Dichloromethane in the environment

A note *for the* *prepared* European
Chlorinated Solvents Association (ECSA) *and the* Halogenated
Solvents Industry Alliance (HSIA)

by Archie McCulloch[*]

Preface

This note sets out to provide a balanced view of the environmental effects of dichloromethane (DCM, also known as methylene chloride, CH_2Cl_2) both now and in the future. It is based on scientific information about the behaviour of DCM in the atmosphere and on commercial, technical and economic information about the potential for change in the volume of production and hence the quantities emitted.

Although there is a natural source of DCM (about 70000 t/y from seawater and biomass burning), most of the material emitted to the atmosphere is man-made. These emissions have remained relatively constant since 2013 and this paper is a response to press reports (for example references 1 and 2) citing an unrealistically high growth rate in DCM emissions and the allegation that these would give rise to significant stratospheric ozone depletion (references 31 and 41).

The high-growth scenarios are shown to be incorrect and show an unreasonable extrapolation of the current production volume. The scenarios in question are extrapolations of sub-sets of historic measurements. The concentrations of DCM in the atmosphere have been measured since 1995 at a number of sites, worldwide, and have been inferred since 1920 from air trapped in Antarctic snow. One of the faulty scenarios uses the average rate of growth of DCM in the lower atmosphere over the period 2006 to 2015 and, even though the uncertainty of this will double every 6 years, the scenario extrapolates this growth for 35 years. The other, more contentious and widely reported scenario, uses growth in the three years from 2011 to 2013, which is then extrapolated for 37 years. Not only are such extrapolations statistically questionable, they also have no commercial or technical rationale.

Production (and hence availability) of DCM is closely linked to the demand for HCFC-22 (chlorodifluoromethane, $CHClF_2$) through chloroform, the raw material for HCFC-22 (itself a raw material for fluoropolymers, mainly PTFE). DCM and chloroform are produced together in plant with limited scope for varying their relative quantities and, as a consequence, the rapid growth in HCFC-22 production, particularly in China, has led to DCM becoming readily (and relatively cheaply) available. Production of HCFC-22 is set to decline in the future due both to controls under the Montreal Protocol and to maturity in the fluoropolymer market. Consequently, production and availability of DCM is unlikely to rise and may well decline. This is borne out by the fact that its emissions have not changed since 2013.

Many of the uses of DCM, particularly solvent applications, can result in emission of the material into the atmosphere unless steps are taken to capture and destroy releases. The principal exception is its use as a chemical feedstock, for example for difluoromethane (HFC-32); because the DCM feedstock is chemically transformed in this process, releases are confined to fugitive emissions which amount to less than 0.1% of use.

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The present level of DCM production, inferred from atmospheric measurements is about 1.3 million t/y, consistent with historic capacity in the developed world of about 700 kt/y and the reported growth of production in China. This makes a contribution to current stratospheric ozone depletion less than 1%, which is small and insignificant, in that it is within the uncertainty of the ozone depletion estimate. It is unlikely to increase.

DCM is defined in the Scientific Assessments of Ozone as a *very short lived substance* (VSLS). Its atmospheric lifetime is 0.4 years and atmospheric concentrations depend on the geographical location, altitude and season of emissions. Its concentration shows very strong seasonal cycles; furthermore, the concentration at the point of injection of air into the stratosphere is about half that at the earth's surface. Due to this variability of the effect of an emission, VSLS cannot be given a conventional ozone depletion potential.

The average atmospheric concentration started to grow in the 1930s, reaching a peak in 1990, thence it fell until 2003. Growth in concentration, fuelled mainly by growth in Chinese chloromethanes production continued until 2013 but, since then, there has been no significant growth. This pattern is consistent with the changes in HCFC-22 production.

In summary, there is no reason to expect long term high growth rates for DCM emissions and the reported scenarios are based on improper extrapolations of selective data.

1. Introduction

As the most widely used of the common chlorinated solvents, this paper centres on DCM (CH_2Cl_2, methylene chloride), with the purpose of setting out the facts about its atmospheric environmental behaviour and differentiating these from the wild speculation in recent press reports[1,2].

DCM has a high solvent power for oils and greases and for some polymeric materials. These properties, coupled with its volatility (boiling point 40.1°C) have led to its wide use as an industrial solvent in applications such chemicals and pharmaceuticals production and to a lower extent as food extraction solvent, for metal cleaning and paint removal. It is also a component of special adhesives and has been used in PU foam blowing, in aerosols, paint strippers and as laboratory agent.[3] Many of these uses can result in much of the DCM employed being emitted into the environment (so-called emissive uses). More recently, smaller quantities of DCM have been used as chemical feedstock to produce HFC-32 (CH_2F_2, difluoromethane) but, except for small losses (fugitive emissions), use as feedstock does not result in emission of DCM.

There is strong evidence for natural production of DCM by phytoplankton in the subsurface layer of seawater at depths of 20 to 150 metres, both from direct measurement[4] and from observations of concentrations higher than expected over the sea surface[5]. Calculations based on the direct measurements indicate a flux into the atmosphere from seawater of about 25 kt/y, considerably less than earlier, less certain estimates (190 kt/y)[6]. Furthermore, an additional source from biomass burning, that may have a large natural component, has been estimated at 60 kt/y[7]. Analysis of air trapped in frozen snow (firn air) from Antarctica suggests that the seawater source amounts to 28 kt/y and biomass burning contributes 40 kt/y, amounts that are small in comparison to anthropogenic emissions[8]. Nevertheless, this indicates that DCM is a natural substance and that small amounts have been present in the environment on a geological timescale.

Anthropogenic emissions have added considerably to the natural flux. Analysis of the firn air from Antarctica shows that the atmospheric concentration was relatively constant at 1.5 pmol/mol in the early part of the 20th century, a consequence of the natural sources mentioned above, and grew rapidly from 1950 to reach a southern hemisphere maximum of 9.4 pmol/mol in 1990[8]. This pattern is consistent with the changes in production and emissions estimated from industrial data in the last part of the 20th century[9,10].

Because of its relatively low solubility in water (2%) and high volatility at ambient temperatures (vapour pressure at 20 °C ca 45 kPa), any DCM released into the environment will tend to migrate into the air where it is removed by natural oxidation. Environmental impacts concern the accumulation of DCM in the atmosphere, which is a balance between its rate of release and the rate at which it is removed, and the effect of this atmospheric burden on local pollution or global climate change and ozone depletion.

