CHFCF ₃	E	296	680 - 1320	17.2	[Gierczak et al., 1996]
1,1,1,3,3,3-Hexafluoropropane	690-39-1	HFC-236fa	CF ₃ CH ₂ CF ₃	E	296	700 - 1500	22.8	[<i>Sihra et al.</i> , 2001]
				E				[Naik et al., 2000]
				E	296	600 - 1350	22.6	[Gierczak et al., 1996]
				E	296	700 - 1400	23.3	[Pinnock et al., 1995]
1,1,1,2,2-Pentafluoropropane	1814-88-6	HFC- 245cb	CF ₃ CF ₂ CH ₃	Е	295	472 - 1490	18.1	[Orkin et al., 2003]
				Е	296	450 - 1550	16.5	[Sihra et al., 2001]
				Е	296	450 - 2000	15.8	[Christidis et al., 1997]
,1,2,3,3-Pentafluoropropane	24270-66- 4	HFC-245ea	CHF ₂ CHFCHF ₂	Е	298	500 - 4000		[Rajakumar et al., 2006]
1,1,1,2,3-Pentafluoropropane	431-31-2	HFC- 245eb	CH ₂ FCHFCF ₃	Е	298	500 - 4000		[Rajakumar et al., 2006]
1,1,1,3,3-Pentafluoropropane	460-73-1	HFC-245fa	CHF ₂ CH ₂ CF ₃	E	295	455 - 1485	19.8	[Orkin et al., 2003]
				Е	296	640 - 1500	19.6	[Sihra et al., 2001]
				Е				[<i>Jain et al.</i> , 2000]
				Е				[<i>Naik et al.</i> , 2000]
				Е		450 - 2325	20.6	[Ko et al., 1999]
1,1,1-Trifluoropropane	421-07-8	HFC-263fb	CH ₃ CH ₂ CF ₃	E	298	500 - 4000		[Rajakumar et al., 2006]
2,2-Difluoropropane	420-45-1	HFC-272ca	CH ₃ CF ₂ CH ₃	Е	296	700 - 1500	5.7	[Sihra et al., 2001]
				Е	296	700 - 1400	5.6	[Pinnock et al., 1995]
			CHE CE CE CE	Е	296	700 - 1435	22.2	[Young et al., 2009b]
,1,1,2,2,3,3,4,4-Nonafluorobutane	375-17-7	HFC-329p	$CIII_2CI_2CI_2CI_3$	1				
1,1,1,2,2,3,3,4,4-Nonafluorobutane	375-17-7 406-58-6	HFC-329p HFC- 365mfc	$CH_{3}CF_{2}CH_{2}CF_{3}$ $CH_{3}CF_{2}CH_{2}CF_{3}$	E	296	665 - 1500	18.8	[Inoue et al., 2008]
1,1,1,2,2,3,3,4,4-Nonafluorobutane	375-17-7 406-58-6	HFC-329p HFC- 365mfc	CH ₃ CF ₂ CH ₂ CF ₃ CH ₃ CF ₂ CH ₂ CF ₃	E E	296	665 - 1500	18.8	[Inoue et al., 2008] [Naik et al., 2000]
1,1,1,2,2,3,3,4,4-Nonafluorobutane	375-17-7 406-58-6	HFC-329p HFC- 365mfc	CH ₃ CF ₂ CH ₂ CF ₃ CH ₃ CF ₂ CH ₂ CF ₃	E E E	296 298	665 - 1500 600 - 1500	18.8	[Inoue et al., 2008] [Naik et al., 2000] [Barry et al., 1997]

		1132a						
Fluoroethene	75-02-5	HFC-1141	CH ₂ =CHF	E	296	770 - 1740	4.8	[Baasandorj et al., 2010]
				E		770 - 1740	4.5	[<i>Stoppa et al.</i> , 2009]
(Z)-1,2,3,3,3-Pentafluoroprop-1- ene	5528-43-8	(Z)-HFC- 1225ye	CF ₃ CF=CHF(Z)	Е	296	706 - 1812	19.3	[<i>Papadimitriou et al.</i> , 2008a]
		•		E	296	710 - 2000	18.3	[<i>Hurley et al.</i> , 2007]
(E)-1,2,3,3,3-Pentafluoroprop-1- ene	5595-10-8	(E)-HFC- 1225ye	CF ₃ CF=CHF(E)	Е	296	810 - 2000	18.4	[Hurley et al., 2007]
(Z)-1,3,3,3-Tetrafluoroprop-1-ene	29118-25- 0	(Z)-HFC- 1234ze	CF ₃ CH=CHF(Z)	Е	296	720 - 2000	16.8	[Nilsson et al., 2009]
2,3,3,3-Tetrafluoroprop-1-ene	754-12-1	HFC- 1234yf	CF ₃ CF=CH ₂	Е	295	500 - 1900	17.2	[Orkin et al., 2010]
		2		Е	296	540 - 1810	16.9	[<i>Papadimitriou et al.</i> , 2008a]
				Е	296	863 - 1745	16.1	[Nielsen et al., 2007]
(E)-1,3,3,3-Tetrafluoroprop-1-ene	1645-83-6	(E)-HFC- 1234ze	trans-CF ₃ CH=CHF	Е	295	500 - 1900	19.9	[Orkin et al., 2010]
				E	296	680 - 2000	19.4	[Søndergaard et al., 2007]
(Z)-1,1,1,4,4,4-Hexafluorobut-2- ene	692-49-9	(Z)-HFC- 1336	CF ₃ CH=CHCF ₃ (Z)	Е	296	1100 - 1500	27.8	[Baasandorj et al., 2011]
3,3,3-Trifluoroprop-1-ene	677-21-4	HFC- 1243zf	CF ₃ CH=CH ₂	Е	298	650 - 2000	12.5	[Andersen et al., 2012a]
3,3,4,4,4-Pentafluorobut-1-ene	374-27-6	HFC- 1345zfc	C ₂ F ₅ CH=CH ₂	Е	298	650 - 2000	13.6	[Andersen et al., 2012a]
3,3,4,4,5,5,6,6,6-Nonafluorohex-1- ene	19430-93- 4		C ₄ F ₉ CH=CH ₂	Е	298	650 - 2000	24.1	[Andersen et al., 2012a]
3,3,4,4,5,5,6,6,7,7,8,8,8- Tridecafluorooct-1-ene	25291-17- 2		C ₆ F ₁₃ CH=CH ₂	Е	298	650 - 2000	29.6	[Andersen et al., 2012a]
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10- Heptadecafluorodec-1-ene	21652-58- 4		C ₈ F ₁₇ CH=CH ₂	E	298	650 - 2000	33.7	[Andersen et al., 2012a]

4358 ² Integrated absorption cross-section in units of 10^{-17} cm² molecule⁻¹ cm⁻¹ for the wavenumber interval specified.

4359 ³ Database: H, HITRAN 2008; G, GEISA 2009.

4361	Table 7. Lifetimes, radiative efficiencies and direct GWPs (relative to CO ₂) for hydrofluorocarbons (HFCs).
4362	Compounds in bold either have significant current atmospheric concentrations or a clear potential for future
4363	emissions. Recommended RE and GWP 100-yr values are indicated in bold. Lifetimes are from WMO [2011]
4364	except those in italic (see text for details). RE and GWP values in italic are based on previous publications (see
4365	text for details).

			Radia	tive Efficie	ency (W	GWP	100-yr
				m ² ppb ²)		
Acronym / name	Formula	Lifetime	AR4	This	This	AR4	This
		(yr)		study –	study –		study –
				const.	lifetime		lifetime
				profile	corr.		corr.
HFC-23	CHF ₃	222.0	0.19	0.18	0.18	14,800	12,400
HFC-32	CH_2F_2	5.2	0.11	0.12	0.11	675	677
HFC-41	CH ₃ F	2.8	0.02	0.03	0.02	92	116
HFC-125	CHF_2CF_3	28.2	0.23	0.23	0.23	3,500	3,170
HFC-134	CHF ₂ CHF ₂	9.7	0.18	0.20	0.19	1,100	1,120
HFC-134a	CH ₂ FCF ₃	13.4	0.16	0.17	0.16	1,430	1,300
HFC-143	CH ₂ FCHF ₂	3.5	0.13	0.14	0.13	353	328
HFC-143a	CH ₃ CF ₃	47.1	0.13	0.16	0.16	4,470	4,800
HFC-152	CH_2FCH_2F	0.4	0.09	0.08	0.04	53	16
HFC-152a	CH_3CHF_2	1.5	0.09	0.12	0.10	124	138
HFC-161	CH ₃ CH ₂ F	66.0 days	0.03	0.04	0.02	12	4
HFC-227ca	CF ₃ CF ₂ CHF ₂	28.2		0.27	0.27		2,640
HFC-227ea	CF ₃ CHFCF ₃	38.9	0.26	0.26	0.26	3,220	3,350
HFC-236cb	CH ₂ FCF ₂ CF ₃	13.1	0.23	0.24	0.23	1,340	1,210
HFC-236ea	CHF ₂ CHFCF ₃	11.0	0.30			1,370	1,330
HFC-236fa	CF ₃ CH ₂ CF ₃	242.0	0.28	0.24	0.24	9,810	8,060
HFC-245ca	CH ₂ FCF ₂ CHF ₂	6.5	0.23		0.24	693	716
HFC-245cb	CF ₃ CF ₂ CH ₃	47.1		0.25	0.24		4,620
HFC-245ea	CHF ₂ CHFCHF ₂	3.2		0.18	0.16		235
HFC-245eb	CH ₂ FCHFCF ₃	3.1		0.23	0.20		290
HFC-245fa	$CHF_2CH_2CF_3$	7.7	0.28	0.26	0.24	1,030	858
HFC-263fb	CH ₃ CH ₂ CF ₃	1.2		0.13	0.10		76
HFC-272ca	CH ₃ CF ₂ CH ₃	2.6		0.08	0.07		144
HFC-329p	CHF ₂ CF ₂ CF ₂ CF ₃	28.4		0.31	0.31		2,360
HFC-365mfc	CH ₃ CF ₂ CH ₂ CF ₃	8.7	0.21	0.23	0.22	794	804
HFC-43-10mee	CF ₃ CHFCHFCF ₂ CF ₃	16.1	0.40		0.42	1,640	1,650
HFC-1132a	$CH_2 = CF_2$	4.0 days		0.10	0.00		0
HFC-1141	CH ₂ =CHF	2.1 days		0.09	0.00		0
(Z)-HFC-1225ye	$CF_3CF=CHF(Z)$	8.5 days		0.26	0.02		0
(E)-HFC-1225ye	$CF_3CF=CHF(E)$	4.9 days		0.25	0.01		0
(Z)-HFC-1234ze	$CF_3CH=CHF(Z)$	10.0 days		0.20	0.02		0
HFC-1234yf	$CF_3CF=CH_2$	10.5 days		0.23	0.02		0
(E)-HFC-1234ze	trans-CF ₃ CH=CHF	16.4 days		0.28	0.04		1
(Z)-HFC-1336	$CF_3CH=CHCF_3(Z)$	22.0 days		0.42	0.07		2
HFC-1243zf	CF ₃ CH=CH ₂	7.0 days		0.17	0.01		0
HFC-1345zfc	C ₂ F ₅ CH=CH ₂	7.6 days		0.19	0.01		0
3,3,4,4,5,5,6,6,6-	C E CII-CII	76 days		0.25	0.02		0
Nonafluorohex-1-ene	$C_4F_9CH=CH_2$	7.0 aays		0.55	0.03		U
3,3,4,4,5,5,6,6,7,7,8,8,							
8-Tridecafluorooct-1-	$C_6F_{13}CH=CH_2$	7.6 days		0.39	0.03		0
ene		-					
3,3,4,4,5,5,6,6,7,7,8,8,	C ₈ F ₁₇ CH=CH ₂	7.6 days		0.44	0.03		0

Table 8. Integrated absorption cross-sections (S) for chlorocarbons and hydrochlorocarbons from the literature. Spectra used in RE calculations in the present study are indicated in bold.

Name	CAS#	Trivial name	Formula	Data ¹	T/K	Wn. range /cm ⁻¹	S^2	Reference	Database ³
1,1,1-Trichloroethane	71-55-6	Methyl chloroform	CH ₃ CCl ₃	E	295	480 - 1490	5.1	[Orkin et al., 2003]	
				E	296	700 - 1500	5.0	[Imasu et al., 1995]	
				E		669 - 1397	4.5	[Fisher et al., 1990]	
Perchloromethane, tetrachloromethane	56-23-5	Carbon tetrachloride	CCl_4	Е	297	750 - 812	6.2	[<i>Nemtchinov and Varanasi</i> , 2003]	G
				E	297	750 - 812	6.2	[Varanasi-priv.com., 2000]	Н
				E	298	730 - 825	5.9	[Orlando et al., 1992]	
				E	298	773 - 802	3.7	[Brown et al., 1987]	
				E	298	786 - 806	3.6	[<i>Massie et al.</i> , 1985]	
				E		616 - 934	4.5	[Fisher et al., 1990]	
Chloromethane	74-87-3	Methyl chloride	CH ₃ Cl	E		661 - 1646	1.4	[Grossman et al., 1997]	
Dichloromethane	75-09-2	Methylene chloride	CH_2Cl_2	А		250 - 3300	3.3	[Bera et al., 2009]	
Trichloromethane	67-66-3	Chloroform	CHCl ₃	Е	295	540 - 1600	5.6	[<i>McPheat and Duxbury</i> , 2000]	
1,2-Dichloroethane	107-06-2		CH ₂ ClCH ₂ Cl	E	293	600 - 1700	2.1	[Vander Auwera, 2000]	

4370 ¹ Type of data: E, Experimental; A, Ab initio.

