



Climate Change Consequences Of VOC Emission Controls

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Executive summary

There are possible climate change consequences of VOC emissions to the atmosphere and from their control by incineration. This report discusses these consequences and documents a simple methodology for quantifying them based on the Global Warming Potential (GWP) concept. The approach is provided with worked examples for assessing the climate change consequences of VOC emission control by incineration, based on calculating the CO₂ equivalent emissions from direct release of a VOC due to its direct or indirect GWP *versus* the CO₂ equivalent emissions arising from the carbon in the fossil fuel used to aid incineration. In this way, it should be straightforward to see whether, and by how much, VOC incineration could mitigate the climate change consequences of direct VOC emission to the atmosphere. The report does not consider health or other environmental impacts arising from any by-products of incineration. It has also not considered other, non-climate change environmental impacts of unabated VOC emissions and use of less efficient VOC control measures. One of the consequences of these will be the potential to form ground-level ozone and human health and wider environmental (damage to crops and materials) associated with this. These are issues which were outside the scope of this study.

Table of contents

1	Intro	oduction	1
2	Climate Change Consequences of VOC Emissions		
3 Calculating Climate Change Consequences of VOC Emission Cont			3
	3.1	CO ₂ Equivalent Emissions from Direct Release of a VOC	3
	3.2	CO ₂ Equivalent Emissions from Incineration of a VOC	4
	3.3	Quantifying the Climate Change Consequences of VOC Incineration Compared with	
		Direct Release	5
	3.4	Worked Examples	6
4	Summary and Conclusions		13
5	References		15
Ann	ex A	Summary of the Solvent Emissions Directive 1999/13/EC	16
Ann	ex B	Global Warming Potentials (GWPs) of some common VOCs.	18
Ann	ex C	Fuel CO ₂ conversion factors for different fuel types	19

1 Introduction

Because of concerns over ground-level ozone formation and regional air quality, the Commission of the European Communities has promulgated a directive dealing with solvent emissions, the Solvents Emissions Directive, SED (OJ, 1999). As a consequence, industry is required to reduce its emissions of volatile organic compounds (VOCs) in general, and solvents in particular. Because solvents are important ozone precursors, the SED will help to reduce ozone formation and meet future air quality targets. Annex A provides a brief summary of what the SED covers.

The choice of optimal VOC emission control measure is highly dependent on the nature of the specific solvent-using process and is highly solvent-specific. One potential VOC emission control measure is incineration. Industry may well question the wisdom of incineration because of the apparent conflict between the climate change consequences of increased fuel usage by the incineration equipment and the requirements of the SED to reduce photochemical ozone formation. However, there may be climate change consequences of the uncontrolled emission of the solvent. The question is whether the climate change penalty of incineration outweighs the climate change benefit from controlling the solvent emission. The ground-level ozone benefits of VOC emission controls are taken for granted within the SED.

This report addresses the climate change consequences of incineration as a potential abatement option for controlling VOC emissions and provides a simple means for quantitatively assessing the CO_2 equivalent emissions of incineration *versus* direct release of the VOC taking into account the VOC's direct global warming potential and the use of any supplementary fuel from fossil fuel feedstocks required to aid incineration. The benefits, or otherwise, of incineration as a means of disposing of VOCs that would otherwise be released to air are only considered in the context of climate change. Other environmental effects of VOC emissions and their incineration, are also outside the scope of the report.

2

Climate Change Consequences of VOC Emissions

Global warming, climate change and the greenhouse effect, however it is termed, are all driven by processes that interfere with the earth's radiation budget. The earth absorbs energy in the form of ultraviolet, visible and infrared radiation from the sun and emits infrared radiation to outer space. These two processes are always in balance. Certain atmospheric trace gases, the radiatively-active trace gases, absorb some of the outgoing infrared radiation and so disturb this radiative balance. The earth's surface and atmosphere react to this disturbance by warming and so re-establish the radiative balance. This process is called radiative forcing and the warming is the greenhouse effect.

The most important radiatively-active trace gases in the atmosphere are water vapour and carbon dioxide. Their presence accounts for the natural greenhouse effect that is estimated to be about 30°C. Our concern here, is with man-made trace gases, some of which act as potent greenhouse gases, that have acted to produce a man-made greenhouse effect with its climate change consequences. It is convenient to measure this potency using the global warming potential GWP index. The GWP of a trace gas is the ratio of the radiative forcing from a given mass emission of the trace gas compared to that from the same mass emission of carbon dioxide, integrated over a given time horizon. Simply stated, the GWP of a VOC is a measure of its climate change impact relative to carbon dioxide.

The GWP of a trace gas depends on its infrared absorption spectrum and whether this overlaps significantly with the wavelength distribution of the outgoing infrared radiation emitted by the earth. It also depends on how long the trace gas remains in the atmosphere once emitted. Methane and halocarbons are important greenhouse gases not only because they have strong infrared absorption bands in the atmospherically-relevant region but also because they are long-lived in the atmosphere. GWPs are calculated by complex global climate models over different time-integrated periods. The time-integration period is important because the radiative forcing effect of a trace gas relative to carbon dioxide depends on the time period it is integrated over because of the dynamic and evolving climate system.