2. The Implications of Atmospheric Reactivity for Ozone Depletion and Climate Change

2.1 Atmospheric Reactivity

The primary mechanism by which DCM is removed from the atmosphere is oxidation by hydroxyl radicals (•OH) to give water, hydrogen chloride and carbon dioxide as the final products. This is a well known process and the reaction kinetics have been studied extensively; Figure 1 shows the variation of the rate constant (k - in $cm^{-3}molecule^{-1}sec^{-1}$) with temperature (degrees K) for the rate determining step - the initial reaction with •OH[11]. While the average concentration of •OH has been shown to be effectively constant, year to year[12], and between hemispheres[13], local concentrations are governed by sunlight and so are influenced by the intensity of sunlight and the duration of daylight.
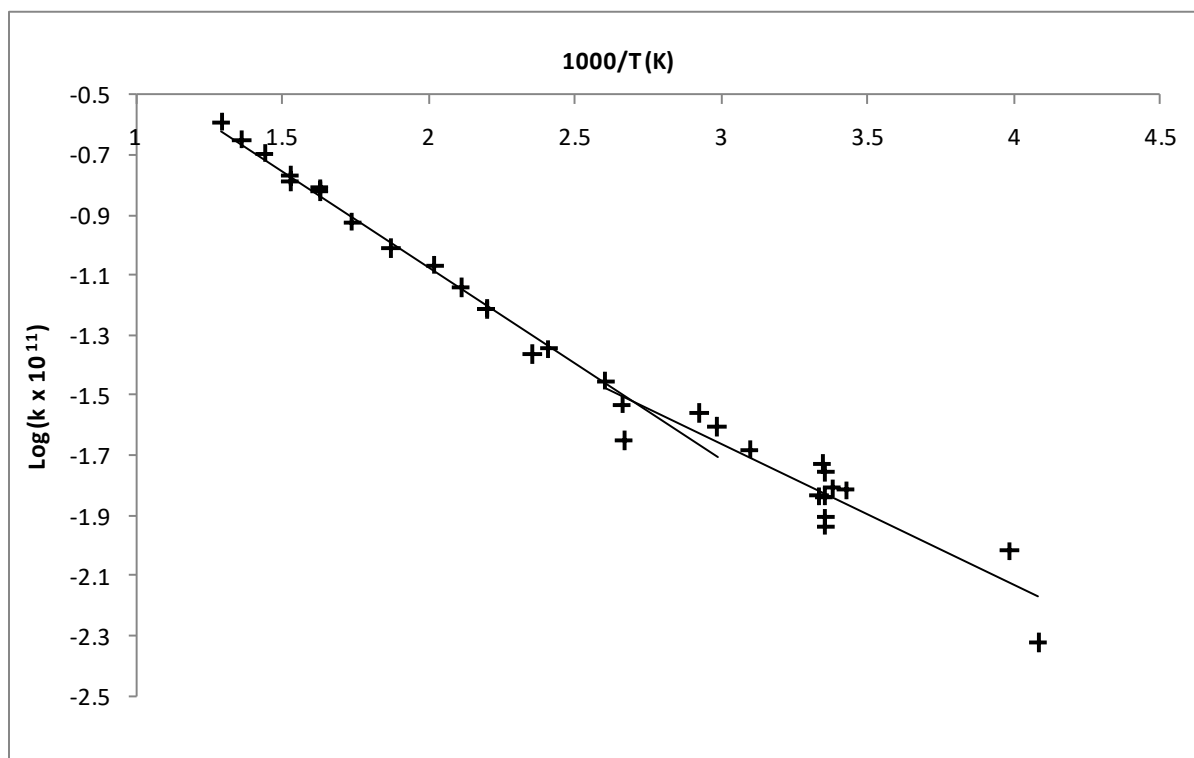

Figure 1. Kinetic parameters for reaction of •OH with CH_2Cl_2 - rate constant k ($cm^3molecule^{-1}sec^{-1}$) variation with temperature (K)

The rate of removal of DCM at the average temperature of the free troposphere gives an average atmospheric lifetime of 0.4 years. This is the value adopted for World Meteorological Organization ozone assessments[14,15,16,17] and Intergovernmental Panel on Climate Change (IPCC) assessments[18].

The reactivity of DCM, characterised by its 0.4 year lifetime, is too low for it to be implicated in the generation of photochemical ozone in the lower atmosphere. It has a Photochemical Ozone Creation Potential (POCP) of between 1 and 7 compared to ethene (100), methane (0.6) and ethane (12.3)[19]. Methane and ethane have sufficiently low POCPs that they are usually considered unreactive with respect to ozone formation in urban areas and accordingly are exempt from some volatile organic compound (VOC) emission regulations and DCM is classed as a material of least concern for transboundary air pollution[20].

The atmospheric lifetime of a substance is a crucial parameter in understanding how that substance will interact with the various mixing regimes in the atmosphere and hence where

and when it is removed. Vertical mixing within the boundary layer (0 to about 1km altitude) at a particular location typically takes less than one day, at the other extreme it takes approximately 40 years for all of the air in the lower atmosphere (troposphere) to circulate through the stratosphere[21]. Tropospheric air, which is contained vertically by the tropopause (at 10 to 20km) is relatively well mixed in each hemisphere, on a timescale of weeks to months, but mixing between the north and south hemispheres is slowed in the Tropics, so that the timescale for interhemispherical mixing is about two years. Most of the air that passes through the stratosphere enters as a result of deep convection over south east Asia and leaves by sinking as it cools over the winter pole (known as the *Brewer-Dobson* circulation)[21].

Clearly, for a substance with an atmospheric lifetime of 0.4 years, only a very small part of any emission will be transported into the stratosphere and that fraction will depend in where and when it is released. Emissions in northern temperate latitudes will undergo significant reaction in the months taken to mix them into tropical air. Emissions in summertime in the northern hemisphere will be even more depleted; not only is there more •OH for longer each day (hydroxyl radical formation depends on sunlight) but the volume of the hemisphere is larger because it effectively incorporates part of the southern tropics. With virtually no emissions in the southern hemisphere, most of the DCM found in the atmosphere there must have been transported from the northern hemisphere. Since this occurs on a timescale of up to two years, the resulting concentration in the southern hemisphere is much lower than that in the north.