4371 ² Integrated absorption cross-section in units of 10^{-17} cm² molecule⁻¹ cm⁻¹ for the wavenumber interval specified.

4372 ³ Database: H, HITRAN 2008; G, GEISA 2009.

4373

Table 9. Lifetimes, radiative efficiencies and direct GWPs (relative to CO_2) for chlorocarbons and 4377 hydrochlorocarbons. Compounds in bold either have significant current atmospheric concentrations or a clear

- 4378 potential for future emissions. Recommended RE and GWP 100-yr values are indicated in bold. Lifetimes are
- 4379 from *WMO* [2011].

			Radiati	ve Efficiency ¹)	(W m ⁻² ppb ⁻	GW	P 100-yr
Acronym / name	Formula	Lifetime (yr)	AR4	This study	This study	AR4	This study
				– const.	– lifetime		– lifetime
				profile	corr.		corr.
Methyl chloroform	CH ₃ CCl ₃	5.0	0.06	0.08	0.07	146	160
Carbon tetrachloride	CCl_4	26.0	0.13	0.18	0.17	1,400	1,730
Methyl chloride	CH ₃ Cl	1.0	0.01			13	12
Methylene chloride	CH_2Cl_2	0.4	0.03			9	9
Chloroform	CHCl ₃	0.4	0.11	0.14	0.08	31	16
1,2-Dichloroethane	CH ₂ ClCH ₂ Cl	65.0 days		0.02	0.01		1

Name	CAS#	Acronym / trivial name	Formula	Data ¹	<i>T /</i> K	Wn. range $/cm^{-1}$	S^2	Reference Datab	base ³
Bromomethane	74-83-9	Methyl bromide	CH ₃ Br	Е	296	450 - 2000	0.7	[Sihra et al., 2001]	
			5	Е	296	450 - 2000	0.8	[Christidis et al., 1997]	
				E		550 - 1600	1.2	[Grossman et al., 1997]	
				E				[Graner, 1981]	
Dibromomethane	74-95-3	Methylene bromide	CH_2Br_2	E	296	450 - 2000	2.1	[Sihra et al., 2001]	
		-		E	296	450 - 2000	2.0	[Christidis et al., 1997]	
Bromodifluoromethane	1511-62-2	Halon-1201	CHBrF ₂	E,A	298	530 - 1460	10.2	[Charmet et al., 2010]	
				E	295	530 - 1400	10.1	[Orkin et al., 2003]	
				E	296	450 - 2000	10.0	[Sihra et al., 2001]	
				E	296	450 - 2000	9.9	[Christidis et al., 1997]	
Dibromodifluoromethane	75-61-6	Halon-1202	CBr_2F_2	E	295	400 - 1600	11.8	[Orkin et al., 2003]	
Bromochlorodifluoromethane	353-59-3	Halon-1211	CBrClF ₂	E	296	450 - 2000	12.4	[Sihra et al., 2001]	
				E	296	450 - 2000	11.5	[Christidis et al., 1997]	
Bromotrifluoromethane	75-63-8	Halon-1301	CBrF ₃	E	298	461 - 2500	16.7	[Charmet et al., 2008]	
				E	298	720 - 1250	15.4	[<i>Drage et al.</i> , 2006]	
				E	295	720 - 1250	16.4	[Orkin et al., 2003]	
				E	296	450 - 2000	17.0	[Sihra et al., 2001]	
				Е		1040 - 1250	16.0	[Varanasi and Chudamani, 1988b]	
				E		1040 - 1250	16.1	[Ramanathan et al., 1985]	
				Е		720 - 1250	15.9	[Person and Polo, 1961]	
2-Bromo-1,1,1- trifluoroethane	421-06-7	Halon-2301	CH ₂ BrCF ₃	Е	295	590 - 1510	12.8	[Orkin et al., 2003]	
2-Bromo-2-chloro-1,1,1- trifluoroethane	151-67-7	Halon-2311 / Halothane	CHBrClCF ₃	E	298	650 - 1500	12.2	[Andersen et al., 2012b]	
				Е	295	480 - 1370	13.0	[Orkin et al., 2003]	
2-Bromo-1,1,1,2- tetrafluoroethane	124-72-1	Halon-2401	CHFBrCF ₃	Е	295	490 - 1480	14.6	[Orkin et al., 2003]	
1,2-Dibromo-1,1,2,2- tetrafluoroethane	124-73-2	Halon-2402	$CBrF_2CBrF_2$	Е	296	450 - 2000	15.4	[Sihra et al., 2001]	

Table 10. Integrated absorption cross-sections (S) for bromocarbons, hydrobromocarbons and halons from the literature. Spectra used in RE calculations in the present
 study are indicated in bold.

- 4384 ¹ Type of data: E, Experimental; A, Ab initio.
- 4385 ² Integrated absorption cross-section in units of 10^{-17} cm² molecule⁻¹ cm⁻¹ for the wavenumber interval specified.
- 4386 ³ Database: H, HITRAN 2008; G, GEISA 2009.

- 4389 Table 11. Lifetimes, radiative efficiencies and direct GWPs (relative to CO_2) for bromocarbons,
- 4390 hydrobromocarbons and halons. Compounds in bold either have significant current atmospheric concentrations
- 4391 or a clear potential for future emissions. Recommended RE and GWP 100-yr values are indicated in bold.
- 4392 Lifetimes are from *WMO* [2011].

			Radiati	ve Efficiency ¹)	GW	P 100-yr	
Acronym / name	Formula	Lifetime (yr)	AR4	This study	This study	AR4	This study
				profile	- metime corr.		- meume corr.
Methyl bromide	CH ₃ Br	0.8	0.01	0.01	0.00	5	2
Methylene bromide	CH_2Br_2	0.3	0.01	0.02	0.01	2	1
Halon-1201	CHBrF ₂	5.2	0.14	0.17	0.15	404	376
Halon-1202	CBr_2F_2	2.9		0.31	0.27		231
Halon-1211	$CBrClF_2$	16.0	0.30	0.31	0.29	1,890	1,750
Halon-1301	CBrF ₃	65.0	0.32	0.31	0.30	7,140	6,290
Halon-2301	CH ₂ BrCF ₃	3.4		0.15	0.14		173
Halon-2311 /	CUD+CICE	1.0		0.19	0.13		41
Halothane	CHBICICF ₃	1.0		0.18	0.15		41
Halon-2401	CHFBrCF ₃	2.9		0.21	0.19		184
Halon-2402	$CBrF_2CBrF_2$	20.0	0.33	0.34	0.31	1,640	1,470

4395	Table 12. Integrated absorption cross-sections (S) for fully fluorinated species from the literature. Spectra used in RE calculations in the present study are indicated in
4396	bold.

Name	CAS#	Acronym	Formula	Data ¹	T/K	Wn. range /cm ⁻¹	S^2	Reference	Database ³
Nitrogen trifluoride	7783-54- 2		NF ₃	Е	296	400 - 2000	7.0	[Robson et al., 2006]	
Sulphur hexafluoride	2551-62- 4		SF_6	Е				[Vlachogiannis et al., 2005]	
				E E	296	900 - 1000	20.7	[Hurley-priv.com., 2003]	G
				Ē	295	925 - 955	18.8	[Varanasi-priv.com., 2000]	Н
				Ē	216	925 - 955	18.9	[Varanasi et al., 1994]	Н
				Ē	-10	640 - 1225	20.2	$[Ko \ et \ al., 1993]$	
				Ē		010 1225	18.0	[<i>Chapados</i> , 1988]	
				Ē			17.6	[$McDowell et al., 1986$]	
				Ē			17.6	[Dunn et al., 1982]	
				Ē			18.3	[Brodbeck et al., 1980]	
				Ē			22.6	[<i>Kim et al.</i> , 1980]	
				Ē			17.9	[Schatz and Hornig, 1953]	
(Trifluoromethyl)sulfur pentafluoride	373-80-8		SF ₅ CF ₃	Е	298	599 - 2500	28.6	[Rinsland et al., 2003]	Н
Pennanderide				Е	296	670 - 1325	25.2	[Hurley-priv.com., 2003]	G
				Е	296	400 - 1330	26.5	[Nielsen et al., 2002]	-
				Е	296	700 - 2000	25.4	[<i>Sihra et al.</i> , 2001]	
				Е	296	670 - 1325	25.4	[<i>Sturges et al.</i> , 2000]	
Sulfuryl fluoride	2699-79- 8		SO_2F_2	Е	296	805 - 1760	13.0	[Andersen et al., 2009]	
	0			Е		500 - 1542	13.6	[Dillon et al 2008]	
				Ē,A	296	500 - 1542	14.0	[<i>Papadimitriou et al.</i> , 2008b]	
Perfluoromethane, tetrafluoromethane	75-73-0	PFC-14	CF_4	А		700 - 1400	19.3	[Bravo et al., 2010b]	
				Е	296	1230 - 1300	19.0	[<i>Hurley et al.</i> , 2005]	
				Е	296	1230 - 1300	21.9	[Hurley-priv.com., 2003]	G
				Е	296	500 - 1400	21.9	[<i>Sihra et al.</i> , 2001]	
				Е	296	1250 - 1290	19.1	[Varanasi-priv.com., 2000]	Н

						<00 1 5 00	a a 1	[D] 1 100 7]	
				A	200	600 - 1500	20.1	[Papasavva et al., 1997]	
				E	300	590 - 1320	18.5	[<i>Roehl et al.</i> , 1995]	
				E	293	1255 - 1310	17.3	[<i>McDaniel et al.</i> , 1991]	
				Е		1255 - 1310	14.0	[Varanasi and Chudamani, 1988b]	
				Е		1255 - 1310	16.9	[Golden et al., 1978]	
Perfluoroethane	76-16-4	PFC-116	C_2F_6	А			26.3	[Bera et al., 2010]	
				E	297	700 - 1400	23.0	[Bravo et al., 2010b]	
				А		700 - 1400	22.5	[Bravo et al., 2010b]	
				E	296	1061 - 1285	21.0	[Zou et al., 2004]	Н
				E	296	450 - 1500	21.6	[Sihra et al., 2001]	
				E	293	675 - 1400	22.8	[Ballard et al., 2000a]	
				Е	253	680 - 1380	22.8	[Highwood and Shine, 2000]	
				E	296	690 - 1360	21.5	[Highwood et al., 1999]	G
				А		600 - 1500	22.7	[Papasavva et al., 1997]	
				Е	300	480 - 1385	21.6	[Roehl et al., 1995]	
				Е				[Varanasi and Chudamani, 1988b]	
				F				$[Mills \ et \ al \ 1958]$	
				E	293	690 - 1360	22.2	[M S F / R A L]	G
Perfluorocyclopropane	931-91-9	PFC-c216	c-C ₂ E ₆	A	275	0 - 2500	16.9	[Bravo et al 2010b]	0
Perfluoropropane	76-19-7	PFC-218	$C_2 F_2$	A		0 2000	30.4	[Bera et al 2010]	
i ennuoropropune	10 17 1	110 210	0318	E	297	700 - 1400	26.8	[Bravo et al., 2010b]	
				A	277	700 - 1400	27.6	[Bravo et al 2010b]	
				E	296	500 - 1500	27.5	[Sihra et al 2001]	
				F	300	500 - 1550	27.5	[Rochl et al., 2001]	
Perfluorocyclobutane	115-25-3	PFC-318	c-C ₄ E ₂	A	500	0 - 2500	22.0	[Rravo et al., 2010b]	
remuoroeyerobulune	115 25 5	110 510		F	297	550 - 1500	21.1	[Vasekova et al. 2006]	
				E	297	550 - 1500	21.7 22.2	[<i>Rallard et al</i> 2000a]	
				F	253	555 - 1460	21.6	[Highwood and Shing 2000]	
				F	295	555 - 1430	21.0	$[M \subseteq F / R \land I]$	G
Perfluorobutane	355-25-9	PFC-31-10	C.E.		271	555 - 1450	36.0	[M.5.1.7, M.1.2.]	U
remuorobutane	555 25 7	110 51 10	C41 10	F	297	450 - 1500	31.7	[Bravo et al 2010]	
				Δ	271	0 - 2500	32.5	[Bravo et al 2010b]	
				Ē	296	450 - 1500	31.7	[Sihra et a] 2001]	
				Ē	300	500 - 1550	27.2	[Roehl et al 1995]	
Perfluorocyclopentene	559-40-0		$c-C_5F_8$	Ē	500	200 1220	24.0	[Bravo et al., 2010b]	

