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# **Forgotten carbon**

Indirect CO<sub>2</sub> in greenhouse gas emission inventories

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	Forgotten carbon:
2	Indirect CO <sub>2</sub> in greenhouse gas emission inventories
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10	
10	Abstract
12	are required to submit greenhouse gas (GHG) inventories accounting for the emissions and removals occurring
14	within their geographic territories. The Intergovernmental Panel on Climate Change (IPCC) provides inventory
	methodology guidance to the Parties of the UNFCCC. This methodology guidance, and national inventories based
16	on it, omits carbon dioxide (CO <sub>2</sub> ) from the atmospheric oxidation of methane, carbon monoxide, and non-methane
10	volatile organic compounds emissions that result from several source categories. The inclusion of this category of
18	"indirect $CO_2$ in GHG inventories increases global anthropogenic emissions (excluding land use and forestry) between 0.5 and 0.7 percent. However, the effect of inclusion on aggregate UNECCC Appendix Derived HG emissions
20	would be to reduce the growth of total emissions, from 1990 to 2004, by 0.2 percentage points. The effect on the
_ •	GHG emissions and emission trends of individual countries varies. The paper includes a methodology for
22	calculating these emissions and discusses uncertainties. Indirect CO <sub>2</sub> is equally relevant for GHG inventories at
24	other scales, such as global, regional, organizational, and facility. Similarly, project-based methodologies, such as
24	those used under the Clean Development Mechanism, may need revising to account for indirect $CO_2$ .
	<i>Keywords</i> : Carbon dioxide emissions, greenhouse gas inventories, IPCC, indirect $CO_2$
26	1 Introduction
_0	
20	Climate change is as pure a global public good problem as humanity has ever faced. Because both
28	treaty making. The fundamental basis for measuring action and determining compliance with treaties is a
30	national greenhouse gas (GHG) inventory
50	A GHG inventory is an accounting of anthronogenically produced GHG emissions from sources
32	(e.g. fossil fuel combustion) and removals through sinks (e.g. managed forest growth or carbon
52	sequestration) based on rigorous technical methodologies and detailed data collection on relevant
34	activities (e.g., fuel consumption).
	National governments that are Parties to the United Nations Framework Convention on Climate
36	Change (UNFCCC) are required to submit GHG inventories accounting for the emissions and removals
	occurring within their geographic territories. Developed countries (i.e., Annex I Parties under the
38	UNFCCC) must submit inventories annually and apply best practice data collection and calculation
	methodologies (UNFCCC, 2000). Developing countries (i.e., non-Annex I Parties) only are required to
40	periodically submit inventories, as part of their national communications, using simplified methodologies

- and a less rigorous and transparent reporting format.<sup>1</sup>
- 42 The Intergovernmental Panel on Climate Change (IPCC) serves as the primary scientific advising body for the Parties to the UNFCCC and the Kyoto Protocol. One of the duties of the IPCC has been the
- 44 development of GHG inventory methodology guidance, which has been formally adopted by Parties as best practice guidance for the preparation of national inventory reports. The first IPCC guidelines were
- 46 completed in 1994 and have been updated several times (IPCC, 1994, 2000; IPCC/UNEP/OECD/IEA,

<sup>&</sup>lt;sup>1</sup> See <u>http://unfccc.int/national\_reports/non-annex\_i\_natcom/items/2716.php/</u>

1997). The most recent version of the IPCC guidelines was completed in 2006 in preparation for a post-

- 2 Kyoto agreement (IPCC, 2006).<sup>2</sup>
  - Although each version of the IPCC guidelines has been considered the state of the art in GHG
- 4 inventory methodologies at the time, each has omitted a category of carbon dioxide (CO<sub>2</sub>) emissions common to all countries. The new category of emissions raises a number of scientific and technical
- issues, which require a detailed understanding of GHG inventory carbon accounting. 6 This paper will describe the scientific basis for inclusion of this new category of CO<sub>2</sub> emissions.
- 8 It will then analyze the effect of the category on global and national-level GHG emissions and discuss methodological uncertainties. Finally, it will discuss the arguments for and against inclusion in national
- 10 inventory reports and future IPCC guidelines. A key finding is that the omission of emissions from this
- category leads to an underestimate of all countries' anthropogenic GHG emissions, and affects the 12 emission trends of individual countries differently.