Annex B presents the GWP indices for a number of VOCs compiled from available information on infrared absorption spectra and atmospheric lifetimes and integrated over a 100 year time horizon. A species with a GWP of 10 means that emitting 1 tonne of the species has the same climate change consequences as emitting 10 tonnes of CO_2 over a 100 year time span. For the halocarbons, these refer to "direct GWPs", that is to say, they refer to warming effects directly caused by the long lifetime and infrared absorption properties of the species themselves. However, the chlorinated HCFCs have an indirect, negative global warming effect as a consequence of the depletion of stratospheric ozone caused by the release of the chlorine during the slow degradation of the HCFCs in the atmosphere. The negative effect arises because ozone itself is a greenhouse gas and the HCFCs act to reduce its concentration. The uncertainties in the indirect radiative forcing effects caused by ozone depletion are high and cannot be represented as a global average as well as the direct radiative forcing effect. The positive direct GWPs of HCFCs are larger than their negative indirect GWPs, but the two cannot be simply added. GWP-weighted emissions of halocarbons reported under UNFCCC reporting guidelines are based on direct GWPs only and the direct GWPs for the HCFCs in Annex B are taken from IPCC (2005).

Hydrocarbons have an indirect, positive radiative forcing through tropospheric chemistry interactions affecting the global distribution of methane and ozone in the lower atmosphere. These VOCs are generally much shorter-lived in the atmosphere than the HCFCs so the indirect radiative forcing is more important than the direct radiative forcing. Annex B includes the positive GWPs for several hydrocarbons for a 100-year time horizon estimated by Collins et al. (2002).

A consequence of the uncontrolled emission of VOCs, in general, and solvents, in particular, is that they may act as greenhouse gases and hence there may be climate change consequences.

3 Calculating Climate Change Consequences of VOC Emission Controls

If a VOC can be incinerated without the need for any supplementary fuel from a fossil fuel feedstock, it will always be beneficial to incinerate the VOC rather than release it to the atmosphere from a global warming point of view. This is because incineration eliminates any direct global warming effect of the VOC and the amount of CO_2 formed by incineration arising from the carbon present in the VOC merely replaces the same amount of CO_2 that would be formed naturally in the atmosphere by the atmospheric degradation of the VOC.

If supplementary fuel from a fossil fuel feedstock is required to incinerate the VOC, the question becomes whether the amount of supplementary fuel produces more CO_2 than the CO_2 mass equivalence of the non-incinerated VOC. If it does, then incineration would not be favoured from a climate change perspective unless the supplementary fuel could be taken from a renewable source (e.g. if it was from a biofuel feedstock) or if heat is recovered from the incinerator in a way that reduces the amount of fossil fuel used elsewhere in the installation. The argument depends on the Global Warming Potential of the VOC and the amount to be incinerated *versus* the amount and type of supplementary fossil fuel required and whether any heat is recovered thus reducing the amount of fossil fuel amount of fossil fuel required and whether any heat is recovered thus reducing the amount of fossil fuel used elsewhere in the plant.

This section provides in general terms a procedure for calculating the CO_2 equivalent emissions using GWPs for a) the direct release of a VOC into the atmosphere and for b) its destruction by a thermal oxidiser (or incinerator) in such a way that the climate change consequences of direct release *versus* destruction covering different options can be quantified. After describing the procedure in general terms, the procedure will be demonstrated in several worked examples.

3.1 CO₂ Equivalent Emissions from Direct Release of a VOC

The VOC will contribute to climate change in two ways:

- a primary contribution arising from the direct effect if the VOC is a halocarbon, due to the atmospheric lifetime and infra-red absorption properties of the VOC and reflected by its direct GWP value shown in Annex B, or the indirect effect if the VOC is a hydrocarbon, due to its chemical effect on the atmosphere shown in Annex B.
- b) a secondary contribution from the CO₂ eventually arising from the atmospheric degradation of the VOC determined by the amount of carbon present in the VOC.

The CO_2 equivalent emissions arising from (a) is simply given by the GWP and the mass of the VOC released. Thus:

$$CO_{2 \text{ primary}} = GWP_{voc} \times m_{voc}$$

where GWP_{voc} is the direct or indirect GWP taken from Annex B for the VOC species and m_{voc} is the number of tonnes of the VOC emitted and $CO_{2 primary}$ is in tonnes CO_{2} equivalent.

The secondary CO_2 equivalent emissions arising from (b) depends on the number of carbon atoms in the VOC, its molecular weight and the mass of the VOC released. Thus:

$$CO_{2 \text{ secondary}} = \frac{44 \text{ x } n_{\text{voc}} \text{ x } m_{\text{voc}}}{MW_{\text{voc}}}$$
(2)

(1)

where n_{voc} is the number of carbon atoms in a molecule of the VOC, MW_{voc} is its molecular weight in g/mole and $CO_{2 \text{ secondary}}$ is in tonnes CO_2 . The figure of 44 refers to the molecular weight of CO_2 .

Then the total CO₂ equivalent emissions (in tonnes) arising from the direct release of the VOC is

$$CO_{2 equiv} = CO_{2 primary} + CO_{2 secondary}$$
 (3)

If the VOC arises from a renewable source (bio-origin), then the secondary effect from the carbon in the VOC should not be included, but the primary effect must still be included because of the radiative forcing effect of the VOC. This might be the case if the VOC was a solvent initially derived from carbon from wood products, such as turpentine, vegetable residues, such as lemon or orange peel or crops, such as rape-seed oil or sugar cane. Then, the climate change consequence of the unabated VOC emission is just that of radiative forcing from the VOC, i.e. the primary contribution and

(4)

where $CO_{2 \text{ equiv, bio}}$ refers to the CO_2 equivalent emissions from the release of a VOC derived from a bio-feedstock.

3.2 CO₂ Equivalent Emissions from Incineration of a VOC

If the VOC is destroyed in an incinerator using a fossil fuel to complete combustion or thermal oxidation, then the CO_2 equivalent emissions have a contribution from the carbon in the VOC that is released from the incinerator as CO_2 and the carbon in the fossil fuel used to complete combustion. However, the CO_2 equivalent emissions may be offset by a reduction in primary fossil fuel combustion used elsewhere in the installation to generate heat if heat is recovered from the incinerator.