				-	205		20.0	
				E	297	550 - 1800	20.9	[Vasekova et al., 2006]
Perfluoropentane	678-26-2	PFC-41-12	$n-C_5F_{12}$	E	297	210 - 2000	36.3	[Bravo et al., 2010b]
				А		0 - 2500	37.2	[<i>Bravo et al.</i> , 2010b]
				E	300	500 - 1550	34.6	[Roehl et al., 1995]
Perfluorohexane	355-42-0	PFC-51-14	$n-C_6F_{14}$	E	297	210 - 2000	38.5	[Bravo et al., 2010b]
				А		0 - 2500	41.8	[<i>Bravo et al.</i> , 2010b]
				E	300	500 - 1550	39.6	[Roehl et al., 1995]
Perfluoroheptane	335-57-9	PFC-61-16	$n-C_7F_{16}$	E	296	500 - 4000	44.7	[Ivy et al., 2012]
		PFC-71-18	C_8F_{18}	E	296	500 - 4000	52.3	[Ivy et al., 2012]
				E	297	700 - 1400	45.6	[Bravo et al., 2010b]
				А		700 - 1400	50.9	[Bravo et al., 2010b]
Perfluorodecalin (mixed)	306-94-5	PFC-91-18	$C_{10}F_{18}$	А		0 - 2500	43.2	[Bravo et al., 2010b]
				Е	296	0 - 1500	39.1	[Shine et al., 2005b]
	60433-					a a r aa		
Perfluorodecalin (cis)	11-6		$c_{10}F_{18}$	А		0 - 2500	43.4	[<i>Bravo et al.</i> , 2010b]
				Е	296	655 - 1370	37.9	[Shine et al., 2005b]
	60433-					0.0500	42.0	
Perfluorodecalin (trans)	12-7		trans- $C_{10}F_{18}$	А		0 - 2500	43.0	[Bravo et al., 2010b]
				Е	296	655 - 1360	35.6	[Shine et al., 2005b]
Perfluoroethene	116-14-3	PFC-1114	$CF_2 = CF_2$	Е	296	1080 - 1400	12.0	[Drage et al., 2006]
			2 2	Е	298	1080 - 1400	12.9	[Acerboni et al., 2001]
Perfluoropropene	116-15-4	PFC-1216	CF ₃ CF=CF ₂	Е	298	970 - 1850	23.5	[Acerboni et al., 2001]
Perfluorobuta-1.3-diene	685-63-2		CF ₂ =CFCF=CF ₂	Е			20.7	[<i>Bravo et al.</i> , 2010b]
, , , , , , , , , , , , , , , , , , ,			- 2 2	А			21.9	[Bravo et al., 2010b]
				E	298	900 - 1850	21.8	[Acerboni et al., 2001]
Perfluorobut-1-ene	357-26-6		CF ₂ CF ₂ CF=CF ₂	Ē	296	635 - 1830	24.0	[Young et al., 2009a]
Perfluorobut-2-ene	360-89-4		$CF_2CF=CFCF_2$	Ē	298	500 - 1410	25.3	[Cometto et al. 2010]
remultioned 2 che	500 07 4			F	296	650 - 1500	23.5	[Voung et al 2009a]
				L	270	050 - 1500	20.0	[10005 01 00., 20070]

4398 ² Integrated absorption cross-section in units of 10^{-17} cm² molecule⁻¹ cm⁻¹ for the wavenumber interval specified.

4399 ³ Database: H, HITRAN 2008; G, GEISA 2009.

- 4401 Table 13. Lifetimes, radiative efficiencies and direct GWPs (relative to CO₂) for fully fluorinated species.
- 4402 Compounds in bold either have significant current atmospheric concentrations or a clear potential for future
- 4403 emissions. Recommended RE and GWP 100-yr values are indicated in bold. Lifetimes are from WMO [2011]
- 4404 except those in italic (see text for details). RE and GWP values in italic are based on previous publications (see
- text for details).

			Radiati	ve Efficiency ¹)	GWP 100-yr		
Acronym / name	Formula	Lifetime (yr)	AR4	This study – const.	This study – lifetime	AR4	This study – lifetime
				profile	corr.		corr.
Nitrogen trifluoride	NF ₃	500.0	0.21	0.21	0.20	17,200	16,100
Sulphur hexafluoride	SF_6	3,200.0	0.52	0.57	0.57	22,800	23,500
(Trifluoromethyl)sulfur	SE CE	800.0	0.57	0.60	0.50	17 700	17 400
pentafluoride	51.201.3	800.0	0.57	0.00	0.59	17,700	17,400
Sulfuryl fluoride	SO_2F_2	36.0		0.21	0.20		4,090
PFC-14	CF_4	50,000.0	0.10	0.09	0.09	7,390	6,630
PFC-116	C_2F_6	10,000.0	0.26	0.25	0.25	12,200	11,100
PFC-c216	$c-C_3F_6$	3,000.0	0.42	0.23	0.23	17,300	9,200
PFC-218	C_3F_8	2,600.0	0.26	0.28	0.28	8,830	8,900
PFC-318	$c-C_4F_8$	3,200.0	0.32	0.32	0.32	10,300	9,540
PFC-31-10	C_4F_{10}	2,600.0	0.33	0.37	0.36	8,860	9,200
Perfluorocyclopentene	$c-C_5F_8$	31.0 days		0.33	0.08		2
PFC-41-12	$n-C_5F_{12}$	4,100.0	0.41	0.41	0.41	9,160	8,550
PFC-51-14	$n-C_6F_{14}$	3,100.0	0.49	0.45	0.44	9,300	7,910
PFC-61-16	$n-C_7F_{16}$	3,000.0		0.51	0.50		7,820
PFC-71-18	C_8F_{18}	3,000.0		0.56	0.55		7,620
Perfluorodecalin (mixed)	$C_{10}F_{18}$	2,000.0	0.56	0.56	0.55	7,500	7,190
Perfluorodecalin (cis)	$cis-C_{10}F_{18}$	2,000.0		0.57	0.56		7,240
Perfluorodecalin (trans)	trans- $C_{10}F_{18}$	2,000.0		0.49	0.48		6,290
PFC-1114	$CF_2 = CF_2$	1.1 days		0.12	0.00		0
PFC-1216	CF ₃ CF=CF ₂	4.9 days		0.25	0.01		0
Perfluorobuta-1,3-diene	$CF_2 = CFCF = CF_2$	1.1 days		0.24	0.00		0
Perfluorobut-1-ene	$CF_3CF_2CF=CF_2$	6.0 days		0.30	0.02		0
Perfluorobut-2-ene	CF ₃ CF=CFCF ₃	31.0 days		0.29	0.07		2

4408	Table 14. Integrated absorption cross-sections (S) for halogenated alcohols and ethers from the literature. Spectra used in RE calculations in the present study are indicated
4409	in bold.

Name	CAS#	Acronym	Formula	Data ¹	T/K	Wn. range /cm ⁻¹	S^2	Reference	Data base ³
(Difluoromethoxy)trifluoromethane	3822-68-2	HFE-125	CHF ₂ OCF ₃	А	277	0 - 1500		[Blowers et al., 2008a]	
				А				[Blowers et al., 2007]	
				E	296	450 - 1650	31.7	[Sihra et al., 2001]	
				E	295	980 - 1510	31.2	[Orkin et al., 1999]	
				А				[Good et al., 1998]	
				E	298	475 - 1590	32.9	[Heathfield et al., 1998]	
				E	296	450 - 2000	29.2	[Christidis et al., 1997]	
(Difluoromethoxy)difluoromethane	1691-17-4	HFE-134 (HG-00)	CHF ₂ OCHF ₂	А		31 - 2500	26.5	[Bravo et al., 2011a]	
				E	296	700 - 1500	25.7	[Andersen et al., 2010a]	
				А	277	0 - 1500		[Blowers et al., 2008a]	
				А				[Blowers et al., 2007]	
				Е	298	25 - 3250	25.0	[Myhre et al., 1999]	
				Е	295	741 - 1443	25.4	[Orkin et al., 1999]	
				А				[Good et al., 1998]	
				Е	298	750 - 1480	25.6	[Heathfield et al., 1998]	
				Е	296	700 - 1500	25.5	[Imasu et al., 1995]	
				Е		770 - 1430	25.3	[Garland et al., 1993]	
Trifluoro(methoxy)methane	421-14-7	HFE-143a	CH ₃ OCF ₃	А		78 - 1503	22.3	[Bravo et al., 2011a]	
•				А	277	0 - 1500		[Blowers et al., 2008a]	
				А				[Blowers et al., 2007]	
				Е	296	550 - 1520	19.9	[Sihra et al., 2001]	
				Е				[Christensen et al., 1999]	
				Ā				[Good et al., 1998]	
1,1,1,2-Tetrafluoro-2- (trifluoromethoxy)ethono	2356-62-9	HFE-227ea	CF ₃ CHFOCF ₃	А				[Blowers et al., 2007]	
(innuorometrioxy)ethane				F	208	485 - 1600	37.0	[Ovaro et al. 2005]	
				E	296	405 - 1000 645 - 1460	37.0	[Takahashi at al 2002]	
				E	290	700 1500	41.0	$\begin{bmatrix} I a kanashi et al., 2002 \end{bmatrix}$	
				E	290	700 - 1500	26.0	[Juin et al., 2001]	
					290	700 - 1300 500 - 2000	20.9	[<i>Imasu et al.</i> , 1995]	
2-Chloro-1-(difluoromethoxy)-1 1 2-				E,A	290	500 - 2000	36.4	[Suga et al., 1994]	
trifluoroethane	13838-16-9	HCFE-235ca2 (enflurane)	CHF ₂ OCF ₂ CHFCl	Е	298	650 - 1500	26.8	[Andersen et al., 2012b]	
						800 - 1500	25.1	[Dalmasso et al., 2006]	
2-Chloro-2-(difluoromethoxy)-1,1,1- trifluoroethane	26675-46-7	HCFE-235da2 (isoflurane)	CHF ₂ OCHClCF ₃	Е	298	650 - 1500	29.1	[Andersen et al., 2010c]	
				Е		400 - 1500	28.5	[Ryan and Nielsen, 2010]	
				Е	296	450 - 1650	27.5	[Sihra et al., 2001]	
				Е	296	450 - 2000	26.3	Christidis et al., 19971	
1-(Difluoromethoxy)-1.1.2.2-tetrafluoroethane	32778-11-3	HFE-236ca	CHF ₂ OCF ₂ CHF ₂	А				[Blowers et al., 2007]	

2-(Difluoromethoxy)-1,1,1,2-tetrafluoroethane	57041-67-5	HFE-236ea2 (desflurane)	CHF ₂ OCHFCF ₃	А		43 - 2500	31.9	[Bravo et al., 2011a]
<pre></pre>			- 2 2	Е	298	650 - 1500	31.3	[Andersen et al., 2010c]
				А				[Blowers et al., 2007]
				Е	298	485 - 1530	30.3	[Ovaro et al., 2005]
				Е	296	700 - 1500	29.9	[Imasu et al., 1995]
1,1,1-Trifluoro-2-(trifluoromethoxy)ethane	20193-67-3	HFE-236fa	CF ₃ CH ₂ OCF ₃	А				[Blowers et al., 2007]
				Е	296	700 - 1500	33.5	[Imasu et al., 1995]
1,1,1,2,2-Pentafluoro-2-methoxy-ethane	22410-44-2	HFE-245cb2	CF ₃ CF ₂ OCH ₃	А		45 - 1501	26.0	[Bravo et al., 2011a]
				А				[Blowers et al., 2007]
				Е	296	700 - 1500	24.6	[Imasu et al., 1995]
1,1-Difluoro-2-(trifluoromethoxy)ethane	84011-15-4	HFE-245fa1	CHF ₂ CH ₂ OCF ₃	А				[Blowers et al., 2007]
				Е	296	700 - 1500	27.9	[Imasu et al., 1995]
2-(Difluoromethoxy)-1,1,1-trifluoroethane	1885-48-9	HFE-245fa2	CHF ₂ OCH ₂ CF ₃	А				[Blowers et al., 2007]
				Е	298	470 - 1550	26.5	[Oyaro et al., 2005]
				Е	296	450 - 1550	26.3	[Sihra et al., 2001]
				Е	296	450 - 2000	25.1	[Christidis et al., 1997]
				Е	296	700 - 1500	26.3	[Imasu et al., 1995]
2,2,3,3,3-Pentafluoropropan-1-ol	422-05-9		CF ₃ CF ₂ CH ₂ OH	Е	298	600 - 4000	20.5	[Antiñolo et al., 2012b]
				Е	298	490 - 1500	18.0	[Sellevåg et al., 2007]
				Е	296	700 - 1500	17.9	[Imasu et al., 1995]
1,1,2,2-Tetrafluoro-1-methoxyethane	425-88-7	HFE-254cb1	CH ₃ OCF ₂ CHF ₂	А		66 - 2500	20.1	[Bravo et al., 2011a]
				А				[Blowers et al., 2007]
				E	298	500 - 1600	19.6	[Heathfield et al., 1998]
				Е	296	700 - 1500	19.1	[Imasu et al., 1995]
1,1,1-Trifluoro-2-methoxyethane	460-43-5	HFE-263fb1	CF ₃ CH ₂ OCH ₃	E	296	600 - 1600	15.5	[Osterstrom et al., 2012]
				А				[Bravo et al., 2011a]
				A				[<i>Blowers et al.</i> , 2007]
				E	298	500 - 1525	15.3	[<i>Oyaro et al.</i> , 2005]
				Е	296	700 - 1500	15.2	[Imasu et al., 1995]
1,1,2,2-Tetrafluoro-1- (trifluoromethoxy)ethane	690-22-2	HFE-263m1	CF ₃ OCH ₂ CH ₃	А		42 - 1562	22.9	[Bravo et al., 2011a]
				А				[Blowers et al., 2007]
				Е	298	550 - 1550	22.0	[Oyaro et al., 2005]
3,3,3-Trifluoropropan-1-ol	2240-88-2		CF ₃ CH ₂ CH ₂ OH	Е	298	500 - 4000	16.6	[Jimenez, et al., 2010]
1 1				Е	298	515 - 1550	13.8	[Sellevåg et al., 2007]
				Е	296	650 - 1530	14.6	[Waterland et al., 2005]
1,1,1,2,2-Pentafluoro-2-(1,1,2,2- tetrafluoroethoxy)ethane	134769-21-4	HFE-329mcc2	CHF ₂ CF ₂ OCF ₂ CF ₃	А				[<i>Blowers et al.</i> , 2007]
				Е	296	700 - 1500	39.2	[Imasu et al., 1995]
2-(Difluoromethoxy)-1,1,1,3,3,3- hexafluoropropane	26103-08-2	HFE-338mmz1	(CF ₃) ₂ CHOCHF ₂	А				[Blowers et al., 2007]
1 1 1 2 2 Dente flarenz 2 /2 2 2				Е	296	700 - 1500	35.4	[Imasu et al., 1995]
1,1,1,2,2-Pentalluoro-2-(2,2,2- trifluoroethoxy)ethane	156053-88-2	HFE-338mcf2	CF ₃ CH ₂ OCF ₂ CF ₃	А				[Blowers et al., 2007]
1,1,1,3,3,3-Hexafluoro-2-	28523-86-6	Sevoflurane (HFE-	(CF ₃) ₂ CHOCH ₂ F	E A	296	700 - 1500 39 - 2500	34.7 32.2	[Imasu et al., 1995] [Bravo et al., 2011a]