2.2 Effect on Stratospheric Ozone
Because of its relatively short lifetime and the resulting highly inefficient transport to the stratosphere of material released into the northern hemisphere boundary layer, DCM is not considered in the ozone assessments to be an ozone depleting substance (ODS). Instead, it is defined as a Very Short Lived Substance (VSLS): "Very short lived substances......have chemical lifetimes comparable with tropospheric transport time scales, with the result that the steady-state mixing ratio of the substance in the troposphere depends on where and when (time of year) it is released. In practice, this happens for species with atmospheric lifetimes of a few months or less".[14] From a regulatory point of view this means that VSLS cannot be included in the normal categories of the Montreal Protocol; not only is their contribution to stratospheric chlorine low but it is highly variable between countries and regions. On average, ozone depletion potentials (ODPs) of VSLS emitted from, say, the Indian subcontinent are 22, 11, and 8 times larger, respectively, than those from Europe, mid-latitude North America, and East Asia[22].

As well as geographical variability, the concentration of DCM reduces with altitude; the surface layer concentration is reduced by 56% at the tropical tropopause (the point of injection of air into the stratosphere) [17]. The small amount of DCM that does get into the stratosphere decomposes rapidly by photolysis at the wavelengths of light in the lower stratosphere[23] and the chlorine released then augments the pool of stratospheric chlorine originating from decomposition of ODS. With a current mean concentration of DCM of about 33 pmol/mol (ppt) in the lower atmosphere (see below), a total equivalent effective stratospheric chlorine loading of approximately 3500 ppt from the ODS[17] and allowing less than complete vertical transport of DCM from the lower atmosphere into the stratosphere[17], the current contribution of all DCM (anthropogenic and natural) to stratospheric ozone depletion is less than 1% of the present total.

As a consequence of the insignificant effect on stratospheric ozone, DCM is not classified as an ODS under the Montreal Protocol and, in the U.S.A., it is specifically allowed for particular applications under Environmental Protection Agency rules[24,25]. In the EU it is not controlled under ODS Regulation[26]

2.3 Climate Change

DCM absorbs infra-red radiation at wavelengths that are important for global warming but its calculated Global Warming Potential (GWP) at a time horizon of 100 years is 9, relative to carbon dioxide[18]. This value is very much less than any threshold for controls under climate change regulations: it is not a controlled greenhouse gas. The absolute contribution of DCM to climate change depends on its atmospheric concentration (currently about 33 ppt) and its radiative efficiency[18], which is comparatively low at 0.03 $Wm^{-2}ppb^{-1}$. The product of these shows that the current radiative forcing from DCM amounts to only 0.001 Wm^{-2}. Total current radiative forcing from all greenhouse gases is 3.5 Wm^{-2}, so that the contribution from DCM is insignificant at 0.03% of the total [27].

Furthermore, modelling studies that include stratospheric ozone in climate forcing calculations have shown that chlorine containing VSLS have reduced climate forcing by a total of 0.005 Wm^{-2} due to their calculated effect on ozone in the lower stratosphere. This global cooling depends directly on the quantities emitted and more than offsets direct radiative forcing from their accumulation in the atmosphere[28].

3. History of Atmospheric Concentrations

3.1 Global

Estimating the environmental effect of a VSLS such as DCM requires accurate atmospheric concentrations to be measured over a wide geographical area. The US National Oceanic and Atmospheric Administration (NOAA) operates a flask sampling system across much of the world and, under the Advanced Global Atmospheric Gases Experiment (AGAGE)[29], DCM has been measured continuously at six sites in the northern hemisphere and two in the southern, commencing in 1995 at Mace Head, Ireland. Prior to that date measurements in the air trapped in Antarctic snow (firn air)[8] have enabled the historical record of southern hemispherical air concentrations shown in Figure 2.
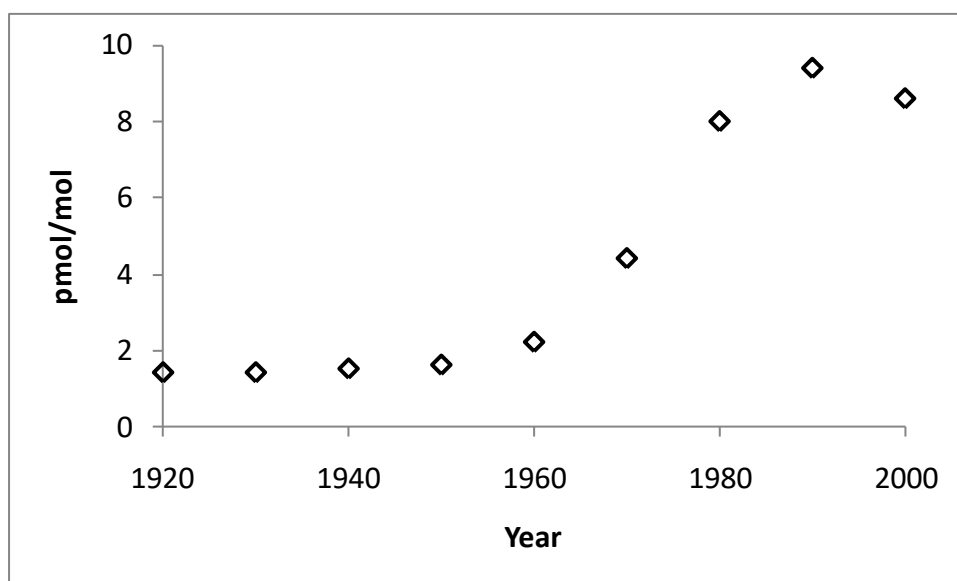

Figure 2. Atmospheric concentrations in the southern hemisphere inferred from measurements in firn air[8].

The level concentrations up to 1940 are indicative of the natural background emissions from seawater and biomass burning and the additional 8 pmol/mol is assigned to anthropogenic emissions which appear to have declined after 1990.