The CO_2 emissions arising from the carbon in the VOC that is incinerated is in fact the same as the secondary CO_2 equivalent emissions arising from (b) if the VOC was directly released, i.e.

$$CO_{2 \text{ incin}} = \frac{44 \times n_{\text{voc}} \times m_{\text{voc}}}{MW_{\text{voc}}} = CO_{2 \text{ secondary}}$$
(5)

In other words, in terms of the contribution to CO_2 made by the carbon present in the VOC it makes no difference whether the VOC is directly released and allowed to degrade to CO_2 in the atmosphere or whether the VOC is oxidised (burned) producing CO_2 in the incinerator: the same amount of CO_2 is generated.

The amount of CO₂ arising from the fossil fuel used to destroy the VOC in the incinerator depends on the type and quantity of fossil fuel used. The type of fossil fuel (i.e. whether it is natural gas, fuel oil, coal) is characterised by a fuel CO₂ conversion factor expressed in tonnes CO₂ per unit of fuel consumed. Fuel CO₂ conversion factors for a number of the most common types of fossil fuels likely to be used to aid incineration, expressed in various consumption units are given in Annex C. These conversion factors refer to fuels used in 2005 and are based on the most recent UK Greenhouse Gas Inventory compiled by AEA Energy & Environment (Baggott et al, 2007, http://www.airquality.co.uk/archive/reports/cat07/0704261626 ukghgi-90-05 main chapters final.pdf) and also underpin Defra's recently launched "*Act on Carbon Calculator*" (available at http://www.defra.gov.uk/news/latest/2007/climate-0620.htm). If the incinerator fuel is from a bio feedstock (biofuel, biogas), then its conversion factor is defined as zero, implying there is no climate change consequence of the use of these fuels to burn the VOC in the incinerator.

The CO₂ arising from the fossil fuel used to destroy the VOC can be calculated by:

$$CO_{2 \text{ fuel}} = F_{\text{fuel}} \times m_{\text{fuel}}$$

(6)

where $CO_{2 \text{ fuel}}$ is in tonnes, F_{fuel} is the fuel CO_2 conversion factor taken from Annex C in units consistent with the amount of fuel used defined by m_{fuel} . $F_{\text{fuel}} = 0$ for biofuels.

The plant operator may recover heat from the incinerator in such a way that it reduces the amounts of fossil fuel (or electricity) used elsewhere in the installation, in which case there will be additional benefits to the CO_2 budget. It is not possible to provide a general formula that allows this CO_2 offset to be calculated other than through using the plant operator's estimates in the reduction in fossil fuel or electricity used on the plant as a result of heat recovery, combined with the fuel CO_2 conversion factors given in Annex C. If this is known, then a formula for the installation's CO_2 offset would be:

$$CO_{2 \text{ offset}} = F_{\text{fuel}} \times \Delta m_{\text{fuel}}$$

(7)

(3)

where Δm_{fuel} is the reduction in fuel or electricity used in the installation by heat recovery from the incinerator and F_{fuel} is the fuel CO₂ conversion factor from Annex C in appropriate units.

Overall, the total CO₂ equivalent emissions (in tonnes) arising from the incineration of the VOC is

$$CO_{2 \text{ equiv}} = CO_{2 \text{ incin}} + CO_{2 \text{ fuel}} - CO_{2 \text{ offset}}$$
(8)

This method and formulae for calculating CO_2 equivalent emissions from VOC incineration are of a general form assuming the operator has data for basic input streams such as amounts of VOC incinerated and fossil fuels consumed. It may be that the operator has other ways of knowing the CO_2 emissions from the incineration process, for example from direct measurements, as will be shown in one of the real-life worked examples in Section 3.4. However, to quantify the climate change consequences of incineration compared with what the consequences would have been had the VOCs been directly released, it remains necessary to work out the contributions of the incinerated VOC and fossil fuel to the measured CO_2 emission rate. This will be demonstrated in the worked example.

3.3 Quantifying the Climate Change Consequences of VOC Incineration Compared with Direct Release

Sections 3.1 and 3.2 have demonstrated methods for calculating the CO_2 equivalent emissions from direct release of VOCs into the atmosphere and from incinerating the same amount of VOCs as an emission control measure. Summarising:

For direct release:

$$CO_{2 equiv} = CO_{2 primary} + CO_{2 secondary}$$

For incineration:

$$CO_{2 \text{ equiv}} = CO_{2 \text{ incin}} + CO_{2 \text{ fuel}} - CO_{2 \text{ offset}}$$
(8)

referring to the same amounts of VOC.

Since $CO_{2 \text{ secondary}} = CO_{2 \text{ incin}}$, then the key parameters defining the difference between the two removal approaches (direct release and incineration) are the primary CO_2 equivalent emissions based on the GWP of the VOC (i.e. $CO_{2 \text{ primary}}$) and the CO_2 arising from the fossil fuel used to destroy the VOC taking into account of heat recovery (i.e. $CO_{2 \text{ fuel}} - CO_{2 \text{ offset}}$). In other words, in quantifying the merits of incineration *vs* direct release from a climate change point of view, the contribution of the carbon in the VOC itself is not required. Then, in quantifying the difference between the two approaches and to see the net climate change consequences of VOC incineration compared with direct release, the equation reduces to:

$$\Delta CO_{2 \text{ equiv}} = CO_{2 \text{ fuel}} - CO_{2 \text{ offset}} - CO_{2 \text{ primary}}$$
(9)

If $\Delta CO_{2 equiv}$ is positive, then the climate change consequences of incineration of a quantity of VOC are disbeneficial compared with direct release into the atmosphere.

If $\Delta CO_{2 \text{ equiv}}$ is negative, then the climate change consequences of incineration of a quantity of VOC are beneficial compared with direct release into the atmosphere.