#### 2 Scientific and technical issues

#### 2.1 14 Atmospheric chemistry

The Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories addresses the issue 16 of "double counting carbon" in estimating carbon dioxide  $(CO_2)$  emissions from fossil fuels (see Appendix 1 in the online supplementary materials for this article) (IPCC/UNEP/OECD/IEA, 1997). In

- 18 one case, by double counting, the IPCC is referring to the fact that some carbon from fossil fuel combustion is emitted as methane  $(CH_4)$ , carbon monoxide (CO), and non-methane volatile organic
- compounds (NMVOCs). Well-accepted atmospheric chemistry theory shows that the fate of the carbon in 20 these compounds is oxidation to  $CO_2$ , which adds to the overall atmospheric burden (i.e., concentration)
- of CO<sub>2</sub> (Seinfeld and Pandis, 1998). The major removal process (i.e., sink) for CH<sub>4</sub>, CO, and NMVOCs 22 from the atmosphere is through a chemical reaction with hydroxyl radicals (OH) in the troposphere
- (IPCC, 2001).<sup>3</sup> 24

This  $CO_2$  resulting from the atmospheric oxidation of  $CH_4$ ,  $CO_2$ , and NMVOCs is referred to as indirect CO<sub>2</sub>. Indirect emissions occur when one emitted gas (i.e., CH<sub>4</sub>, CO, and NMVOCs) affects the 26 atmospheric burden of another GHG gas (i.e., CO<sub>2</sub>).

- 28 Indirect CO<sub>2</sub> resulting from the oxidation of  $CH_4$ , CO, and NMVOCs produced by fossil fuel combustion are included in all versions of the IPCC guidelines and are reported in national GHG
- 30 inventories. The IPCC methodology used by all countries for estimating CO<sub>2</sub> emissions from fuel combustion is based on fuel consumption statistics and assumes that all the carbon in the fuel-minus the

32 portion that remains as soot or ash solids—is oxidized to CO<sub>2</sub>. The methodology accepts that a portion of the carbon in fuels is actually emitted as  $CH_4$ , CO, and NMVOCs, which later oxidizes to  $CO_2$ . The

34 fraction of carbon from fossil fuel combustion (average) that is initially emitted as CH<sub>4</sub>, CO, or NMVOCs is roughly 1 to 4 percent, and varies significantly by the efficiency of combustion and use of emission 36 control equipment.

GHG inventory methods intentionally double count some carbon atoms (e.g., once as an atom in a  $CH_4$  molecule and once in a  $CO_2$  molecule) in order to develop a more comprehensive estimate of the

38 long-term atmospheric  $CO_2$  burden and therefore the radiative forcing<sup>4</sup> effect of fossil fuel combustion

emissions. 40

<sup>&</sup>lt;sup>2</sup> The 2006 IPCC guidelines will not be used for the preparation of inventories under the Kyoto Protocol because they were prepared after the agreement was negotiated.

<sup>&</sup>lt;sup>3</sup> See also http://www.epa.gov/methane/scientific.html/ for a description of atmospheric methane sinks.

<sup>&</sup>lt;sup>4</sup> "Radiative forcing is the change in the net vertical irradiance (expressed in Watts per square metre: Wm<sup>2</sup>) at the tropopause due to an internal change or a change in the external forcing of the climate system, such as, for example, a change in the concentration of carbon dioxide or the output of the Sun. Usually radiative forcing is computed after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with all tropospheric properties held fixed at their unperturbed values. Radiative forcing is called instantaneous if no change in stratospheric temperature is accounted for" (IPCC, 2001).

GHG inventories include emissions of multiple chemical species. The IPCC has developed an
index—the Global Warming Potential (GWP)—for comparing and combining the time-integrated (e.g., 100 year) radiative forcing effects of various gases (IPCC, 2001). Gases with long atmospheric lifetimes
that directly contribute to radiative forcing have a GWP value relative to CO<sub>2</sub> and are included in GHG inventories. In addition to CO<sub>2</sub>, these gases include CH<sub>4</sub>, nitrous oxide (N<sub>2</sub>O), hydrofluorocarbons
(HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF<sub>6</sub>). Methane has an atmospheric lifetime of

approximately 12 years.
 The production of CO<sub>2</sub> from the atmospheric oxidation of CH<sub>4</sub> is not accounted for by the GWP for methane. The IPCC Third Assessment Report contains the following text explaining this point

10 (Section 6.12.3.1 Methane) (IPCC, 2001):