The AGAGE data (publicly available at *https://agage.mit.edu/data/agage-data*) are much more temporally and spatially resolved than the firn data. DCM is measured on an effectively continuous basis at 8 stations worldwide. Figure 3 shows their geographical locations: Cape Grim, Tasmania and American Samoa (both southern hemisphere): Jungfraujoch, Switzerland; Mace Head, Ireland; Monte Cimone, Italy; Ragged Point, Barbados; Trinidad Head, California and Zeppelin Mountain, Svalbard (all northern hemisphere). Of the northern hemispherical stations, all but Ragged Point and Zeppelin Mountain are located in the temperate band from 30ºN to 60ºN.

Figure 4 shows the monthly means of the background concentrations of DCM measured at each station. Generally, the means are calculated from over one hundred individual measurements at each site, after pollution events have been filtered out, and the AGAGE database carries uncertainty estimates for each value. The uncertainties are affected as much by atmospheric conditions at the measuring station as by precision of the measurements themselves and vary from an average of 2% at Zeppelin Mountain to 12% at Jungfraujoch and Monte Cimone. However, for reasons of clarity, uncertainties are not shown in Figure 4.

Figure 3. Indicative geographical locations of the 8 AGAGE stations reporting continuous measurements of DCM.
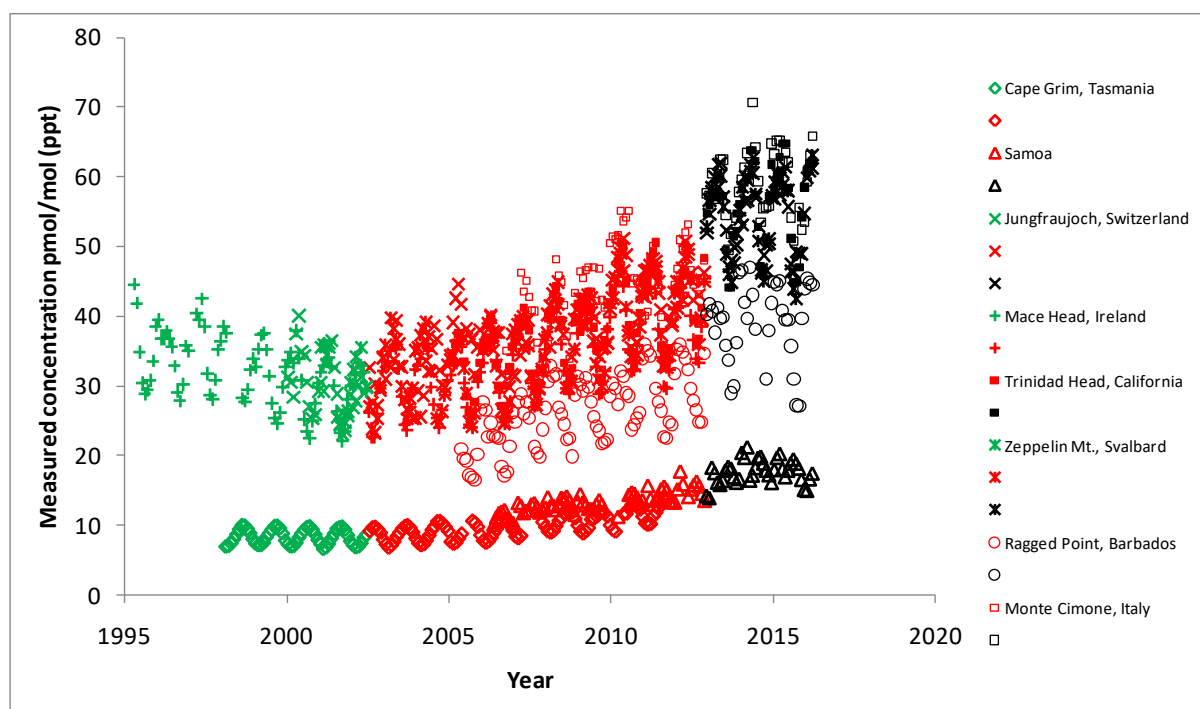

Figure 4. Monthly means of background concentrations (mixing ratios) of DCM measured at the stations cited. Colours differentiate periods in time by apparent rate of change in concentration (see text and Figure 5).

It is immediately clear that there is a seasonal cycle in each station's measurements, with the lowest concentration occurring in summer and the highest in winter. This is a consequence of the seasonal variability of hydroxyl radical discussed above and is entirely expected. It is also apparent from the Cape Grim and Samoan measurements that air in the southern hemisphere is well mixed, in fact rather better mixed than northern hemispherical air where temperate and polar regions have very similar concentrations but the tropics, as typified by Ragged Point, Barbados, show generally lower concentrations. This is consistent with emissions being predominantly in the northern mid-latitudes[30] and with removal of DCM by atmospheric oxidation during transport of the air mass into the northern tropics, hence the Ragged Point measurements show as outliers below those in the general northern hemisphere data. Outlying points above the general data may be due to local pollution that has not been effectively screened out, or from local meteorological effects (most of the outliers are from the high altitude stations at Jungfraujoch and Monte Cimone, both of which have the highest uncertainty).

Despite the outlying points, there appears to be a broad trend of reducing concentrations up to year 2003. This is most apparent in the northern hemisphere record and is shown in the green points of Figure 4. While there is a clear increase after 2003 (red points), it is by no means clear that this is sustained beyond 2013. In fact, the average after 2013, shown in black, may be constant; this is most easily seen in the southern hemisphere data. In the northern hemisphere, after an apparent step change in 2013, the rate of increase in 2014 to 2016 is lower than previously; this is even shown in the Ragged Point, Barbados record. The trend lines from 2003 to 2013 and 2013 to 2016 of *all* points in latitude band 30 to 60°N and *all* points in the southern hemisphere calculated by linear regression are shown in Figure 5, together with their 95% confidence limits. While there is a positive trend in both hemispheres between 2003 and 2013, after that year there is no statistically significant trend. Potential reasons for this are discussed in section 4.