Although not needed in the calculation of <u>the differences</u> in climate change consequences, the following worked examples will work through the calculation of the full CO_2 equivalent emissions of direct release and incineration to see how this is done with relevant input data.

3.4 Worked Examples

The following six worked examples show how the CO_2 equivalent emissions can be calculated from a given set of input conditions in order to weigh up the climate changes consequences of direct release of the VOCs to be disposed of compared with climate changes consequences of their incineration. The worked examples are not necessarily meant to be realistic in terms of practicalities of incineration, but are meant to illustrate how CO_2 equivalent calculations can be done for different types of input data scenarios.

3.4.1 Case A

Scenario:

In this case, 25 tonnes of methylene dichloride (dichloromethane) are to be disposed of in an incinerator fired by 8 ktherm natural gas. Heat may be recovered from the incinerator such that 1 ktherm natural gas can be saved from other parts of the installation. None of the fuels are from renewable sources.

CO2 equivalent emissions from direct release to air

The GWP of methylene dichloride from Annex B is 10 Therefore, from equation (1):

CO_{2 primary} = 10 x 25 = 250 tonnes CO₂ equivalent due to the direct GWP of methylene dichloride

The molecular weight of methylene dichloride, MW_{voc} is 84.9 g/mole The number of carbon atoms in a molecule of methylene dichloride is 1 Therefore, from equation (2):

 $CO_{2 \text{ secondary}} = \frac{44 \times 1 \times 25}{84.9} = 13.0 \text{ tonnes } CO_2 \text{ equivalent}$ due to the carbon in the VOC

Therefore, the total CO₂ equivalent emissions from direct release to air (Eqn 3) is:

CO_{2 equiv} = 250 + 13.0 = 263 tonnes CO₂ equivalent

CO2 equivalent emissions from incineration

The CO_2 emissions arising from the carbon in the VOC that is incinerated (Eqn 5) is:

CO_{2 incin} = CO_{2 secondary} = 13.0 tonnes CO₂ equivalent

Natural gas is used to fire the incinerator with a fuel CO_2 conversion factor, F_{fuel} , taken from Annex C of 6.023 tonnes CO_2 per ktherm gas.

The CO₂ emissions arising from the 8 ktherm natural gas used in the incinerator is (Eqn 6)

CO_{2 fuel} = 6.023 x 8 = 48.2 tonnes CO₂ equivalent

The installation's CO₂ offset from the heat recovery is based on a 1 ktherm natural gas saved is Δm_{fuel} From Equation 7:

$$CO_{2 \text{ offset}} = 6.023 \text{ x } 1 = 6.023 \text{ tonnes } CO_2 \text{ equivalent}$$

Then the total CO₂ equivalent emissions from incineration is (Eqn 8):

CO_{2 equiv} = 13.0 + 48.2 - 6.023 = 55.2 tonnes CO₂ equivalent

<u>Difference in CO₂ equivalent emissions from incineration compared with direct release</u> The difference is: $\Delta CO_{2 \text{ equiv}} = 55.2 - 263 = -208 \text{ tonnes CO}_2 \text{ equivalent}$

The negative value indicates there are overall climate change benefits in incineration compared with direct release of the methylene dichloride for these particular conditions.

3.4.2 Case B

Scenario:

In this case, 10 tonnes of methylene dichloride (dichloromethane) are to be disposed of in an incinerator fired by 6 tonnes of gas oil which are based on a renewable source. Heat cannot be recovered from the incinerator.

CO₂ equivalent emissions from direct release to air

The GWP of methylene dichloride from Annex B is 10 Therefore, from equation (1):

CO_{2 primary} = 10 x 10 = 100 tonnes CO₂ equivalent due to the direct GWP of methylene dichloride

The molecular weight of methylene dichloride, MW_{voc} is 84.9 g/mole The number of carbon atoms in a molecule of methylene dichloride is 1 Therefore, from equation (2):

 $CO_{2 \text{ secondary}} = \frac{44 \text{ x } 1 \text{ x } 10}{84.9} = 5.2 \text{ tonnes } CO_2 \text{ equivalent}$ due to the carbon in the VOC

Therefore, the total CO₂ equivalent emissions from direct release to air (Eqn 3) is:

$CO_{2 equiv} = 100 + 5.18 = 105.2 \text{ tonnes } CO_2 \text{ equivalent}$

CO2 equivalent emissions from incineration

The CO₂ emissions arising from the carbon in the VOC that is incinerated (Eqn 5) is:

CO_{2 incin} = CO_{2 secondary} = 5.2 tonnes CO₂ equivalent

Gas oil is used to fire the incinerator with a fuel CO_2 conversion factor, but is based on a renewable source, so $F_{fuel} = 0$.

The CO₂ emissions arising from the renewable gas oil used in the incinerator is (Eqn 6)

CO_{2 fuel} = 0 tonnes CO₂ equivalent

No heat is recovered and hence:

CO_{2 offset} = 0 tonnes CO₂ equivalent

Then the total CO₂ equivalent emissions from incineration is (Eqn 8):

 $CO_{2 \text{ equiv}} = 5.2 + 0 - 0 = 5.2 \text{ tonnes } CO_2 \text{ equivalent}$

Difference in CO₂ equivalent emissions from incineration compared with direct release The difference is:

 $\Delta CO_{2 \text{ equiv}} = 5.2 - 105.2 = -100 \text{ tonnes } CO_2 \text{ equivalent}$

In other words, in this case, because the incineration fuel is from a renewable source, the difference is based soley on the direct GWP of the methylene dichloride. The negative value indicates there are overall climate change benefits in incineration compared with direct release of the methylene dichloride for these particular conditions.