(fluoromethoxy)propage		347mmz1)						
(indofonieuloxy)propane		34/IIIII21)		F	298	650 - 1500	30.2	[Anderson et al 2010c]
				F	270	650 - 1500	30.6	[Ryan and Nielson 2010]
1 1 1 2 2 3 3-Hentafluoro-3-methoxypropage	375-03-1	HEE_347mcc3 (HEE_7000)	CH-OCE-CE-CE-			51 - 2500	31.1	[Rravo et al. 2011a]
1,1,1,2,2,3,5-11eptantioro-5-methoxypropane	575-05-1	III L-34/Ince3 (III L-7000)	CH30CF 2CF 2CF 3	F		700 1400	28.2	[Brave at al 2010a]
						700 - 1400	20.2	$\begin{bmatrix} Blowers et al. 2007 \end{bmatrix}$
				E		700 1500	27.4	[<i>Ninoming et al.</i> 2000]
				E	200	700 - 1500	27.4	[<i>Ivinomiya el al.</i> , 2000]
1 (2.2 Diffuerentherry) 1 1 2 2 2				E	290	/00 - 1300	29.5	[<i>Imasu et al.</i> , 1995]
n-(2,2-Diffuoroethane	171182-95-9	HFE-347mcf2	CHF ₂ CH ₂ OCF ₂ CF ₃	А				[Blowers et al., 2007]
pentanuoroethane				Е	296	700 - 1500	30.2	[Imasu et al., 1995]
1,1,2,2-Tetrafluoro-1-(2,2,2-	406-78-0	HFE-347pcf2	CHF ₂ CF ₂ OCH ₂ CF ₃	А				[Blowers et al., 2007]
trifuoroetnoxy)etnane				Б	208	500 1600	22.2	[Heathfield at al. 1008]
1 1 1 2 3 3 3 Hentafluoro 2 methovypropage	22052 84 2	HEE 3/7mmv1	(CE) CEOCH		298	500 - 1000	32.2	[<i>Revers et al.</i> 2007]
1,1,1,2,5,5,5-Heptanuoro-2-methoxypropane	22032-04-2	III E-547 IIIIIy I	(CF3)2CFOCF13	E	206	700 1500	28.6	[Image et al. 1005]
1 1 1 2 2 2 Haveflyon 2 methowymenes	202 24 2	LIEE 256maa2	CU OCE CUECE		290	700 - 1300	20.0	[<i>Imusu et al.</i> , 1995]
1,1,1,2,3,3-Hexanuolo-3-meuloxyplopane	362-34-3	HrE-550mec5	CH ₃ OCI ² CHI ⁴ CI ⁴ ₃	E	206	700 1500	25.8	[Imagy et al. 1005]
	222 26 0	LIEE 256mfP	CE CH OCH CE		290	700 - 1300	23.0	[<i>Imusu et al.</i> , 1995]
	333-30-8	HFE-550IIII12	$CF_3CH_2OCH_2CF_3$	A	200	500 1600	27.2	[Diowers et al., 2007]
				E	290	500 - 1600	27.2	[<i>Oyaro et al.</i> , 2004]
				E	290	500 - 1500	28.1	[Sthra et al., 2001]
				E	293	500 - 1600	21.1	[<i>Urkin et al.</i> , 1999]
1 (2.2 Diffuerentherry) 1 1 2 2				E				[wallington et al., 1998]
tetrafluoroethane	50807-77-7	HFE-356pcf2	CHF ₂ CH ₂ OCF ₂ CHF ₂	А				[Blowers et al., 2007]
				Е	296	700 - 1500	24.9	[Imasu et al., 1995]
3-(Difluoromethoxy)-1,1,2,2- tetrafluoropropane	35042-99-0	HFE-356pcf3	CHF2OCH2CF2CHF2	А				[Blowers et al., 2007]
······································				E	296	700 - 1500	24.8	[Imasu et al., 1995]
1.1.2.2.3.3-Hexafluoro-1-methoxypropane	160620-20-2	HFE-356pcc3	CH ₂ OCF ₂ CF ₂ CHF ₂	Ā	-/ *			[Blowers et al., 2007]
-,-,-,-,-,-,				E	296	700 - 1500	23.4	[Imasu et al., 1995]
1.1.1.3.3.3-Hexafluoro-2-methoxypropane	13171-18-1	HFE-356mmz1	(CF ₂) ₂ CHOCH ₂	Ă	270	100 1000	2011	[Blowers et al., 2007]
1,1,1,0,0,0,0 Heiminuoro 2 meniorijpropune	101/1 10 1		(013)201100113	E	298	475 - 1550	25.8	[Ovaro et al., 2004]
				Ē	296	700 - 1500	25.7	[Imasu et al., 1995]
1 1 1 2 2-Pentafluoro-3-methoxypropane	378-16-5	HFE-365mcf3	CE ₂ CE ₂ CH ₂ OCH ₂	Ē	296	650 - 1500	20.7	[Thomsen et al. 2011]
1,1,1,2,2 Tentandoro 5 medioxypropule	570 10 5			<u>А</u>	270	050 1500	20.7	[Blowers et al 2007]
				F	298	490 - 1525	19.5	[Ovaro et al. 2004]
				F	296	700 - 1500	19.5	[Imasu et al. 1995]
1-Ethoxy-11222-pentafluoroethane	22052-81-9	HEE_365mcf2	CE-CE-OCH-CH-		270	96 - 1520	27.8	[Rrayo at al 2011o]
1 Ethoxy 1,1,2,2,2-pentantioroethane	512 51 6	HEE 374pc2	CHE CE OCH CH	A A		70 - 1520	27.0	$\begin{bmatrix} Blowers et al. 20071 \end{bmatrix}$
1-Luioxy-1,1,2,2-ten anuoroeniane	512-51-0	111 L-3/4pc2		F	208	500 - 1600	20.9	[Heathfield et al 1998]
				E	290	700 1500	20.9	[Incumpleta et al., 1990]
4.4.4 Trifluorobutan 1 ol	461 19 7		CE (CH) CH OH	E	290	500 - 1500	20.7 10.6	[Imasu et al., 1993]
+,+,+- 1111001000000000000000000000000000000	+01-10-/		CF3(CF2)2CF2OF	E	290	500 - 4000	10.0	[Junenez, et al., 2010]
propanol	2378-02-1		(CF ₃) ₃ COH	E	296	700 - 1500	37.4	[Imasu et al., 1995]
2,2,3,3,4,4,5,5-Octafluorocyclopentanol	16621-87-7		-(CF ₂) ₄ CH(OH)-	Е	296	700 - 1500	21.1	[Imasu et al., 1995]