For the southern hemisphere, the AGAGE measurements, which are based on automatic equipment that gathers and analyses hourly samples of air, are consistent with the results from periodical flask sampling reported by NOAA[31] shown in Figure 6. However, in the 30 to 60°N band, the NOAA flask samples seem to show consistently higher concentrations of DCM, ending in 2013 to 2015 at values similar to those of the winter maximum. Notwithstanding this discrepancy, the growth pattern in the NOAA data is the same as that shown by AGAGE: there was significant growth during the period 2004 to 2013 and virtually no growth thereafter. The growth trend for this period and the concentrations shown in Figures 4 and 5 are consistent with the determinations of concentration in the high troposphere, at the point of injection of air into the stratosphere obtained in NASA's ATTREX campaign[32]. The provenance of the error bars on the northern hemispheric data is not clear from reference 31, but they appear to reflect the seasonal variability of the determinations and have been treated as such from the point of view of calculating trend lines and uncertainties. If the error bars reflect sampling and analytical uncertainties, then the overall uncertainty of the NOAA data would be much greater.

Also shown in Figure 6 are the growth scenarios envisaged by Hossaini and colleagues[31]. These are stated to be representative of the concentration of DCM that might be injected into the stratosphere and so, in the historical record, are close to global average concentrations. Both scenarios follow the global trends (the average of northern and southern hemispherical measurements) of the NOAA database up to 2013 but neither scenario takes account of the plateau in concentration between 2013 and 2016. From 2015 onwards, Scenario 1 is a linear extrapolation of the 2004 to 2013 database, even though the values on which it is based are shown as constant from 2013 to 2015. Scenario 2 is even stranger, taking off from 2014 at a growth rate that occurred over only two years in the measured data. These scenarios are projected for 35 years (at least 3 times the observational database). Even
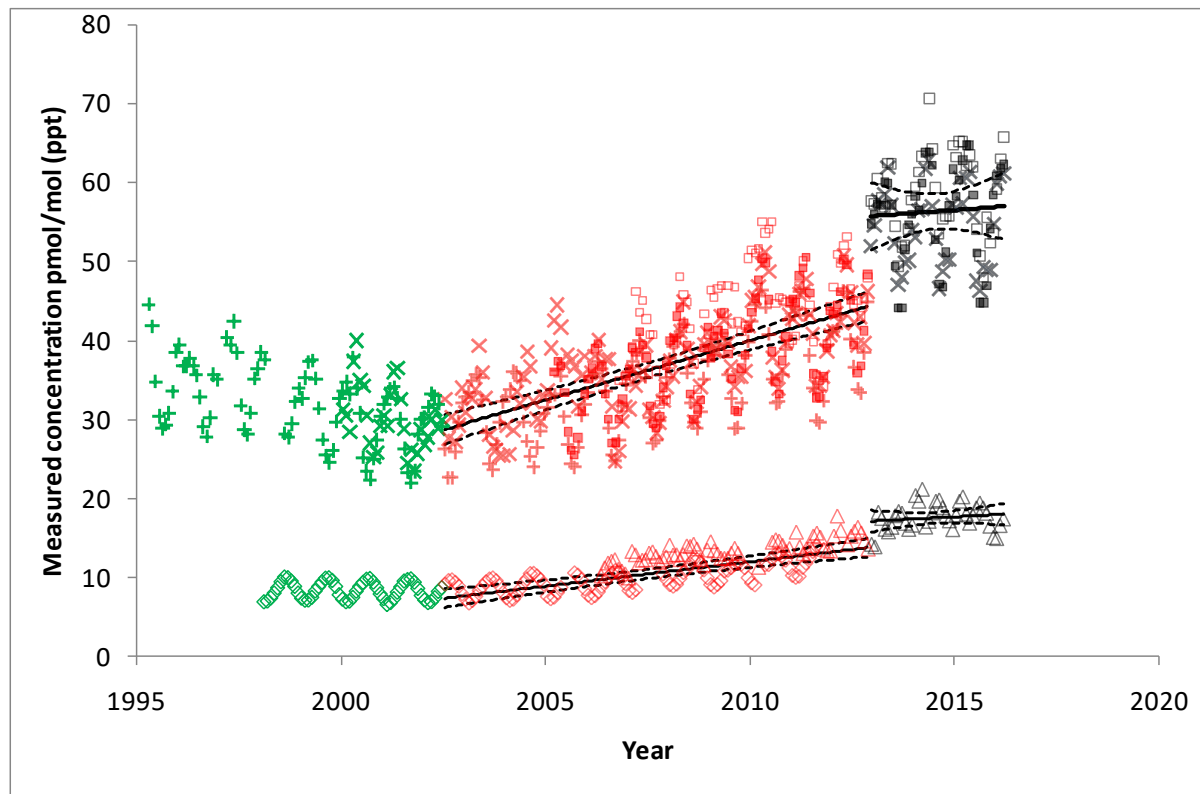
Figure 5. Calculated trends from all AGAGE measurements within the spatial and temporal domains shown by each coloured band.
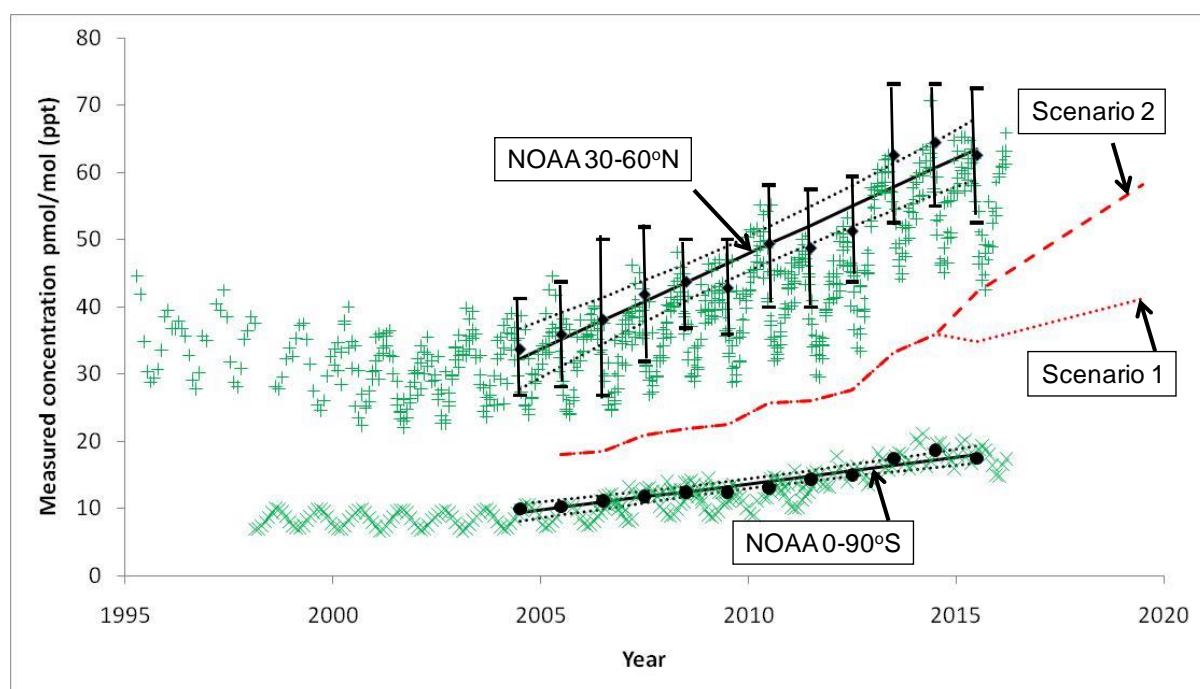