3.4.3 Case C

Scenario:

In this case, 10 tonnes of HFC-152a are to be disposed of in an incinerator fired by 170 MWh fuel oil. Heat may be recovered from the incinerator such that 0.7 ktherm natural gas can be saved from other parts of the installation. None of the fuels are from renewable sources.

CO2 equivalent emissions from direct release to air

The GWP of HFC-152a from Annex B is 122 Therefore, from equation (1):

CO_{2 primary} = 122 x 10 = 1220 tonnes CO₂ equivalent due to the direct GWP of HFC-152a.

The molecular weight of HFC-152a (CH_3CHF_2), MW_{voc} is 66 g/mole The number of carbon atoms in a molecule of HFC-152a is 2 Therefore, from equation (2):

 $CO_{2 \text{ secondary}} = \frac{44 \text{ x } 2 \text{ x } 10}{66} = 13.3 \text{ tonnes } CO_2 \text{ equivalent}$ due to the carbon in the VOC

Therefore, the total CO₂ equivalent emissions from direct release to air (Eqn 3) is:

 $CO_{2 equiv} = 1220 + 13.3 = 1233$ tonnes CO_2 equivalent

CO2 equivalent emissions from incineration

The $\overline{CO_2}$ emissions arising from the carbon in the VOC that is incinerated (Eqn 5) is:

CO_{2 incin} = CO_{2 secondary} = 13.3 tonnes CO₂ equivalent

Fuel oil is used to fire the incinerator with a fuel CO_2 conversion factor, F_{fuel} , taken from Annex C of 0.281 tonnes CO_2 per MWh fuel oil.

The CO₂ emissions arising from the 170 MWh fuel oil used in the incinerator is (Eqn 6)

The installation's CO_2 offset from the heat recovery is based on a 0.7 ktherm natural gas saved is Δm_{fuel} From Equation 7:

CO_{2 offset} = 6.023 x 0.7 = 4.2 tonnes CO₂ equivalent

Then the total CO₂ equivalent emissions from incineration is (Eqn 8):

CO_{2 equiv} = 13.3 + 47.8 - 4.2 = 56.9 tonnes CO₂ equivalent

<u>Difference in CO₂ equivalent emissions from incineration compared with direct release</u> The difference is: $\Delta CO_{2 \text{ equiv}} = 56.9 - 1233 = -1176 \text{ tonnes CO}_2 \text{ equivalent}$

The negative value indicates there are overall climate change benefits in incineration compared with direct release of the HFC-152a for these particular conditions.

3.4.4 Case D

Scenario:

In this case, 20 tonnes of a hydrocarbon solvent with a molecular formula C_7H_{16} are to be disposed of in an incinerator. The incinerator is self-sustaining and no additional fuel is required. Heat cannot be recovered from the incinerator. The solvent is not from renewable sources.

CO2 equivalent emissions from direct release to air

The GWP of the solvent is not given in Annex B, but a value of 10 is assumed due to the indirect effect of the VOC.

Therefore, from equation (1):

 $CO_{2 \text{ primary}} = 10 \times 20 = 200 \text{ tonnes } CO_2 \text{ equivalent}$ due to the indirect GWP of the hydrocarbon.

The molecular weight of the solvent (C_7H_{16}), MW_{voc} is 100 g/mole The number of carbon atoms in a molecule of C_7H_{16} is 7 Therefore, from equation (2):

 $CO_{2 \text{ secondary}} = \frac{44 \times 7 \times 20}{100} = 61.6 \text{ tonnes } CO_2 \text{ equivalent} \text{ due to the carbon in the VOC}$

Therefore, the total CO₂ equivalent emissions from direct release to air (Eqn 3) is:

 $CO_{2 equiv} = 200 + 61.6 = 261.6 \text{ tonnes } CO_2 \text{ equivalent}$

CO2 equivalent emissions from incineration

The CO_2 emissions arising from the carbon in the VOC that is incinerated (Eqn 5) is:

CO_{2 incin} = CO_{2 secondary} = 61.6 tonnes CO₂ equivalent

No additional fuel is used to fire the incinerator. Hence

CO_{2 fuel} = 0 tonnes CO₂ equivalent

No heat is recovered and hence:

CO_{2 offset} = 0 tonnes CO₂ equivalent

Then the total CO₂ equivalent emissions from incineration is (Eqn 8):

 $CO_{2 \text{ equiv}} = 61.6 + 0 - 0 = 61.6 \text{ tonnes } CO_2 \text{ equivalent}$

Difference in CO₂ equivalent emissions from incineration compared with direct release The difference is: $\Delta CO_{2 \text{ equiv}} = 61.6 - 261.6 = -200 \text{ tonnes CO}_2 \text{ equivalent}$

In other words, in this case, because no additional incineration fuel is used, the difference is based solely on the indirect GWP of the hydrocarbon. The negative value indicates there are overall climate change benefits in incineration compared with direct release of the hydrocarbon by effectively removing the consequence of the indirect GWP for these particular conditions

3.4.5 Case E

Scenario:

In this case, 150 tonnes of a hydrocarbon solvent manufactured from a renewable source with a molecular formula C_6H_{12} are to be disposed of in an incinerator fired by 1100 tonnes of gas oil. Heat may be recovered from the incinerator such that 500 tonnes gas oil can be saved from other parts of the installation. The fuel is not from a renewable source.

CO₂ equivalent emissions from direct release to air

The GWP of the solvent is not given in Annex B, but a value of 10 is assumed due to the indirect effect of the VOC.

Therefore, from equation (1):

 $CO_{2 \text{ primary}} = 10 \times 150 = 1,500 \text{ tonnes } CO_2 \text{ equivalent}$ due to the indirect GWP of the hydrocarbon.