1-Diffusionmethoxy)-1,1,2.2- tetrifluoroefhancy 18809-7.9- (diffusionmethoxy)-1,1,2.2- tetrifluoroefhancy 18809-7.9- (diffusionmethoxy)-1,1,2.2- (diff									
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1-(Difluoromethoxy)-2- ((difluoromethoxy)difluoromethoxy)-1,1,2,2- tetrafluoroethane	188690-77-9	HFE-43-10pccc124 (H- Galden 1040x, HG-11)	CHF2OCF2OC2F4OCHF2	А		21 - 2500	80.9	[Bravo et al., 2011a]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					Е	296	700 - 1440	67.9	[Wallington et al., 2009]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					E	296	450 - 1600	66.5	[Sibra et al. 2001]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					E	205	963 1587	84.0	[Cavalli of al 1008]
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $					E	295	450 2000	64.9	[Cavalli et al., 1996]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		1 (2702 07 (C F OCH	E	290	450 - 2000	05.5	[Christials et al., 1997]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1,1,1,2,2,3,3,4,4-Nonafluoro-4-methoxybutane	163/02-07-6	HFE-449s1 (HFE-/100)	$C_4F_9OCH_3$	A				[Bravo et al., 2011a]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					Е	296	450 - 1550	36.0	[Sihra et al., 2001]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					E		700 - 1400	34.4	[<i>Bravo et al.</i> , 2010a]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					E	295			[Wallington et al., 1997]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		163702-07-6	n-HFE-7100	$n-C_4F_9OCH_3$	А		35 - 1501	36.0	[Bravo et al., 2011a]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					А				[Blowers et al., 2007]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					Е	296	450 - 1520	33.7	[Sihra et al., 2001]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		163702-08-7	<i>i</i> -HFE-7100	$i-C_4F_9OCH_3$	А		59 - 1501	39.3	[Bravo et al., 2011a]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					А				[Blowers et al., 2007]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					E	296	450 - 1500	37.6	[Sihra et al., 2001]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1-Ethoxy-112233444-nonafluorobutane	163702-05-4	HFE-569sf2 (HFE-7200)	C (E)OC H	A	270	150 1500	57.0	[Bravo et al. 2011a]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1 Euloxy 1,1,2,2,5,5,4,4,4 Holiandolobutane	105702 05 4	III E 505312 (III E 7200)	6419662113	F	206	500 1500	37.1	[Sibra et al. 2001]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					E	290	700 1400	205	$\begin{bmatrix} Sinra \ ei \ ai., 2001 \end{bmatrix}$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					E		700 - 1400	30.5	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		1 (2702 05 4	LIFE 7200		E		21 1510	20.1	[Christensen et al., 1998]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		163/02-05-4	<i>n</i> -HFE-7200	$n-C_4F_9OC_2H_5$	A		31 - 1519	38.1	[Bravo et al., 2011a]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					A				[Blowers et al., 2007]
$ \begin{array}{c} & & & & & & & & & & & & & & & & & & &$		163702-06-5	<i>i</i> -HFE-7200	$i-C_4F_9OC_2H_5$	А		37 - 1519	41.4	[Bravo et al., 2011a]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					А				[Blowers et al., 2007]
Bis (difluoromethoxy) difluoromethane78522-47-1HFE-236cal2 (HG-10)CHF2OCF2OCHF2A36 - 250047.1[Brave et al., 2011a] L^2 -Bis (difluoromethoxy)-1,1,2,2- tetrafluoroethane188690-78-0HFE-338pcc13 (HG-01)CHF2OCF2CF2OCHF2A28 - 250053.6[Brave et al., 2011a] $1,2$ -Bis (difluoromethoxy)-1,1,2,2- tetrafluoroethane188690-78-0HFE-338pcc13 (HG-01)CHF2OCF2CF2OCHF2A28 - 250053.6[Brave et al., 2011a] $1,1,3,3,3$ -Hexafluoroptopan-2-ol 1-(Difluoromethoxy)-2,(2-(difluoromethoxy)- 1,2,2-tetrafluoroethoxy)-1,1,2,2- tetrafluoroethane920-66-1(CF3)2CHOHE296700 - 150025.4[Imasu et al., 1998] $1,1,3,3,4,4,6,6,7,7,9,9,10,0,12,12-Hexadecafluoro-2,58,11-tetraoxadodecane(Difluoromethoxy)(difluoromethoxy)16-03HF2C-(OCF2CF2)_2-OCF2HA20 - 250080.4[Brave et al., 2011a]1,1,3,3,5,5,7,7,8,8,10,10-Dodecafluoro-2,4,6,9-tetraoxadecane249932-25-0HG-20HF2C-(OCF2CF2)_2-OCF2HA35 - 250070.3[Brave et al., 2011a]1,1,3,3,5,5,7,7,8,9,10,10-Dodecafluoro-2,4,6,9-tetraoxadecane249932-25-0HG-20HF2C-(OCF2CF2)_2-OCF2HA35 - 250070.3[Brave et al., 2011a]1,1,3,3,5,5,7,7,8,8,10,10-Dodecafluoro-2,4,6,9-tetraoxadecane249932-25-0HG-20HF2C-(OCF2)_2-OCF2DA24 - 2500108.0[Brave et al., 2011a]1,1,3,3,5,5,7,7,8,9,10,01-2-Didecafluoro-2,4,6,9-tetraoxadecane249932-26-1HG-20HF2C-(OCF2)_2-OCF2DA30 - 2500103.3[Brave e$					Е	296	450 - 1400	32.7	[Sihra et al., 2001]
$ \begin{array}{c} & & & & & & & & & & & & & & & & & & &$	Bis(difluoromethoxy)difluoromethane	78522-47-1	HFE-236ca12 (HG-10)	CHF ₂ OCF ₂ OCHF ₂	А		36 - 2500	47.1	[Bravo et al., 2011a]
I.2-Bis(difluoromethoxy)-1,1,2,2- tetrafluoroethaneI88690-78-0HFE-338pcc13 (HG-01)CHF2OCF2CF2OCHF2A $28 \cdot 2500$ 53.6 [<i>Bravo et al.</i> , 2011a]I.1,1,3,3,3-Hexafluoroptan-2-ol I-(Difluoromethoxy)-2-(2-(diffuoromethoxy)- 1,1,2,2-tetrafluoroethane920-66-1(CF3)2CHOHE 296 $700 \cdot 1500$ 25.4 [<i>Mayhre et al.</i> , 1998]I.1,1,3,3,4.4.6,6,7,7,9,9,10,10,12,12- Hexadecafluoro-2,5,8,11-tetraoxadodecane (Difluoromethoxy)(diffuoromethoxy) $17350 \cdot 37 \cdot 3$ HG-03HF2C-(OCF2CF2)2-OCF2HA $20 \cdot 2500$ 80.4 [<i>Bravo et al.</i> , 2011a]I.1,3,3,5,5,7,7,8,8,10,10-Dodecafluoro- 2,4,6,9-tetraoxadoceane (I,1,3,3,5,5,7,7,9,9)-Decafluoro-2,4,6,8-HG-21 $HF2C-(OCF2CF2)CF2OCF2O-CF2HA24 \cdot 2500103.0[Bravo et al., 2011a]I.1,3,3,5,5,7,7,9,9-Decafluoro-2,4,6,8-tetraoxanonane188690-77-9HG-30HF2C-(OCF2CF2)OCF2HA30 \cdot 2500103.3[Bravo et al., 2011a]$					E	298	25 - 3250	44.9	[Myhre et al., 1999]
1,2-Bis(difluoromethoxy)-1,1,2,2- tetrafluoroethane188690-78-0HFE-338pcc13 (HG-01)CHF2OCF2CF2OCHF2A28 - 250053.6[Brave et al., 2011a]1,1,1,3,3,3-Hexafluoropropan-2-ol 1-(Difluoromethoxy)-2-(2-(difluoromethoxy)- 1,2,2-tetrafluoroethane920-66-1(CF3)2CHOHE296700 - 150025.4[Imasu et al., 1998]1,1,3,3,3-Hexafluoropropan-2-ol 1-(Difluoromethoxy)-2-(2-(difluoromethoxy)- 1,2,2-tetrafluoroethane920-66-1(CF3)2CHOHE296700 - 150025.4[Imasu et al., 1998]1,1,3,3,4,6,6,7,7,9,9,10,10,12,12- Hexadecafluoro-2,5,8,11-tetraoxadodecane (Difluoromethoxy)(difluoromethoxy)/difluoro methoxy)(difluoromethoxy)/difluoro methoxy)(difluoromethoxy)/difluoro methoxy)(difluoromethoxy)/difluoro methoxy)(difluoromethoxy)/difluoro methoxy)(difluoromethoxy)173350-37-3HG-03HF2C-(OCF2CF2)_3-OCF2HA17 - 2500114. 1[Brave et al., 2011a]1,1,3,3,5,7,7,8,8,10,10-Dodecafluoro- 2,4,6,9-tetraoxadecane249932-25-0HG-21HF2C- OCF2CF2OCF2O- CF2HA24 - 2500108. 0[Brave et al., 2011a]1,1,3,3,5,5,7,7,9,9-Doceafluoro-2,4,6,8- tetraoxanonane18690-77-9HG-30HF2C-(OCF2)_3-OCF2HA30 - 2500103. 3[Brave et al., 2011a]					Е	295	978 - 1584	51.9	[Cavalli et al., 1998]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1,2-Bis(difluoromethoxy)-1,1,2,2- tetrafluoroethane	188690-78-0	HFE-338pcc13 (HG-01)	CHF2OCF2CF2OCHF2	А		28 - 2500	53.6	[<i>Bravo et al.</i> , 2011a]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					Е	298	25 - 3250	54.7	[<i>Myhre et al.</i> , 1999]
1,1,1,3,3,3-Hexafluoropropan-2-ol 1-(Difluoromethoxy)-2-(2-(difluoromethoxy)- 1,1,2,2-tetrafluoroethane920-66-1(CF_3)_2CHOHE295700 - 150025.4[Imasu et al., 1995]1,1,2,2-tetrafluoroethoxy)-1,1,2,2- tetrafluoroethane205367-61-9HG-02HF_2C-(OCF_2CF_2)_2-OCF_2HA20 - 250080.4[Bravo et al., 2011a]1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12- Hexadecafluoro-2,5,8,11-tetraoxadodecane (Difluoromethoxy)(difluoromethoxy)difluoro methoxy)(difluoromethoxy)difluoro methoxy)(difluoromethoxy)difluoro methoxy)(difluoromethoxy)173350-37-3HG-03HF_2C-(OCF_2CF_2)_3-OCF_2HA17 - 2500114. 1[Bravo et al., 2011a]1,1,3,3,5,5,7,7,8,8,10,10-Dodecafluoro- 2,4,6,9-tetraoxadecane249932-25-0HG-21 $OCF_2CF_2OCF_2O-F_2O-F_2O-F_2O-F_2O-F_2O-F_2O-F_2O-$					Ē	295	930 - 1501	60.4	[Cavalli et al 1998]
$\begin{array}{c} (CI_{3}) (CIICIT & E & E & E & E & E & E & E & E & E & $	1 1 1 3 3 3-Hevafluoropropan-2-ol	920-66-1		(CE ₂) ₂ CHOH	E	295	700 - 1500	25.4	[Imagy et al 1995]
111 <th< td=""><td>1 (Difluoromethoxy) 2 (2 (difluoromethoxy)</td><td>920-00-1</td><td></td><td>(013)2011011</td><td>L</td><td>290</td><td>700 - 1500</td><td>23.4</td><td>[<i>Imasa et al.</i>, 1995]</td></th<>	1 (Difluoromethoxy) 2 (2 (difluoromethoxy)	920-00-1		(013)2011011	L	290	700 - 1500	23.4	[<i>Imasa et al.</i> , 1995]
1,1,2,2-tetrahuoroethoxy)-1,1,2,2-205367-81-9HG-02HG-02HF2C-(OCF2CF2)2-OCF2HA20 - 250080.4[Bravo et al., 2011a]tetrafluoroethane1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12- Hexadecafluoro-2,5,8,11-tetraoxadodecane173350-37-3HG-03HF2C-(OCF2CF2)3-OCF2HA17 - 2500114. 1[Bravo et al., 2011a](Difluoromethoxy)(difluoro methoxy)difluoro methoxy)difluoro ethoxy)difluoro- 2,4,6,9-tetraoxadecane249932-25-0HG-20HF2C-(OCF2)2-OCF2HA35 - 250070.3[Bravo et al., 2011a]1,1,3,3,5,5,7,7,8,8,10,10-Dodecafluoro- 2,4,6,9-tetraoxadecane249932-26-1HG-21OCF2CF2OCF2O- CF2HA24 - 2500108. 0[Bravo et al., 2011a]1,1,3,3,5,5,7,7,9,9-Decafluoro-2,4,6,8- tetraoxanonane188690-77-9HG-30HF2C-(OCF2)3-OCF2HA30 - 2500103. 3[Bravo et al., 2011a]	1 + 2 + 2 + 2 + 2 + 2 + 2 + 2 + 2 + 2 +	205267 61 0	11C 02		٨		20 2500	00.4	[Dames of al. 2011a]
tetranuoroetnane1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12- Hexadecafluoro-2,5,8,11-tetraoxadodecane (Difluoromethoxy)(difluoro methoxy)difluoro methoxy)difluoro173350-37-3HG-03HF2C-(OCF2CF2)_3-OCF2H HF2C-(OCF2)_2-OCF2HA17 - 2500114. 1[Bravo et al., 2011a](Difluoromethoxy)(difluoromethoxy)difluoro methoxy)difluoromethane249932-25-0HG-20HF2C-(OCF2)_2-OCF2H OCF2CF2OCF2O- CF2HA35 - 250070.3[Bravo et al., 2011a]1,1,3,3,5,5,7,7,8,8,10,10-Dodecafluoro- 2,4,6,9-tetraoxadecane249932-26-1HG-21HG-21HF2C- OCF2CF2OCF2O- CF2HA24 - 2500108. 0[Bravo et al., 2011a]1,1,3,3,5,5,7,7,9,9-Decafluoro-2,4,6,8- tetraoxanonane188690-77-9HG-30HF2C-(OCF2)_3-OCF2HA30 - 2500103. 3[Bravo et al., 2011a]	1,1,2,2-tetralluoroetnoxy)-1,1,2,2-	205307-01-9	HG-02	$HF_2C = (OCF_2CF_2)_2 = OCF_2H$	А		20 - 2500	80.4	[Bravo et al., 2011a]
1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12- Hexadecafluoro-2,5,8,11-tetraoxadodecane (Difluoromethoxy)(difluoro methoxy)difluoro methoxy)difluoro 249932-25-0HG-03HF2C-(OCF2CF2)3-OCF2H HG-20A17 - 2500114. 1[Bravo et al., 2011a]1,1,3,3,5,5,7,7,8,8,10,10-Dodecafluoro- 2,4,6,9-tetraoxadecane249932-26-1HG-21HG-21HF2C- OCF2CF2OCF2O- CF2HA24 - 2500108. 0[Bravo et al., 2011a]1,1,3,3,5,5,7,7,9,9-Decafluoro-2,4,6,8- tetraoxanonane188690-77-9HG-30HF2C-(OCF2)3-OCF2HA30 - 2500103. 3[Bravo et al., 2011a]	tetrafluoroethane								
Hexadecafluoro-2,5,8,11-tetraoxadodecaneHexadecafluoroHe	1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12-	173350-37-3	HG-03	HE ₂ C-(OCE ₂ CE ₂) ₂ -OCE ₂ H	А		17 - 2500	114.	[Bravo et al., 2011a]
(Difluoromethoxy)((difluoromethoxy)difluoro 249932-25-0 HG-20 HF2C-(OCF2)2-OCF2H A 35 - 2500 70.3 [Bravo et al., 2011a] $1,1,3,3,5,5,7,7,8,8,10,10$ -Dodecafluoro- 2,4,6,9-tetraoxadecane 249932-26-1 HG-21 HG-21 HF2C- OCF2CF2OCF2OCF2O- CF2H A 24 - 2500 108. 0 [Bravo et al., 2011a] $1,1,3,3,5,5,7,7,9,9$ -Decafluoro-2,4,6,8- tetraoxanonane 188690-77-9 HG-30 HF2C-(OCF2)3-OCF2H A 30 - 2500 103. 3 [Bravo et al., 2011a]	Hexadecafluoro-2,5,8,11-tetraoxadodecane	1,0000 0, 0	110 00				1, 2000	1	
methoxy)difluoromethane $249932-25-0$ HG-20H	(Difluoromethoxy)((difluoromethoxy)difluoro	240032 25 0	HG 20	HEC (OCE) OCE H	٨		35 2500	70.3	[Brave at al 2011a]
$1,1,3,3,5,5,7,7,8,8,10,10$ -Dodecafluoro- $2,4,6,9$ -tetraoxadecane $HG-21$ HF_2C- $OCF_2CF_2OCF_2OCF_2O-$ CF_2H $24 - 2500$ $108.$ 0 $[Bravo et al., 2011a]$ $1,1,3,3,5,5,7,7,9,9$ -Decafluoro-2,4,6,8- tetraoxanonane $188690-77-9$ $HG-30$ $HF_2C-(OCF_2)_3-OCF_2H$ A $30 - 2500$ $103.$ 3 $[Bravo et al., 2011a]$	methoxy)difluoromethane	249932-23-0	110-20	$111_{2}C = (0C1_{2})_{2} = 0C1_{2}11$	А		55 - 2500	70.5	[<i>Diavo et al.</i> , 2011a]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 1 2 2 5 5 7 7 8 8 10 10 Dedees from			HF ₂ C-				100	
$\begin{array}{c} CF_{2}H \\ 1,1,3,3,5,5,7,7,9,9-Decafluoro-2,4,6,8-\\ tetraoxanonane \\ \end{array} \\ \begin{array}{c} 0 \\ F \\ F_{2}C-(OCF_{2})_{3}-OCF_{2}H \\ A \\ \end{array} \\ \begin{array}{c} 30 \\ -2500 \\ 3 \\ \end{array} \\ \begin{array}{c} 103.\\ 3 \\ 3 \\ \end{array} \\ \left[\textit{Bravo et al., 2011a} \right] \end{array}$	1,1,3,3,3,3,7,7,8,8,10,10-Douecanuoro-	249932-26-1	HG-21	OCF2CF2OCF2OCF2O-	А		24 - 2500	108.	[Bravo et al., 2011a]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2,4,0,9-tetraoxadecane			CF ₂ H				0	_ / 4
tetraoxanonane $HF_2C-(OCF_2)_3-OCF_2H$ A $30-2500$ [Bravo et al., 2011a]	1.1.3.3.5.5.7.7.9.9-Decafluoro-2.4.6.8-	100 500 55 0					20 2500	103.	
	tetraoxanonane	188690-77-9	HG-30	$HF_2C-(OCF_2)_3-OCF_2H$	A		30 - 2500	3	[Bravo et al., 2011a]