Figure 6. Annual average concentrations of DCM derived from NOAA flask samples reported in reference 31 with trendlines and their 95% confidence limits. AGAGE determinations from Figs 4 and 5 are shown in green. Also shown are the scenarios apparently derived from the NOAA data.

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if such an extrapolation were legitimate and based on actual behaviour, because the uncertainty in the basic NOAA observations doubles every 6 years, the prediction for 2050 would have little utility. Scenarios are discussed in greater detail in section 5.

3.2 Local and Regional Enhancements of Concentration

Increases in atmospheric concentration of DCM in urban and industrial environments is well known. Indeed filtering such "pollution incidents" from the background air measurements is essential from the point of view of establishing global trends[29]. Enhanced concentrations have been demonstrated in Australia[33], U.S.A.[34] where, against a rural background of 28 pmol/mol, urban concentrations were enhanced 5-fold to 146 pmol/mol and China[35] where the air outflowing from the Pearl River Delta contained 200 to 1750 pmol/mol, a maximum enhancement factor of 50 over the northern hemisphere background.

A trend of reducing pollution was shown for Europe[29] over the period 1995 to 2005, with the 24 month rolling average of enhancements in concentration falling from 20 pmol/mol to less than 5 pmol/mol. The was not the case for more recent years in India; samples collected during commercial airliner flights between 1998 and 2012 in the CARIBIC experiment showed a significant increase in emissions from the Indian subcontinent, estimated to have increased from between 3 and 14 kt/y in 1998 to 2000 to between 16 and 25 kt/y in 2008[36]. The timing of this increase is wholly consistent with global trends and the magnitude is consistent with global commerce discussed below.

4. Commercial History and its Influence on Future Scenarios

4.1 Uses of DCM
DCM is a highly effective solvent that has been used extensively since the middle of the 20th century[3]. These uses have changed through the years; the major requirement in the manufacture of photographic film has now shrunk to virtually nothing but other industrial solvent use has grown[30]. Unless it is recovered and destroyed, material used in solvent applications will be emitted into the environment and get into the atmosphere and the growth in use in developed countries was reflected in a peak in atmospheric concentration in about 1990. Since then use and emissions in the developed world have been falling, for example at between 4%/y in Europe and 5%/y in U.S.A. in the early 21st century[3].

Use as a chemical feedstock effectively destroys the feedstock; it is converted into the desired product and the only emissions are of material that has not been effectively contained. These so called *fugitive* emissions amount to a maximum of 0.5% of the total usage. This is the default value proposed by the Intergovernmental Panel on Climate Change for fugitive emissions of similar chemicals that are greenhouse gases[37]. The actual rate of emissions is far smaller, for example the European emission rate for ozone depleting substances used as feedstock amounts to 0.06% (2016) having shrunk from 0.1% (2012)[38]. DCM is the feedstock in the main route to difluoromethane (HFC-32), production of which has expanded rapidly this century, particularly in China where 6197 tonnes was produced in 2005 and 18387 tonnes in 2009[39]. While there are no reliable global data on production of HFC-32, an estimate based on measured emissions suggests that about 60000 tonnes was produced in 2015[40]. HFC-32 is mainly used in the refrigerant blends that are replacing HCFC-22; nevertheless it is a greenhouse gas that is controlled under both the Kyoto and the revised Montreal Protocols and so its production and use will be capped.

At the current rate of production and current fugitive emission rates, the quantity of DCM released into the atmosphere from this source is less than 100 t/y. Given that the cap on HFC-32 production is likely to be much less than 100 times the current production, fugitive emissions of DCM will not become significant and will be much less than the natural flux, which is about 70000 t/y[8].

4.2 Production
Most of the global production of DCM is from chloromethanes plants that make methyl chloride, chloroform and carbon tetrachloride as well. While some of the processes involve direct chlorination of methane, in a significant majority methanol is first reacted with hydrogen chloride to give methyl chloride, which is then chlorinated directly at high temperature. This route makes more effective use of chlorine (because hydrogen chloride generated during the direct chlorination may be recycled to the first stage) and makes for easier control of the mix of products from the second stage. This control is effected mainly by varying the ratio of chlorine to methyl chloride, with some additional flexibility from recycling underchlorinated product (unreacted methyl chloride and DCM). Nevertheless, the product is always a mixture, generally DCM and chloroform, with a relatively small amount of carbon tetrachloride[3].

Process economics are determined by the range of this product mixture (the scope for change of which is limited by process configuration) and the contemporary demand for, and hence value of, the individual products. It is apparent that, in a modern chloromethanes plant (as in China), the ratio of DCM to chloroform can be changed from 60% DCM: 40% chloroform to 40% DCM: 60% chloroform[41].

At present, the demand for carbon tetrachloride is relatively low. Its production and consumption (excluding feedstock use) were phased out under the Montreal Protocol (MP) in

all countries in 2010. The only significant outlet for any carbon tetrachloride made in a chloromethanes plant is as a chemical feedstock. It is used to make tetrachloroethene (perchloroethylene (PER)), some HFCs and insecticide intermediates but about 25% of production either has to be incinerated or is emitted into the environment[42]. To minimise production of carbon tetrachloride, a "shallower" chlorination is dictated and, inevitably, the product mix will contain substantial amounts of DCM, even if chloroform is the more desirable product. By far the largest use for chloroform (more than 95%) is as a chemical feedstock for production of HCFC-22[3].