The solvent is from a renewable source, so the carbon it is made up from does not contribute to climate change and hence:

 $CO_{2 \text{ secondary}} = 0$, and the total CO_2 equivalent emissions from direct release to air (Eqn 4) is

CO_{2 equiv} = CO_{2 primary} = **1,500 tonnes CO₂ equivalent**

CO2 equivalent emissions from incineration

The CO₂ equivalent emissions arising from the carbon in the VOC that is incinerated (Eqn 5) is:

CO_{2 incin} = CO_{2 secondary} = 0 tonnes CO₂ equivalent

because the VOC is from a renewable source.

Gas oil is used to fire the incinerator with a fuel CO_2 conversion factor, F_{fuel} , taken from Annex C of 3.19 tonnes CO_2 per tonne gas oil.

The CO₂ emissions arising from the 1100 tonnes of gas oil used in the incinerator is (Eqn 6)

The installation's CO₂ offset from the heat recovery is based on a 500 tonnes gas oil saved is Δm_{fuel} From Equation 7:

CO_{2 offset} = 3.19 x 500 = 1,595 tonnes CO₂ equivalent

Then the total CO₂ equivalent emissions from incineration is (Eqn 8):

CO_{2 equiv} = 0 + 3,509 - 1,595 = 1,914 tonnes CO₂ equivalent

<u>Difference in CO₂ equivalent emissions from incineration compared with direct release</u> The difference is: $\Delta CO_{2 \text{ equiv}} = 1,914 - 1,500 = 414 \text{ tonnes CO}_2 \text{ equivalent}$

In this case, because the solvent has a low indirect GWP and was being incinerated with a large amount of fossil fuel, the difference has a positive value indicating overall climate change disbenefits in incineration under these conditions compared with direct release of the solvent

3.4.6 Case F

Scenario:

This case involves the destruction of methylene dichloride (dichloromethane) in an incinerator, but the calculations are based on different sets of information provided by the plant operator. Instead of knowing the amounts of methylene dichloride to be disposed of and the amounts of fuel used, the operator provides information that states that 60 tonnes CO_2 and 22 tonnes of HCl are released per year. Heat cannot be recovered from the incinerator. We need to work back from this information the amount of methylene dichloride disposed of in order to know the CO_2 equivalent emissions that would arise from the release of the methylene dichloride to air.

It can be assumed that all the chlorine atoms in the methylene dichloride are released as HCl in the incineration process. The molecular formula of methylene dichloride is CH_2Cl_2 so one mole of methylene dichloride produces 2 moles of HCl.

The molecular weight of HCl is 36.5 g/mole.

Thus the number of moles HCl released from the incinerator = $\frac{22 \times 10^6}{36.5}$ = 6.0 x 10⁵ moles

This amount of HCl must have arisen from $\frac{1}{2} \times (6.0 \times 10^5) = 3.0 \times 10^5$ moles moles of methylene dichloride.

The molecular weight of methylene dichloride, MW_{voc} is 84.9 g/mole, so this equates to 84.9 x 3.0 x $10^5 = 2.5 \times 10^7$ g of methylene dichloride, or **25 tonnes.**

Then the normal calculations can commence to estimate the CO_2 equivalent emissions from direct release to air.

CO₂ equivalent emissions from direct release to air

The GWP of methylene dichloride from Annex B is 10 Therefore, from equation (1):

CO_{2 primary} = 10 x 25 = 250 tonnes CO₂ equivalent due to the direct GWP of methylene dichloride

The molecular weight of methylene dichloride, MW_{voc} is 84.9 g/mole The number of carbon atoms in a molecule of methylene dichloride is 1 Therefore, from equation (2):

$$CO_{2 \text{ secondary}} = \frac{44 \text{ x } 1 \text{ x } 25}{84.9} = 13.0 \text{ tonnes } CO_2 \text{ equivalent}$$
 due to the carbon in the VOC

Therefore, the total CO₂ equivalent emissions from direct release to air (Eqn 3) is:

CO_{2 equiv} = 250 + 13.0 = 263 tonnes CO₂ equivalent

CO2 equivalent emissions from incineration

This quantity does not have to be calculated because the operators have already stated the total CO_2 emissions from the incinerator, including contributions from both the methylene dichloride itself and the additional fuel is **60 tonnes CO**₂.

In other words,

 $CO_{2 \text{ incin}} + CO_{2 \text{ fuel}} = 60 \text{ tonnes } CO_{2} \text{ equivalent}$

Since heat is not recovered from the incinerator,

CO_{2 offset} = 0 tonnes CO₂ equivalent

Then the total CO₂ equivalent emissions from incineration is (Eqn 8):

$CO_{2 \text{ equiv}} = 60 - 0 = 60 \text{ tonnes } CO_2 \text{ equivalent}$

Difference in CO₂ equivalent emissions from incineration compared with direct release The difference is: $\Delta CO_{2 \text{ equiv}} = 60 - 263 = -203 \text{ tonnes CO}_2 \text{ equivalent}$

The negative value indicates there are overall climate change benefits in incineration compared with direct release of the methylene dichloride for these particular conditions.

These worked examples cover a number of different scenarios and almost all of them have show an overall climate change benefit in incineration compared with direct release of the VOC. In fact, only when the VOC has a low direct or indirect GWP and is burned with a large excess of fossil fuel in the incinerator with little heat recovery is it likely to be less favourable to incinerate rather than directly release the VOC to air from a climate change point of view.

4 Summary and Conclusions

This report has discussed the climate change consequences of emitting VOCs into the atmosphere and how to quantify the carbon dioxide equivalent emissions through the use of the Global Warming Potential concept. It has discussed the direct global warming effect of halocarbons due to their long atmospheric lifetime and infra-red absorption properties and the indirect global warming effect of hydrocarbons due to their atmospheric degradation and perturbation on the distribution of other greenhouse gases such as methane and ozone.