1-Ethoxy-1,1,2,2,3,3,3-heptafluoropropane	22052-86-4		CF ₃ CF ₂ CF ₂ OCH ₂ CH ₃	А		67 - 1519	33.0	[Bravo et al., 2011a]
(2,2,2-Trifluoroethoxy)ethene	406-90-6	Fluoroxene	CF ₃ CH ₂ OCH=CH ₂	А		47 - 2500	23.5	[Bravo et al., 2011a]
1,1,2,2-Tetrafluoro-1-(fluoromethoxy)ethane 2-Ethoxy-3 3 4 4 5-pentafluorotetrahydro-2 5-	37031-31-5		CH ₂ FOCF ₂ CF ₂ H	А		43 - 2500	25.0	[Bravo et al., 2011a]
bis[1,2,2,2-tetrafluoro-1-	920979-28-8		$C_{12}H_5F_{19}O_2$	Е	294	700 - 1400	55.9	[Javadi et al., 2007]
(trifluoromethyl)ethyl]-furan	160.00.0							
Fluoro(methoxy)methane	460-22-0		CH ₃ OCH ₂ F	A				[Blowers et al., 2008a]
Difluoro(methoxy)methane	359-15-9		CH ₃ OCHF ₂	A				[Blowers et al., 2008a]
				A				[Blowers et al., 2007]
Fluoro(fluoromethoxy)methane	462-51-1		CH ₂ FOCH ₂ F	A				[Blowers et al., 2008a]
Difluoro(fluoromethoxy)methane	461-63-2		CH ₂ FOCHF ₂	A				[Blowers et al., 2008a]
Trifluoro(fluoromethoxy)methane	2261-01-0		CH ₂ FOCF ₃	А				[Blowers et al., 2008a]
1,1,2,2-Tetrafluoro-1,2-dimethoxyethane	73287-23-7	HG'-01	CH ₃ OCF ₂ CF ₂ OCH ₃	А		16 - 2500	29.5	[Bravo et al., 2011a]
				Е	296	200 - 1800	23.0	[Andersen et al., 2004]
1,1,2,2-Tetrafluoro-1-methoxy-2-(1,1,2,2-	185300 16 0	HC' 02	CH-O(CE-CE-O)-CH-	٨		20 2500	58.2	[Brave at al 2011a]
tetrafluoro-2-methoxyethoxy)ethane	405599-40-0	110-02	CH30(CF2CF2O)2CH3	л		29 - 2500	56.2	[<i>Dravo et al.</i> , 2011a]
				Е	296	200 - 1800	45.5	[Andersen et al., 2004]
2,5,8,11-tetraoxadodecane	485399-48-2	HG'-03	CH ₃ O(CF ₂ CF ₂ O) ₃ CH ₃	А		20 - 2500	82.7	[Bravo et al., 2011a]
2,0,0,11 (0110)110000000110				Е	296	200 - 1800	63.4	[Andersen et al., 2004]
Difluorodimethoxymethane	54796-90-6	HG'-10	CH2OCE2OCH2	A	270	64 - 2500	26.1	[Bravo et al., 2011a]
Diffuoroumentoxymethalie	51790 90 0	HG'-20	$CH_2O(CE_2O)_2CH_2$	A		49 - 2500	51.8	[Bravo et al., 2011a]
		HG'-30	$CH_2O(CF_2O)_2CH_2$	Δ		41 - 2500	78.8	[Bravo et al 2011a]
1,1,1,2,3,3-Hexafluoro-3-	120151 60 6	HEF 220m-2	CE CELICE OCE			41 2500	/0.0	
(trifluoromethoxy)propane	428454-68-6	HFE-329me3	CF ₃ CFHCF ₂ OCF ₃	A				[Blowers et al., 2007]
1 (Diffueremethows) 1 1 2 2 2 2				Е	296	670 - 1450	42.4	[Wallington et al., 2004]
hexafluoropropane	56860-85-6	HFE-338mec3	CF ₃ CFHCF ₂ OCF ₂ H	А				[Blowers et al., 2007]
				Е	298	620 - 1450	34.2	[Oyaro et al., 2005]
				Е	296	680 - 1450	36.3	[Wallington et al., 2004]
3.3.4.4.5.5.6.6.7.7.7-Undecafluoroheptan-1-ol	185689-57-0		CF ₃ (CF ₂) ₄ CH ₂ CH ₂ OH	Е	296	670 - 1510	26.8	[Waterland et al., 2005]
3.3.4.4.5.5.6.6.7.7.8.8.9.9.9-				_				
Pentadecafluorononan-1-ol	755-02-2		CF ₃ (CF ₂) ₆ CH ₂ CH ₂ OH	Е	296	600 - 1480	30.9	[Waterland et al., 2005]
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-	87017-97-8		CF ₃ (CF ₂) ₈ CH ₂ CH ₂ OH	Е	296	645 - 1450	24.7	[Waterland et al., 2005]
Nonadecafluoroundecan-1-ol 2-Chloro-1 1 2-trifluoro-1-methoxyethane	125-87-6		CH_OCE_CHEC1	F	208	800 - 1500	17.0	[Dalmasso et al. 2006]
1-(Difluoro(trifluoromethoxy)methoxy)-	425-67-0	PFPMIE		L	290	800 - 1500	17.0	[Dumusso et u., 2000]
1.1.2.3.3.3-hexafluoro-2-	1309353-34-1	(perfluoropolymethylisopr	CF ₃ OCF(CF ₃)CF ₂ OCF ₂ OC	Е	296	650 - 1500	59.2	[Young et al., 2006]
(trifluoromethoxy)propane		opvl)	F ₃					[]
1.1.2-Trifluoro-2-(trifluoromethoxy)ethene	1187-93-5	HFE-216	CE2OCE=CE2	Е		890 - 1865	29.8	[Mashino et al., 2000]
Trifluoro(trifluoromethoxy)methane	1479-49-8		CF ₂ OCF ₂	Ā		0,0 1000	27.0	[Blowers et al., 2008a]
Trifluoromethyl formate	85358-65-2		HCOOCE	A		89 - 2500	30.9	[Bravo et al., 2011b]
Perfluoroethyl formate	313064-40-3		HCOOCE ₂ CE ₂	A		59 - 1847	35.6	[Bravo et al., 2011b]
Perfluoropropyl formate	271257-42-2		HCOOCE	A		64 - 1847	41.2	[Bravo et al., 2011b]
Perfluorobutyl formate	197218-56-7		HCOOCE	Δ		37 - 1847	46.6	[Bravo et al 2011b]
2.2.2.Trifluoroethyl formate	32042_38_0		HCOOCH ₂ CF ₂ CF ₂ CF ₃	Δ		24 _ 1808	25.0	[Bravo et al 2011b]
2,2,2-11110010ethy110111ate	52042-30-9		ncoocn ₂ cr ₃	A		24 - 1000	25.0	[Dravo et al., 20110]

3,3,3-Trifluoropropyl formate	1344118-09-7		HCOOCH ₂ CH ₂ CF ₃	А		37 - 1806	26.1	[Bravo et al., 2011b]
1,2,2,2-Tetrafluoroethyl formate	481631-19-0		HCOOCHFCF ₃	А		41 - 2500	29.2	[Bravo et al., 2011b]
1,1,1,3,3,3-Hexafluoropropan-2-yl formate	856766-70-6		HCOOCH(CF ₃) ₂	А		37 - 2500	36.5	[Bravo et al., 2011b]
Perfluorobutyl acetate	209597-28-4		CH ₃ COOCF ₂ CF ₂ CF ₂ CF ₃	А		35 - 2500	49.8	[Bravo et al., 2011b]
Perfluoropropyl acetate	1344118-10-0		CH ₃ COOCF ₂ CF ₂ CF ₃	А		60 - 2500	44.4	[Bravo et al., 2011b]
Perfluoroethyl acetate	343269-97-6		CH ₃ COOCF ₂ CF ₃	А		52 - 2500	38.6	[Bravo et al., 2011b]
Trifluoromethyl acetate	74123-20-9		CH ₃ COOCF ₃	А		71 - 2500	34.0	[Bravo et al., 2011b]
Methyl carbonofluoridate	1538-06-3		FCOOCH ₃	А		118 - 2500	18.3	[Bravo et al., 2011b]
Fluoromethyl carbonofluoridate	2838-04-2		FCOOCFH ₂	А		29 - 2500	23.5	[Bravo et al., 2011b]
Difluoromethyl carbonofluoridate	70411-09-5		FCOOCF ₂ H	А		37 - 2500	30.5	[Bravo et al., 2011b]
Trifluoromethyl carbonofluoridate	3299-24-9		FCOOCF ₃	A		77 - 1928	37.1	[Bravo et al., 2011b]
Perfluoroethyl carbonofluoridate	623950-74-3		FCOOCE ₂ CE ₃	A		49 - 1928	41.7	[Bravo et al., 2011b]
2.2.2.Trifluoroethyl carbonofluoridate	112915-23-8		FCOOCH ₂ CF ₂	A		0 - 2500	29.9	[Bravo et al., 2011b]
1 1-Difluoroethyl carbonofluoridate	1344118-11-1		FCOOCE ₂ CH ₂	A .		76 - 2500	32.2	[Bravo et al., 2011b]
Perfluoropropyl carbonofluoridate	1344118-12-2		FCOOCE	A		0 - 1928	47 A	[Bravo et al 2011b]
Trifluoromethyl 2.2.2.trifluoroacetate	30410-93-6		$CE_{2}COOCE_{2}$	Δ		22 - 1883	43.2	[Bravo et al 2011b]
Perfluoroactive 2.2.2-trifluoroacetate	206436-37-5		CE-COOCE-CE-	Δ		10 - 1883	47.5	[Bravo et al 2011b]
1 1 Diffuoroathyl 2.2.2 triffuoroactate	1244119 12 2		CF COOCE CH	A		19 - 1003	47.5	$\begin{bmatrix} D \ a v o \ et \ a l., 2011 b \end{bmatrix}$
1,1,1,2,2,2 Haveflyoronnon 2, yl 2,2,2	1544110-15-5		CI ³ COOCI ² CH ₃	A		21 - 1075	38.0	[<i>Bravo et al.</i> , 2011b]
trifluoroogetete	42031-15-2		CF ₃ COOCH(CF ₃) ₂	А		24 - 1858	48.5	[Bravo et al., 2011b]
Influoroacetate	422 28 2		CE COOCU, CU			25 1724	27.6	[Durana et al. 2011b]
Vinyi 2,2,2-trifluoroacetate	433-28-3		CF3COOCH=CH2	A		35 - 1734 40 - 1924	27.0	[Bravo et al., 2011b]
	383-03-1		CF ₃ COOCH ₂ CH ₃	A		49 - 1854	25.5	[Bravo et al., 2011b]
2,2,2-1 filluoroethyl 2,2,2-trilluoroacetate	407-38-5		CF ₃ COOCH ₂ CF ₃	A		23 - 1844	37.0	[Bravo et al., 2011b]
Allyl 2,2,2-trifluoroacetate	383-67-5		CF ₃ COOCH ₂ CHCH ₂	A		22 - 1833	28.0	[Bravo et al., 2011b]
Methyl 2,2,2-trifluoroacetate	431-47-0		CF ₃ COOCH ₃	A		24 - 1839	23.2	[Bravo et al., 2011b]
Phenyl 2,2,2-trifluoroacetate	500-73-2		CF ₃ COOPh	A		23 - 1842	31.9	[Bravo et al., 2011b]
Methyl 2-fluoroacetate	453-18-9		H ₂ CFCOOCH ₃	A		63 - 1805	14.0	[Bravo et al., 2011b]
Difluoromethyl 2,2-difluoroacetate	2002-63-3		$HCF_2COOCHF_2$	A		31 - 1855	30.2	[Bravo et al., 2011b]
Methyl 2,2-difluoroacetate	433-53-4		HCF ₂ COOCH ₃	A		21 - 1836	17.2	[Bravo et al., 2011b]
Difluoromethyl 2,2,2-trifluoroacetate	2024-86-4		CF ₃ COOCHF ₂	A		27 - 1857	36.1	[Bravo et al., 2011b]
2,2,3,3,4,4,4-Heptafluorobutan-1-ol	375-01-9		C ₃ F ₇ CH ₂ OH	Е		700 - 1400	21.4	[Bravo et al., 2010a]
1,1,2-Trifluoro-2-(trifluoromethoxy)-ethane	84011-06-3		CHF ₂ CHFOCF ₃	Α				[Blowers et al., 2007]
				E	298	465 - 1600	28.2	[<i>Oyaro et al.</i> , 2005]
1-Ethoxy-1,1,2,3,3,3-hexafluoropropane	380-34-7		CF ₃ CHFCF ₂ OCH ₂ CH ₃	А				[Blowers et al., 2007]
				Е	298	675 - 1450	27.4	[<i>Oyaro et al.</i> , 2005]
1,1,1,2,2,3,3-Heptafluoro-3-(1,2,2,2-	2220 15 2		CE CE CE OCUECE					
tetrafluoroethoxy)-propane	3330-13-2		$CF_3CF_2CF_2OCHFCF_3$	A				[Blowers et al., 2007]
				Е	298	500 - 1450	43.7	[Oyaro et al., 2005]
2,2,3,3-Tetrafluoro-1-propanol	76-37-9		CHF ₂ CF ₂ CH ₂ OH	Е	298	600 - 4000	19.2	[Antiñolo et al., 2012b]
			2 2 2	Е	298	505 - 1500	13.6	[Sellevåg et al., 2007]
2.2.3.4.4.4-Hexafluoro-1-butanol	382-31-0		CF ₃ CHFCF ₂ CH ₂ OH	Е	298	450 - 1500	29.2	[Sellevåg et al., 2007]
2.2.3.3.4.4.4-Heptafluoro-1-butanol	375-01-9		CF ₃ CF ₂ CF ₂ CH ₂ OH	Е	298	450 - 1500	21.4	[Sellevåg et al., 2007]
1 1 2 2-Tetrafluoro-3-methoxy-propage	60598-17-6		CHF ₂ CF ₂ CH ₂ OCH ₂	Ă				[Blowers et al. 2007]
.,.,_,_ reduitable 5 methoxy propute	00000 17 0			E	298	500 - 1520	13.9	[Ovaro et al., 2004]
1 1 1 2 2 4 5 5 5-Nonafluoro-4-		perfluoro_2_methyl_3_		Ъ	270	500 1520	15.7	[ofmo trun, 2007]

3,3,3-Trifluoro-propanal	460-40-2	CF ₃ CH ₂ CHO	Е	298	600 - 1850	16.7	[Antiñolo et al., 2011]
			Е	298	400 - 1900	14.2	[Sellevag et al., 2004a]
4,4,4-Trifluorobutanal	406-87-1	CF ₃ (CH ₂) ₂ CHO	Е		1000 - 1850	17.0	[Antiñolo et al., 2012a]
2-Fluoroethanol	371-62-0	CH ₂ FCH ₂ OH	E	293	100 - 1600	6.2	[Sellevag et al., 2004b]
2,2-Difluoroethanol	359-13-7	CHF ₂ CH ₂ OH	E	293	100 - 1600	8.0	[Sellevag et al., 2004b]
2,2,2-Trifluoroethanol	75-89-8	CF ₃ CH ₂ OH	E	293	100 - 1600	15.9	[Sellevag et al., 2004b]
			E	296	700 - 1500	14.3	[Imasu et al., 1995]
1,1'-Oxybis[2-(difluoromethoxy)-1,1,2,2- tetrafluoroethane	205367-61-9	HCF2O(CF2CF2O)2CF2H	Е	295	650 - 1500	92.5	[Andersen et al., 2010b]
1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12- hexadecafluoro-2,5,8,11-Tetraoxadodecane	173350-37-3	HCF ₂ O(CF ₂ CF ₂ O) ₃ CF ₂ H	Е	295	650 - 1500	85.2	[Andersen et al., 2010b]
1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12,13,13,15,15 -eicosafluoro-2,5,8,11,14- Pentaoxapentadecane	173350-38-4	HCF ₂ O(CF ₂ CF ₂ O) ₄ CF ₂ H	Е	295	650 - 1500	70.2	[Andersen et al., 2010b]

4411 ² Integrated absorption cross-section in units of 10^{-17} cm² molecule⁻¹ cm⁻¹ for the wavenumber interval specified.