4.3 Influence of HCFC-22 Demand

HCFC-22 is used in two ways: the commercial product, used in the refrigeration and air conditioning industry, may be eventually emitted into the atmosphere, and so production and consumption for this are controlled under the MP. It is also a chemical feedstock: the raw material for the manufacture of PTFE (polytetrafluoroethylene) and other fluoropolymers, effectively being destroyed in the process and not controlled under the MP. The estimated global production of HCFC-22 for both uses is shown in Figure 7. It is apparent that production in the developed countries that are not operating under Article 5 of the MP remained almost constant until 2008 in the range of 300 to 400 kt/y. From then on production in these countries has fallen but is still in the region of 200 kt/y. From 1996 onwards, production in India and China has grown rapidly and in 2015 65% of the global total was produced in China[43]. Production in other Article 5 countries (Argentina, North and South Korea, Mexico and Venezuela) is small.
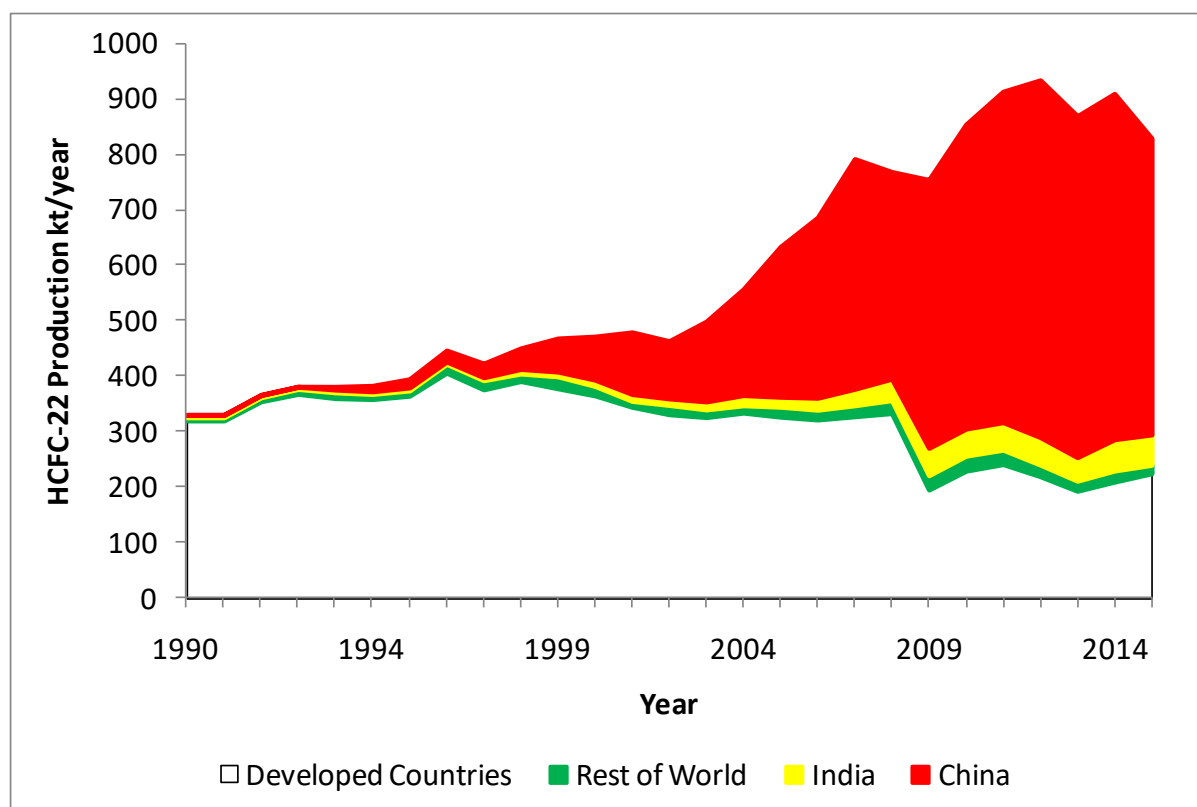

Figure 7. Global production of HCFC-22, showing contributions from developed countries (not under Article 5 of the Montreal Protocol), India, China and the rest of the world.[43]

Total global production rose sharply from 462 kt/y in 2002 to reach a peak of 934 kt/y in 2012, slightly more than doubling in 10 years and almost all of that growth was in China. The increase in demand was a result of requirements both for refrigeration and air conditioning

(RAC) and for feedstock use in the manufacture of fluoropolymers. The RAC use is potentially dispersive so that production and consumption for it have been controlled under the MP, with restriction of production from 2003 onwards in developed countries and 2015 in Article 5 countries.

Since it is effectively a destruction technology, use as a chemical feedstock for fluoropolymers is not controlled. It was a major component in the rapid growth of Chinese HCFC-22 production before 2010 and subsequently has remained roughly constant[44].

The sharp drop in production in developed countries is consistent with the closure of plants in U.S.A. and Europe that is reflected in byproduct emission reports[45,46]. Demand for feedstock not satisfied could have been met by imports from China.

Relative to China, in the developed world growth in HCFC-22 was slow, so that the infrastructure of plants to provide chloroform feedstock grew up over several decades. This allowed time for uses for co-produced DCM to be developed and for the chloromethanes plants to be tuned to meet the quantities of each product that the market required. As a result, despite local and short term imbalances that gave rise to temporary fluctuations in the relative values of the products, the DCM/chloroform/HCFC-22/fluoropolymer system was in balance both technically and commercially.