The report has discussed the consequences of VOC emission control through incineration and the climate change contribution made by the combustion of supplementary incineration fuel.

This report has provided a simple approach with worked examples for assessing the climate change consequences of VOC emission control by incineration, based on calculating the CO_2 equivalent emissions from direct release of a VOC due to its direct or indirect GWP *versus* the CO_2 equivalent emissions arising from the carbon in the fossil fuel used to complete combustion. In terms of the contribution to CO_2 made by the carbon present in the VOC it makes no difference whether the VOC is directly released and allowed to degrade to CO_2 in the atmosphere or whether the VOC is oxidised (burned) producing CO_2 in the incinerator: the same amount of CO_2 is generated.

If fuel from a fossil fuel feedstock is required to incinerate the VOC, the question becomes whether the amount of supplementary fuel produces more CO₂ than the CO₂ mass equivalence of the non-incinerated VOC. If it does, then incineration would not be favoured unless the supplementary fuel could be taken from a renewable source (e.g. if it was from a biofuel feedstock) or if heat is recovered from the incinerator in a way that reduces the amount of fossil fuel used elsewhere in the installation. The argument depends on the Global Warming Potential of the VOC and the amount to be incinerated *versus* the amount and type of supplementary fossil fuel used elsewhere in the installation. Only when the VOC has a low direct or indirect GWP and is burned with a large excess of fossil fuel in the incinerator with little heat recovery is it likely to be less favourable to incinerate rather than directly release the VOC to air from a climate change point of view.

The report has highlighted that chlorinated HCFCs have an indirect, negative global warming effect as a consequence of the depletion of stratospheric ozone. The uncertainties in the indirect radiative forcing effects caused by ozone depletion are high and cannot be represented as a global average as well as the direct radiative forcing effect. For this reason, these effects were not considered in the report's methodology. This is consistent with UNFCCC guidelines for reporting GWP-weighted emissions of halocarbons that are based on direct GWPs.

Overall, one can say that the direct global warming effect from the release of a VOC into air caused by its infra-red absorption properties and its atmospheric lifetime is known with high certainty. The same can be said about the secondary contribution caused by atmospheric degradation of the VOC or by its incineration aided by the combustion of a fossil fuel. This assumes that the quantity of the VOC and fossil fuel are known accurately. The indirect global warming effect of hydrocarbons such as propane, butane, propylene etc. released into the atmosphere as a result of their atmospheric degradation causing an impact on the global distribution of other trace greenhouse gases such as methane and ozone are known less accurately and rely on the uncertainties of various key parameters in global climate models. Less certain still are the indirect negative global warming effects of chlorinated HCFCs released into the atmosphere which reduces levels of ozone in the stratosphere. These effects cannot be so readily quantified on a global scale, as mentioned above. These two indirect global warming effects (one having a positive warming effect, the other a negative cooling effect) are removed by incinerating a VOC, implying that the climate change consequences of removing VOCs by incineration can be quantified more accurately than the climate change consequences of their direct release into the atmosphere.

The discussions and proposed methodologies have assumed that combustion in the incinerator is complete so no unburnt VOCs from the compound being incinerated or from the additional fuel are released into the atmosphere. The report also does not consider health or other environmental impacts arising from any by-products of incineration. One of the products from incineration of

Climate Change Consequences of VOC Emission Control

halocarbons will be the halo-acids such as HCI. The report has also not considered other, non-climate change environmental impacts of unabated VOC emissions and use of less efficient VOC control measures. One of the consequences of these will be the potential to form ground-level ozone and human health and wider environmental (damage to crops and materials) associated with this.

5 References

Baggott SL, Cardenas L, Garnett E, Jackson J, Mobbs DC, Murrells T, Passant N, Thomson A, Watterson JD, UK Greenhouse Gas Inventory, 1990 to 2005. Annual Report for submission under the Framework Convention on Climate Change (April 2007), Report for Defra, Welsh Assembly Government, the Scottish Executive and the Department of the Environment for Northern Ireland, AEAT/ENV/R/2429, ISBN ISBN 0-9554823-1-3.

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Annex A Summary of the Solvent Emissions Directive 1999/13/EC

The Solvent Emissions Directive (SED) is the term for the Council Directive 1999/13/EC on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations. The pupose of the Directive is to prevent or reduce the direct and indirect effects of emissions of VOCs into the environment and the potential risks to public health by providing measures and procedures to be implemented for certain activities operating above defined solvent consumption thresholds.

Annex I of the Directive lists the solvent using activities covered. These include:

- Adhesive coating
- Coating activities applied to
 - vehicle bodies,
 - o trailers,
 - o metallic and plastic surfaces including those on aircraft, ships, trains etc.
 - wooden surfaces
 - o textile, fabric, film and paper surfaces
 - leather
- Steel, copper and aluminium coil coatings
- Dry cleaning
- Footware manufacture
- Manufacture of coating preparations, varnishes, inks and adhesives
- Manufacture of pharmaceutical products
- Printing and reproduction activities
- Rubber conversions
- Surface cleaning processes
- Vegetable oil and animal fat extraction and refining processes
- Vehicle refinishing
- Winding wire coating
- Wood impregnation
- Wood and plastic lamination

The Directive provides limits on emissions from these installations when solvent consumption is above a certain threshold expressed in tonnes per year. The solvent consumption thresholds and VOC emission limit values are set for different types of activities and existing installations must comply with these limits by 31st October 2007.

The emission limits may be set on the the final discharged waste gases into air from a stack or abatement equipment, as fugitive emissions (expressed as a percentage of solvent input) and/or both. Fugitive emissions refer to any emissions not in the waste gases and include uncaptured emissions released to the outside environment via windows, doors, vents and similar openings.