4412 ³ Database: H, HITRAN 2008; G, GEISA 2009.

4413

4414

- 4416 Table 15. Lifetimes, radiative efficiencies and direct GWPs (relative to CO₂) for halogenated alcohols and
- 4417 ethers. Compounds in bold either have significant current atmospheric concentrations or a clear potential for
- 4418 future emissions. Recommended RE and GWP 100-yr values are indicated in bold. Lifetimes are from WMO
- 4419 [2011] except those in italic (see text for details). RE and GWP values in italic are based on previous
- 4420 publications (see text for details).

			Radiati	ve Efficiency	(W m ⁻² ppb ⁻	GWP 100-yr	
Acronym / name	Formula	Lifetime (yr)	AR4	This study – const. profile	This study – lifetime corr.	AR4	This study – lifetime corr.
HFE-125	CHF ₂ OCF ₃	119.0	0.44	0.41	0.41	14,900	12.400
HFE-134 (HG-00)	CHF ₂ OCHF ₂	24.4	0.45	0.46	0.44	6,320	5,560
HFE-143a	CH ₃ OCF ₃	4.8	0.27	0.19	0.18	756	523
HFE-227ea	CF ₃ CHFOCF ₃	51.6	0.40	0.45	0.44	1,540	6,450
HCFE-235ca2 (enflurane)	CHF ₂ OCF ₂ CHF Cl	4.3		0.45	0.41		583
HCFE-235da2 (isoflurane)	CHF ₂ OCHClCF 3	3.5	0.38	0.47	0.42	350	491
HFE-236ca	CHF ₂ OCF ₂ CHF	20.8		0.58	0.56		4,240
HFE-236ea2 (desflurane)	CHF ₂ OCHFCF ₃	10.8	0.44	0.47	0.45	989	1,790
HFE-236fa	CF ₃ CH ₂ OCF ₃	7.5	0.34	0.38	0.36	487	979
HFE-245cb2	CF ₃ CF ₂ OCH ₃	4.9	0.32	0.36	0.33	708	654
HFE-245fa1	CHF ₂ CH ₂ OCF ₃	6.6	0.30	0.33	0.31	286	828
HFE-245fa2	CHF ₂ OCH ₂ CF ₃	5.5	0.31	0.39	0.36	659	812
2,2,3,3,3- Pentafluoropropan-1-ol	CF ₃ CF ₂ CH ₂ OH	0.3	0.24	0.27	0.14	42	19
HFE-254cb1	CH ₃ OCF ₂ CHF ₂	2.5	0.28	0.30	0.26	359	301
HFE-263fb1	CF ₃ CH ₂ OCH ₃	23.0 days	0.20	0.21	0.04	11	1
HFE-263m1	CF ₃ OCH ₂ CH ₃	0.4		0.22	0.13		29
3,3,3-Trifluoropropan-1-ol	CF ₃ CH ₂ CH ₂ OH	12.0 days		0.20	0.02		0
HFE-329mcc2	$CHF_2CF_2OCF_2$ CF_3	22.5	0.49	0.54	0.53	919	3,070
HFE-338mmz1	(CF ₃) ₂ CHOCHF	21.2	0.41	0.45	0.44	380	2,620
HFE-338mcf2	CF ₃ CH ₂ OCF ₂ C F ₃	7.5	0.43	0.47	0.44	552	929
Sevoflurane (HFE- 347mmz1)	(CF ₃) ₂ CHOCH ₂ F	2.2		0.37	0.32		216
HFE-347mcc3 (HFE- 7000)	$CH_3OCF_2CF_2C$ F_3	5.0	0.34	0.37	0.35	575	530
HFE-347mcf2	$CHF_2CH_2OCF_2$ CF_3	6.6	0.41	0.45	0.42	374	854
HFE-347pcf2	$CHF_2CF_2OCH_2$ CF_3	6.0	0.25	0.52	0.48	580	889
HFE-347mmy1	$(CF_3)_2 CFOCH_3$	3.7	0.31	0.35	0.32	343	363
HFE-356mec3	CH ₃ OCF ₂ CHFC F ₃	3.8	0.30	0.33	0.30	101	387
HFE-356mff2	CF ₃ CH ₂ OCH ₂ C F ₃	105.0 days		0.36	0.17		17
HFE-356pcf2	$\begin{array}{c} CHF_2CH_2OCF_2\\ CHF_2 \end{array}$	5.7	0.37	0.40	0.37	265	719
HFE-356pcf3	CHF ₂ OCH ₂ CF ₂ CHF ₂	3.5	0.39	0.42	0.38	502	446
HFE-356pcc3	CH ₃ OCF ₂ CF ₂ C	3.8	0.33	0.36	0.32	110	413

HFE-356mmz1	HF ₂ (CF ₃) ₂ CHOCH ₃	97.1 days	0.30	0.33	0.15	27	14
HFE-365mcf3	CF ₃ CF ₂ CH ₂ OC	19.3 days	0.27	0.29	0.05	11	1
HFE-365mcf2	CF ₃ CF ₂ OCH ₂ C H ₃	0.6		0.41	0.26		58
HFE-374pc2	CHF ₂ CF ₂ OCH ₂ CH ₃	5.0	0.25	0.32	0.30	557	627
4,4,4-Trifluorobutan-1-ol	CF ₃ (CH ₂) ₂ CH ₂ O H	4.0 days		0.12	0.01		0
1,1,1,3,3,3-Hexafluoro-2- (trifluoromethyl)-2- propanol	(CF ₃) ₃ COH			0.38			
2,2,3,3,4,4,5,5- Octafluorocyclopentanol	-(CF ₂) ₄ CH(OH)-	0.3	0.30	0.33	0.16	73	13
HFE-43-10pccc124 (H- Galden 1040x, HG-11)	$CHF_2OCF_2OC_2$ F_4OCHF_2	13.5	1.37	1.06	1.02	1,870	2,820
HFE-449s1 (HFE-7100)	C ₄ F ₉ OCH ₃	4.7	0.31	0.40	0.36	297	421
<i>n</i> -HFE-7100	$n-C_4F_9OCH_3$	4.7		0.46	0.42		486
<i>l</i> -HFE-/100	$1-C_4F_9OCH_3$	4.7	0.30	0.38	0.35	50	407
$n_{\rm FE}$ -309812 ($n_{\rm FE}$ -7200) $n_{\rm FE}$ -7200	$C_4 \Gamma_9 O C_2 \Pi_5$	0.8	0.50	0.44	0.30	39	57
<i>i</i> -HFE-7200	i-C ₄ F ₉ OC ₂ H ₅	0.8		0.49	0.33		03 44
	CHF2OCF2OCH	0.0		0.50	0.20		
HFE-236ca12 (HG-10)	F ₂	25.0	0.66	0.67	0.65	2,800	5,350
HFE-338pcc13 (HG-01)	CHF ₂ OCF ₂ CF ₂ OCHF ₂	12.9	0.87	0.89	0.86	1,500	2,910
1,1,1,3,3,3- Hexafluoropropan-2-ol	(CF ₃) ₂ CHOH	1.9	0.28	0.31	0.26	195	182
HG-02	HF_2C- (OCF_2CF_2)_2- OCF_2H	12.9		1.29	1.24		2,730
HG-03	HF_2C- (OCF_2CF_2)_3- OCF_2H	12.9		1.83	1.76		2,850
HG-20	HF ₂ C–(OCF ₂) ₂ – OCF ₂ H HF C	25.0		0.94	0.92		5,300
HG-21	OCF ₂ CF ₂ OCF ₂ OCF ₂ O-CF ₂ H	13.5		1.78	1.71		3,890
HG-30	HF ₂ C–(OCF ₂) ₃ – OCF ₂ H	25.0		1.69	1.65		7,330
1-Ethoxy-1,1,2,2,3,3,3- heptafluoropropane	CF ₃ CF ₂ CF ₂ OC H ₂ CH ₃	0.8		0.41	0.28		61
Fluoroxene	$CF_3CH_2OCH=C$ H_2	3.6 days		0.28	0.01		0
1,1,2,2-Tetrafluoro-1- (fluoromethoxy)ethane 2-Ethoxy-3,3,4,4,5-	H2 CH2FOCF2CF2 H	6.2		0.37	0.34		871
pentafluorotetrahydro-2,5- bis[1,2,2,2-tetrafluoro-1- (trifluoromethyl)ethyl]- fump	$C_{12}H_5F_{19}O_2$	1.0		0.66	0.49		56
Fluoro(methoxy)methane	CH ₂ OCH ₂ F	73.0 davs		0,165	0.07		13
Difluoro(methoxy)methan e	CH ₃ OCHF ₂	1.1		0.23	0.17		144
Fluoro(fluoromethoxy)me thane	CH ₂ FOCH ₂ F	0.9		0.27	0.19		130
Difluoro(fluoromethoxy)	CH ₂ FOCHF ₂	3.3		0.34	0.30		617

methane							
Trifluoro(fluoromethoxy) methane	CH ₂ FOCF ₃	4.4		0.36	0.33		751
HG'-01	CH ₃ OCF ₂ CF ₂ O CH ₃	2.0		0.35	0.29		222
HG'-02	CH ₃ O(CF ₂ CF ₂ O) ₂ CH ₃	2.0		0.67	0.56		236
HG'-03	$CH_3O(CF_2CF_2O)_2CH_2$	2.0		0.91	0.76		221
HG'-10	CH ₃ OCF ₂ OCH ₃			0.26			
HG'-20	CH ₃ O(CF ₂ O) ₂ C H ₃			0.72			
HG'-30	CH ₃ O(CF ₂ O) ₃ C H ₃			1.14			
HFE-329me3	CF ₃ CFHCF ₂ OC F ₃	40.0		0.48	0.48		4,550
HFE-338mec3	CF ₃ CFHCF ₂ OC F ₂ H			0.51			
3,3,4,4,5,5,6,6,7,7,7- Undecafluoroheptan-1-ol	$CF_3(CF_2)_4CH_2C$ H_2OH	20.0 days		0.37	0.06		0
3,3,4,4,5,5,6,6,7,7,8,8,9,9, 9-Pentadecafluorononan-	$CF_3(CF_2)_6CH_2C$ H_2OH	20.0 days		0.41	0.07		0
3,3,4,4,5,5,6,6,7,7,8,8,9,9, 10,10,11,11,11- Nonadecafluoroundecan-	$\begin{array}{c} CF_3(CF_2)_8 CH_2 C\\ H_2 OH \end{array}$	20.0 days		0.31	0.05		0
2-Chloro-1,1,2-trifluoro- 1-methoxyethane	CH ₃ OCF ₂ CHFC 1	1.4		0.27	0.21		122
PFPMIE (perfluoropolymethyliso	$CF_3OCF(CF_3)C$ $F_2OCF_2OCF_3$	800.0	0.65	0.66	0.65	10,300	9,710
HFE-216	CF ₃ OCF=CF ₂	8.4 days		0.30	0.02		0
Trifluoro(trifluoromethox	CF ₃ OCF ₃			0.53			
y)methane Trifluoromethyl formate	HCOOCE.	3.5		0.35	0.31		599
Perfluoroethyl formate	HCOOCE ₃	3.5		0.33	0.31		580
Perfluoropropyl formate	HCOOCF ₂ CF ₂ C F_3	2.6		0.58	0.50		376
Perfluorobutyl formate	HCOOCF ₂ CF ₂ C F ₂ CF ₃	3.0		0.63	0.56		392
2,2,2-Trifluoroethyl formate	HCOOCH ₂ CF ₃	0.4		0.27	0.16		33
3,3,3-Trifluoropropyl formate	HCOOCH ₂ CH ₂ CF ₃	0.3		0.27	0.13		17
1,2,2,2-Tetrafluoroethyl formate	HCOOCHFCF ₃	3.2		0.39	0.35		470
1,1,1,3,3,3- Hexafluoropropan-2-yl formate	HCOOCH(CF ₃) ²	3.2		0.37	0.33		333
Perfluorobutyl acetate	CH ₃ COOCF ₂ CF ₂ CF ₂ CF ₃	21.9 days		0.70	0.12		2
Perfluoropropyl acetate	CH ₃ COOCF ₂ CF ₂ CF ₃	21.9 days		0.60	0.11		2
Perfluoroethyl acetate	CH ₃ COOCF ₂ CF	21.9 days		0.56	0.10		2
Trifluoromethyl acetate	CH ₃ COOCF ₃	21.9 days		0.41	0.07		2
Methyl carbonofluoridate Fluoromethyl	FCOOCH ₃ FCOOCFH ₂	1.8		0.08 0.19	0.07		95