Chinese growth, on the other hand, was very rapid up to 2010. At one point in the early 2000s, demand for HCFC-22 in fluorpolymer production was growing at 33%/y[47], although it has remained roughly constant since 2010[44]. This led to a similarly rapid growth for chloroform feedstock and a large number of chloromethane plants was constructed; by 2010, Chinese production of all chloromethanes was 3 million t/y, of which 90,000 tonnes was carbon tetrachloride[48]. At this time, the chloroform required for HCFC-22 production would have been about 800,000 t/y. It is not known how much additional chloroform was produced in China and either used in other processes or exported, nor is there information about production of methyl chloride. However, the growth in DCM capacity shown in Figure 8 is consistent with the estimated chloroform production.
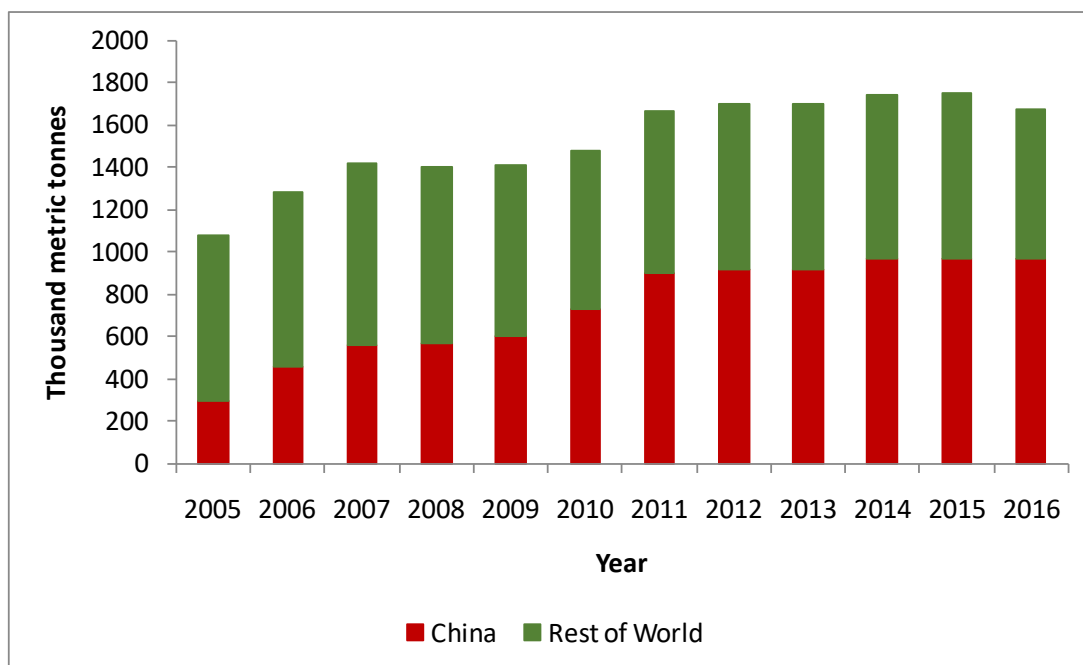

Figure 8. Global DCM capacity *(ECSA/HSIA personal communication)*

Furthermore, the pattern of growth in the atmospheric concentration (and hence in emissions) of DCM matches the growth in HCFC-22 production up to 2010 and the subsequent plateau. The global average atmospheric concentration of DCM at its lowest point in 2003 would

require emissions of 630,000 t/y and between 2010 and 2015 the concentration would have been sustained by emissions of 1.3 million t/y. The extra 700,000 t/y is consistent with the change in Chinese chloromethanes capacity over the same time period.

The fact that the pattern of change in the atmospheric concentration of DCM is very similar to the pattern of change in HCFC-22 production is unlikely to be a coincidence, given the close relationship between HCFC-22 and chloromethanes production. Unlike the situation with developed countries, where growth occurred slowly enough for the production and economic systems to remain roughly balanced, the rapid Chinese growth in HCFC-22 resulted in a similarly rapid growth in the requirement for chloroform that, because of the relative inflexibility of chloromethanes production, has driven up the availability of DCM. Inevitably, what amounts to a surplus of DCM has driven down its price. The consequence of this is wider usage (in applications that might not have been attractive at higher prices) and also less incentive to conserve material.

Furthermore, international trade in DCM is, again, consistent with the decline of North American and European importance as producers and exporters and the rise of China (as a producer and exporter) and India (as a consumer and importer) [49].

5. Rational Future Scenarios

In view of the relative complexity of the DCM market, with interactions between
       supply (as a co-product of the more desirable chloroform),
       use in emissive solvent applications,
       use as an industrial feedstock and solvent which does not lead to emission and
       the changing trade between countries,

simple extrapolation of an historic trend does not lead to a rational scenario for future emissions. When short term trends are "cherry-picked" from the historical database, the resulting scenario is meaningless.

It is to be expected that, in the next few years (perhaps up to 2030), demand for HCFC-22 will remain, at most, approximately constant or slowly decline, depending on the extent to which the requirements for fluoropolymer manufacture match the reductions in production for dispersive uses required by the Montreal Protocol[44]. Thus the global requirement for chloroform is not likely to change much. Because the productive capacity for this already exists, one side effect of a limited demand for chloroform is that the availability of DCM becomes fixed in a range controlled by the limits of operation of the chloromethanes plants. Fixing the availability of DCM will not only limit the quantity available to be emitted but will tend to promote better husbandry and emission control as its supply becomes limited and its value increases.

The first signs of this are already evident in the emission record which shows, in Figures 4, 5 and 6, that, after growth from 2003 to 2012, emissions were stable between 2012 and 2015. In the period up to 2030, for the reasons discussed above, emissions are unlikely to change much: the most likely scenario is a slow reduction. In the longer term, if demand for fluoropolymers were to grow, then the requirement for feedstock HCFC-22 could reach the point where it matches current capacity for chloroform (and DCM) production, but this is critically dependent on the growth rate for fluoropolymers, in particular PTFE. As a commodity material, the expected growth rate would be close to the growth in global gross domestic product (GDP) and any significant increase in demand is likely to occur considerably later than 2030, always assuming that technology remains the same as now. In the event that technology advances, the projected demand for fluoropolymers may not materialise.

In summary, the concentration of DCM in the atmosphere is not likely to change much in the foreseeable future. Based on the measurements shown in Figure 4, the present global average at the earth's surface is in the region of 33 to 37 pmol/mol, less than half of which could be transported into the stratosphere[17], setting a maximum contribution of 0.04 ppb to effective equivalent stratospheric chlorine (EESC, a metric for the contribution of halogen chemistry to stratospheric ozone loss). This represents a contribution of approximately 1% to total EESC[17], which is both small and not significantly different from the uncertainty in the estimate of EESC.

To create a problem from DCM emissions, these would have to grow at a sustained rate of up to 4 times the historic average for 35 years which, given the lack of commercial drivers for such growth is absurd. Because the current economic and commercial situation for chloromethanes has resulted in virtually no growth, the problem scenario is actually 12 times recent average growth, which is even less plausible.

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