The solvent consumption thresholds, VOC emission limit values and details of the activities covered under the SED are given in Annex IIA of the Official Journal of the European Communities document L85/1-L85/22 (OJ, 1999). For the vehicle coating sector, emission limits are expressed in relation to the surface area of product and amount of solvent emitted per vehicle body. Consumption thresholds for this sector are also expressed in relation to annual production of the coating items.

Activities which cannot be operated under contained conditions may be exempt from the controls of Annex IIA providing an alternative reduction scheme is used. The purpose of the reduction scheme is to allow the operator to achieve by other means emission reductions equivalent to those achieved if the emission limit values were to be applied. In this case, the operator must forward an emission reduction plan which includes decreases in average solvent content and/or increased efficiency to Unclassified AEAT/ENV/R/2475

achieve a reduction in total emissions from the installation to a given percentage of a defined annual reference emission rate, termed the target emission. Details of this are given in Annex IIB of the SED document (OJ, 1999).

The Directive provides guidance on carrying out a solvent management plan (Annex III) based on the quantities of solvent used and their outputs following a mass balance approach.

The SED has provision for Member States to define and implement national plans to achieve emission reductions across certain activities. The Plan must result in a reduction of annual emissions from existing installations covered by the SED by at least the same amount and within the same time frame as would have been achieved by applying the emission limits to individual plant set out in Annex IIA. A national plan may exempt certain existing installations from emission limit values providing the overall reductions of annual emissions are achieved.

Annex B Global Warming Potentials (GWPs) of some common VOCs.

VOC Common name	Chemical formula	Other name	GWP, 100
			horizon
dimethylether	CH ₃ OCH ₃		1 ^a
methylene dichloride	CH ₂ Cl ₂	Dichloromethane	10 ^a
methyl chloride	CH₃CI	Chloromethane	16 ^a
methyl bromide	CH₃Br	Bromomethane	5 ^ª
methylchloroform	CH ₃ CCI ₃	1,1,1-Trichloroethane	144 ^a
HCFC-22	CHCIF ₂	Chlorodifluoromethane	1,780 ^a
HCFC-123	CHCl ₂ CF ₃	Dichlorotrifluoroethane	76 ^a
HCFC-124	CHCIFCF ₃	Chlorotetrafluoroethane	599 ^a
HCFC-141b	CH₃CCI₂F	Dichlorofluoroethane	713 ^a
HCFC-142b	CH ₃ CCIF ₂	Chlorodifluoroethane	2,270 ^a
HCFC-225ca	CHCl ₂ CF ₂ CF ₃	Dichloropentafluoropropane	120 ^a
HCFC-225cb	CHCIFCF ₂ CCIF ₂	Dichloropentafluoropropane	586 ^a
HFC-23	CHF ₃	Trifluoromethane	14,310 ^a
HFC-32	CH ₂ F ₂	Difluoromethane	670 ^a
HFC-125	CHF ₂ CF ₃	Pentafluoroethane	3,450 ^a
HFC-134a	CH ₂ FCF ₃	1,1,1,2-Tetrafluoroethane	1,410 ^a
HFC-143a	CH ₃ CF ₃	1,1,1-Trifluoroethane	4,400 ^a
HFC-152a	CH ₃ CHF ₂	1,1-Difluoroethane	122 ^a
HFC-227ea	CF ₃ CHFCF ₃	1,1,1,2,3,3,3-Heptafluoropropane	3,140 ^a
HFC-236fa	CF ₃ CH ₂ CF ₃	1,1,1,3,3,3-Hexafluoropropane	9,500 ^a
HFC-245fa	CHF ₂ CH ₂ CF ₃	1,1,1,3,3-Pentafluoropropane	1,020 ^a
HFC-365mfc	CH ₃ CF ₂ CH ₂ CF ₃	1,1,1,3,3-Pentafluorobutane	782 ^a
HFC-43-10mee	CF ₃ CHFCHFCF ₂ CF ₃	1,1,1,2,3,4,4,5,5,5-Decafluoropentane	1,610 ^a
HFE-449s1	CH ₃ O(CF ₂) ₃ CF ₃		397 ^a
HFE-569sf2	CH ₃ CH ₂ O(CF ₂) ₃ CF ₃		56 ^a
HFE-347pcf2	CF ₃ CH ₂ OCF ₂ CHF ₂		540 ^a
ethane			8.4 ^b
propane			6.3 ^b
butane			7.0 ^b
ethylene			6.8 ^b
propylene			4.9 ^b

Notes:

a) Taken from Table 2.6 (pp160-161) in IPCC (2005) calculated using the methodologies therein

b) Indirect GWPs taken from Collins et al. (2002) and Table 2.8 in IPCC (2005) representing the impact of the VOC on the global distribution of methane and ozone

c) If the VOC of interest is not listed, assume default values of 0.1 and 10 for a hydrocarbon, spanning the range between its likely direct and indirect effects, and 100 to 5,000 for a fluorocarbon

Annex C Fuel CO₂ conversion factors for different fuel types

Fuel type	Fuel factor (tonnes CO ₂)	Fuel consumption units
Natural gas	0.206	per MWh gas ¹
	6.023	per ktherm gas ¹
Gas oil	3.19	per tonne gas oil
	0.265	per MWh gas oil ¹
	2.674	per thousand litres gas oil
Fuel oil	3.223	per tonne fuel oil
	0.281	per MWh fuel oil ¹
Coal	2.457	per tonne coal
	0.346	per MWh coal ¹
Electricity	0.523	per MWh electricity

¹ Based on Net Calorific Values.

These conversion factors refer to fuels used in 2005 and are based on the 2005 UK Greenhouse Gas Inventory compiled by AEA Energy & Environment (Baggott et al, 2007, http://www.airquality.co.uk/archive/reports/cat07/0704261626 ukghgi-90-05 main chapters final.pdf)



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