It should be noted that the climate forcing caused by  $CO_2$  produced from the oxidation of  $CH_4$  is not included in these GWP estimates. As discussed in the [Second Assessment Report], it is often the case

- that this  $CO_2$  is included in national carbon production inventories. Therefore, depending on how the
- 14 inventories are combined, including the  $CO_2$  production from  $CH_4$  could result in double counting this  $CO_2$ .
- 16 Carbon monoxide and NMVOCs do not have a direct radiative forcing effect and have shorter atmospheric lifetimes that vary from a few minutes to a few months (IPCC, 2001; Seinfeld and Pandis,

18 1998).<sup>5</sup>

#### 2.2 GHG inventory accounting

20 Methane, CO, and NMVOCs are emitted from a variety of combustion, industrial, agricultural, and waste management processes. Although it is well known within the scientific community that the fate 22 of the carbon in these gases is oxidation to CO<sub>2</sub>, GHG inventory methodologies have not consistently treated the issue of the atmospheric oxidation of these gases (Gillenwater et al., 2002). Indirect CO<sub>2</sub> from

24 the atmospheric oxidation of  $CH_4$ , CO, and NMVOCs is included in inventories for some source categories, correctly excluded for some categories, and incorrectly excluded for others. The source

26 categories falling into these first two groups are:

Fossil fuel combustion and fueling activities including the atmospheric oxidation of CH<sub>4</sub>, CO, and
 NMVOCs to CO<sub>2</sub> is accounted for by the methodology used by all countries to calculate CO<sub>2</sub>

emissions from fossil fuel combustion.<sup>6</sup> This methodology is based on fuel consumption statistics and data on the carbon content of each fuel; it assumes that all carbon in the fuel is oxidized to  $CO_2$  in the atmosphere, except the small fraction of carbon remaining as un-oxidized solids, for example soot or

as as (IPCC, 2000, 2006; IPCC/UNEP/OECD/IEA, 1997).<sup>7</sup> The implicit assumption for all countries' estimates of  $CO_2$  emissions from fossil fuel combustion, which is by far the dominant source of greenhouse gas emission globally, is that indirect  $CO_2$  is included in GHG inventories.

Several managed biological systems (e.g., livestock) also emit CH<sub>4</sub>, CO, and NMVOCs. The carbon

36 in these gases is derived from rapidly cycling (non-fossil) sources. For example, the carbon content of  $CH_4$  from enteric fermentation is derived from plant matter, which has converted atmospheric CO<sub>2</sub> to

38 organic compounds. The atmospheric oxidation of  $CH_4$  merely completes a natural cycle and is not treated as a net anthropogenic contribution to the atmosphere's  $CO_2$  burden. Any net changes in the

40 biogenic carbon stocks found in plant matter are assumed to be captured in GHG inventories through estimates of  $CO_2$  emissions and removals from land-use and land-use changes and forestry.

<sup>&</sup>lt;sup>5</sup> CO and NMVOCs do have an indirect radiative forcing effect, primarily through chemical reactions that affect the concentration of CH<sub>4</sub>, CO<sub>2</sub>, and formation of tropospheric ozone (ozone is a GHG) (IPCC, 2001).

<sup>&</sup>lt;sup>6</sup> This includes evaporative emissions of NMVOCs associated with immediate fueling activities for mobile or stationary sources where the mass of carbon associated with these emissions is accounted for in the fuel consumption activity data used in the combustion-related emission estimates for CO<sub>2</sub>.

<sup>&</sup>lt;sup>7</sup> If a direct measurement method is used to estimate  $CO_2$  emissions from fuel combustion then  $CO_2$  emissions from the atmospheric oxidation of  $CH_4$ , CO, and NMVOCs will not be included and must be estimated separately.