carbonofluoridate					
Difluoromethyl carbonofluoridate	FCOOCF ₂ H		0.33		
Trifluoromethyl carbonofluoridate	FCOOCF ₃		0.32		
Perfluoroethyl carbonofluoridate	FCOOCF ₂ CF ₃		0.48		
2,2,2-Trifluoroethyl carbonofluoridate	FCOOCH ₂ CF ₃		0.33		
carbonofluoridate	FCOOCF ₂ CH ₃	0.3	0.33	0.17	27
Perfluoropropyl	FCOOCF ₂ CF ₂ C		0.53		
Trifluoromethyl 2,2,2-	F ₃		0.40		
trifluoroacetate	CF_3COOCF_3		0.49		
trifluoroacetate	CF_3COUCF_2CF		0.62		
1,1-Difluoroethyl 2,2,2- trifluoroacetate	CF ₃ COOCF ₂ CH	0.3	0.53	0.27	31
1,1,1,3,3,3- Hexafluoropropan-2-yl	CF ₃ COOCH(CF ₃) ₂		0.49		
Vinyl 2,2,2- trifluoroacetate	CF ₃ COOCH=C		0.39		
Ethyl 2,2,2- trifluoroacetate	CF ₃ COOCH ₂ C H ₃	21.9 days	0.30	0.05	1
2,2,2-Trifluoroethyl 2,2,2- trifluoroacetate	CF ₃ COOCH ₂ CF	54.8 days	0.43	0.15	7
Allyl 2,2,2-trifluoroacetate	CF ₃ COOCH ₂ C HCH ₂		0.35		
Methyl 2,2,2- trifluoroacetate	CF ₃ COOCH ₃	0.6	0.28	0.18	52
Phenyl 2,2,2- trifluoroacetate	CF ₃ COOPh		0.39		
Methyl 2-fluoroacetate	H ₂ CFCOOCH ₃		0.08		
Difluoromethyl 2,2- difluoroacetate	$HCF_2COOCHF_2$		0.44		
Methyl 2,2-difluoroacetate	HCF ₂ COOCH ₃	40.1 days	0.19	0.05	3
Difluoromethyl 2,2,2- trifluoroacetate	CF ₃ COOCHF ₂	0.3	0.49	0.24	27
Heptafluorobutan-1-ol	C ₃ F ₇ CH ₂ OH	0.6	0.32	0.20	34
(trifluoromethoxy)-ethane	CHF ₂ CHFOCF ₃	9.8	0.36	0.35	1,240
1-Ethoxy-1,1,2,3,3,3- hexafluoropropane	CF ₃ CHFCF ₂ OC H ₂ CH ₃	0.4	0.35	0.19	23
1,1,1,2,2,3,3-Heptafluoro- 3-(1,2,2,2- tetrafluoroethoxy)-	CF ₃ CF ₂ CF ₂ OC HFCF ₃	67.0	0.59	0.58	6,490
propane 2,2,3,3-Tetrafluoro-1-	CHF ₂ CF ₂ CH ₂ O	91.3 days	0.25	0.11	13
2,2,3,4,4,4-Hexafluoro-1- butanol	CF ₃ CHFCF ₂ CH ₂ OH	94.9 days	0.43	0.19	17
2,2,3,3,4,4,4-Heptafluoro- 1-butanol	CF ₃ CF ₂ CF ₂ CH ₂ OH	0.3	0.31	0.16	16
1,1,2,2-Tetrafluoro-3-	CHF ₂ CF ₂ CH ₂ O	14.2 days	0.25	0.03	1
Perfluoro-2-methyl-3-	$CF_3CF_2C(O)CF($	7.0 days	0.41	0.03	0

pentanone	$CF_3)_2$				
3,3,3-Trifluoro-propanal	CF ₃ CH ₂ CHO	2.0 days	0.16	0.00	0
4,4,4-Trifluorobutanal	$CF_3(CH_2)_2CHO$		0.16		
2-Fluoroethanol	CH ₂ FCH ₂ OH	20.4 days	0.10	0.02	1
2,2-Difluoroethanol	CHF ₂ CH ₂ OH	40.0 days	0.13	0.04	3
2,2,2-Trifluoroethanol	CF ₃ CH ₂ OH	0.3	0.20	0.10	20
1,1'-Oxybis[2- (difluoromethoxy)- 1,1,2,2-tetrafluoroethane	$\begin{array}{l} HCF_2O(CF_2CF_2\\ O)_2CF_2H \end{array}$	26.0	1.18	1.15	4,920
1,1,3,3,4,4,6,6,7,7,9,9,10,1 0,12,12-hexadecafluoro- 2,5,8,11- Tetraoxadodecane	HCF ₂ O(CF ₂ CF ₂ O) ₃ CF ₂ H	26.0	1.46	1.43	4,490
1,1,3,3,4,4,6,6,7,7,9,9,10,1 0,12,12,13,13,15,15- eicosafluoro-2,5,8,11,14- Pentaoxapentadecane	HCF ₂ O(CF ₂ CF ₂ O) ₄ CF ₂ H	26.0	1.50	1.46	3,630

4425 та	able 16. GWP and	GTP for selected	gases.
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					GWP			GTP	
Acronym / name	Formula	Lifetime (yr)	$\frac{\text{RE (W m}^{-1})}{\text{ppb}^{-1}}$	20-yr	100-yr	500-yr	20-yr	50-yr	100-yr
CFC-11	CCl ₃ F	45.0	0.26	6,900	4,660	1,490	6,890	4,890	2,340
CFC-12	CCl_2F_2	100.0	0.32	10,800	10,200	4,590	11,300	11,000	8,450
CFC-113	CCl_2FCClF_2	85.0	0.30	6,490	5,820	2,390	6,730	6,250	4,470
HCFC-22	CHClF ₂	11.9	0.21	5,280	1,760	503	4,200	832	262
HCFC-141b	CH ₃ CCl ₂ F	9.2	0.16	2,550	782	223	1,850	271	111
HCFC-142b	CH ₃ CClF ₂	17.2	0.19	5,020	1,980	567	4,390	1,370	356
HFC-23	CHF ₃	222.0	0.18	10,800	12,400	8,720	11,500	13,000	12,700
HFC-134a	CH_2FCF_3	13.4	0.16	3,710	1,300	371	3,050	703	201
HFC-152a	CH_3CHF_2	1.5	0.10	506	138	39	174	24	19
Methyl chloroform	CH ₃ CCl ₃	5.0	0.07	578	160	46	317	34	22
Carbon tetrachloride	CCl_4	26.0	0.17	3,480	1,730	504	3,280	1,570	479
Sulphur hexafluoride	SF ₆	3,200.0	0.57	17,500	23,500	31,500	18,900	23,800	28,200
PFC-14	CF_4	50,000.0	0.09	4,880	6,630	9,410	5,270	6,690	8,040





Figure 1. Atmospheric concentrations of 10 halocarbons from 1977-2010 averaged over the
greenhouse gas monitoring network (between 7 and 10 stations) [from *WMO/GAW*, 2011].



Figure 2. Schematic figure showing the main parameters required to compute climate impact metrics, and the additional inputs required in the calculation of those parameters. Dashed lines show where simpler techniques (based on the more complex models) are often employed (as is the case in this review).



Figure 3. IR spectra of CF_4 (top panel), CF_2Cl_2 (middle panel), and CF_3CFH_2 (bottom panel) 4461 measured using 0.5 cm⁻¹ spectral resolution in 700 Torr of air diluent at 296 K [*Forster et al.*, 4462 2005; *Hurley et al.*, 2005; *Sihra et al.*, 2001].



Figure 4. Comparison of experimental and theoretical (B3LYP/6-31G**, MP2/6-31G**) 4469 spectra for n-C₄F₁₀. The theoretical spectra were modeled using Gaussian functions of 14 cm⁻¹ 4470 full width. Data taken from *Bravo et al.* [2010b].



Figure 5. Radiative forcing efficiency (for a 0-1 ppb increase in mixing ratio) per unit cross section compared
between the *Pinnock et al.* [1995] study and this study. The top panel shows the progression from the original
Pinnock plot (using the Reading Narrow Band Model (NBM)) on incorporating an updated global-annual mean
atmosphere (GAM) and then incorporating three atmospheres representing the tropics and extra-tropics, all at a
resolution of 10 cm⁻¹. The middle panel shows a comparison of the Reading NBM and the Oslo Line-by-Line (LBL) model averaged to 10 cm⁻¹ resolution, using atmospheres representing the tropics and extra-tropics. The bottom panel shows the results from the Oslo LBL model at a resolution of 1 cm⁻¹.



Figure 6. Relative difference in calculation of RE using 1 cm^{-1} and 10 cm^{-1} with the Pinnock 4489 plot shown in Figure 5 of the compounds investigated in this study. The original LBL 4490 calculations are performed with 0.2 cm⁻¹ and then converted to 1 cm^{-1} and 10 cm^{-1} .



4502 Figure 7. Annual average distribution of HFC-161 mixing ratio (ppb) at the surface (top panels) and averaged
4503 zonally (bottom) for the reference simulation with emission distribution as for CFC-11 (left) and the sensitivity
4504 simulation with emission distribution as for BC (right) calculated with the Oslo CTM2 model (see text for
4505 details).



Figure 8. Vertical profiles of CFC-11 mixing ratio (ppt) in the tropics (left) and the extratropics (right) from MIPAS observations [*Hoffmann et al.*, 2008], the Oslo radiation code, and the Oslo CTM2 model. The profiles have been scaled to the year 1994 tropospheric mixing ratio of 269 ppt as in *Minschwaner et al.* [2012].







Figure 9. Factor needed to correct RE to account for non-uniform vertical and horizontal distribution versus atmospheric lifetime. The red symbols are for compounds whose main loss mechanism is stratospheric photolysis while the blue symbols are for compounds which are mainly lost in the troposphere by reaction with OH. Dark blue symbols have been used in the calculation of the S-shaped fit and dark red symbols have been used in the calculation of the exponential fit. Light blue and light red symbols are shown for comparison. The curve from Sihra et al. [2001] represents an empirical least squares fit to the fractional correction factors from Jain et al. [2000]. The parentheses designate whether the results are from the simulations with "CFC-11-like" or "BC-like" emission distribution. For the compounds where several different absorption bands have been used in the RF calculations, both the mean and the standard deviation of the fractional corrections are shown.

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Figure 10. Impulse response functions from the four IPCC assessments and from the recent
multi-model study of *Joos et al.* [2013]. Note that the IRF from FAR [*IPCC*, 1990] and SAR
[*IPCC*, 1995] did not include climate-carbon cycle feedbacks, while these are included in
IRFs from TAR [*IPCC*, 2001], AR4 [*IPCC*, 2007] and *Joos et al.* [2013].



4564 Figure 11. Absorption spectrum of CFC-11 at 296 K in 933 hPa (700 Torr) air diluent from
4565 *Sihra et al.* [2001] (solid line) and Oslo simulation of Pinnock curve (dotted line).



4570 Figure 12. Absorption spectrum of HCFC-22 at 293 K in 800 hPa air diluent from *Ballard et*4571 *al.* [2000b] (solid line) and Oslo simulation of Pinnock curve (dotted line).





4577 Figure 13. Absorption cross-section of HFC-134a from *Forster et al.* [2005] (solid line) and
4578 Oslo simulation of Pinnock curve (dotted line). The spectrum is a composite of measurements
4579 from five laboratory groups and has been measured under various temperatures and diluent
4580 gas pressures.



4584 Figure 14. Absorption spectrum of CCl₄ at 296 K from *Nemtchinov and Varanasi* [2003]
4585 (solid line) and Oslo simulation of Pinnock curve (dotted line).



4592 Figure 15. Absorption spectrum of Halon-1301 at 296 K in 933 hPa (700 Torr) air diluent
4593 from *Sihra et al.* [2001] (solid line) and Oslo simulation of Pinnock curve (dotted line).



et al. [2001] (solid line) and Oslo simulation of Pinnock curve (dotted line).





4619 Figure 18. Comparison of radiative efficiencies calculated in this study (lifetime-corrected adjusted cloudy-sky) 4620 and from AR4 [Forster et al., 2007]. Green dots represent compounds where the RE in this study is less than 5% 4621 different from AR4, while red and black dots represent compounds where the REs are significantly different 4622 (>5% and >10%, respectively). Black dots have been labeled and represent compounds where the RE calculated 4623 here is more than 10% different from AR4. Two compounds are off scale and therefore not shown in the plot: HFE-43-10pccc124 (H-Galden 1040x, HG-11) with a RE of 1.02 W m⁻² ppb⁻¹ calculated in the present study 4624 4625 (compared to 1.37 W m⁻² ppb⁻¹ in AR4), and HFE-338pcc13 (HG-01) with a RE of 0.86 W m⁻² ppb⁻¹ calculated 4626 in the present study (compared to 0.87 W m⁻² ppb⁻¹ in AR4).









Figure 19. GWP 100-yr of all compounds calculated in this study.