2	such as coal mining as well as petroleum and natural gas exploration, processing and storage. The carbon
	emitted in the form of CH <sub>4</sub> , CO, or NMVOCs from these fugitive emission source categories is not
4	captured in fuel consumption statistics because it occurs prior to the collection of data on fossil fuel
	consumption. Therefore, indirect $CO_2$ from these fugitive sources is not accounted for by IPCC
6	methodologies or in national GHG inventories. <sup>8</sup>
	Some industrial processes in which carbon from fossil fuel sources is used as a production
8	feedstock (e.g., petrochemical production) may also be sources of indirect CO <sub>2</sub> . The carbon emitted in the
	form of CH <sub>4</sub> , CO, or NMVOCs from these industrial processes may be included in a country's non-
10	energy use of fossil fuel statistics or they may be estimated separately. <sup>9</sup> Carbon dioxide emissions from
	industrial processes that use carbon feedstocks as reducing agents (e.g., iron and steel production) are
12	typically included in GHG inventories based on the assumption that the carbon in the reducing agent is
	fully oxidized. Depending on the assumptions and methods used to estimate storage and emissions from

Methane, CO, or NMVOCs are also emitted as fugitives from fossil fuel production activities

- 14 those non-energy use and feedstock categories (e.g., solvent use), indirect CO<sub>2</sub> resulting from emissions of CH<sub>4</sub>, CO, and NMVOCs may or may not be accounted for in GHG inventories. IPCC (2006) includes
- 16 detailed guidance on the estimation of emissions from non-energy uses of fossil fuels.
- See Appendix 2 in the online supplementary materials for this article for a list of the source categories relevant to the accounting of indirect  $CO_2$  and describes how the accounting should be performed to consistently include all indirect  $CO_2$  in GHG inventories.

#### 20 2.3 Estimation methodology

The methodologies for calculating indirect CO<sub>2</sub> from the atmospheric oxidation of CH<sub>4</sub>, CO and NMVOC are simple and for countries that already have detailed inventories of CH<sub>4</sub>, CO, and NMVOC emissions, no additional data collection should be necessary. Indirect CO<sub>2</sub> emissions are calculated by

converting previously estimated emissions of  $CH_4$ , CO, or NMVOCs to  $CO_2$  based on the carbon content of each gas.

The emissions of  $CO_2$  from the atmospheric oxidation of  $CH_4$  are calculated by applying a factor of 44/16—the ratio of molecular weight of  $CO_2$  to the molecular weight of  $CH_4$ —to emissions from the appropriate source categories (e.g., coal mining, petroleum and natural gas systems) (Equation 1).

30  $Emissions_{CO2} = Emissions_{CH4} \times 44/16$ 

A similar process is used to calculate indirect CO<sub>2</sub> from the atmospheric oxidation of CO; however, a factor of 44/28 is used to account for the lower mass fraction of carbon in carbon monoxide
 (Equation 2).

- 36  $Emissions_{CO2} = Emissions_{CO} \times 44/28$
- 38 To estimate indirect CO<sub>2</sub> from NMVOC emissions the following steps are proposed for the preparation of national GHG inventories:
- Separate the portion of national NMVOCs emissions resulting from biogenic materials from the portion of NMVOC emissions resulting from petroleum or other fossil fuel products.

[Equation 2]

[Equation 1]

<sup>&</sup>lt;sup>8</sup> The United States' GHG Inventory submitted in 2002 to the UNFCCC did include indirect  $CO_2$  from the atmospheric oxidation of  $CH_4$ , but it was excluded from subsequent year submissions.

<sup>&</sup>lt;sup>9</sup> Non-energy products from fossil fuels include industrial applications of fossil carbon material such as in the manufacture of ammonia from natural gas. Under the IPCC guidelines, countries are to collect statistics on these non-energy uses and estimate and report any emissions separately from the oxidation of feedstock carbon.

14

- Identify the portion of the fossil-based NMVOC emissions resulting from relevant energy and industrial process source categories (as determined using the table in Appendix 2 in the online supplementary materials for this article).
- For the portion of these NMVOC emissions resulting from solvent use, determine the average carbon content (on a mass basis) based on a chemical speciation profile (see Appendix 3 in the online
- 6 supplementary materials for this article). If information on the speciation profile is not available, assume a default average carbon content of 60 percent by mass (default) for use in Equation 3.
- 8 For the remaining portion of relevant NMVOC emissions from other source categories, determine carbon content values using a chemical speciation profile. If information on the speciation profile is
- 10 not available, assume an average carbon content of 85 percent by mass (default) for use in Equation 3.
- 12  $Emissions_{CO2} = Emissions_{NMVOCs} \times Percent \ carbon \ in \ NMVOCs \ by \ mass \times 44/12$  [Equation 3]
  - NMVOCs do not represent a single molecular species, but instead a broad range of volatile
- hydrocarbon species with varying molecular weights and carbon contents. Therefore, an accurate estimate of emissions of  $CO_2$  from the atmospheric oxidation of NMVOCs requires a chemical speciation profile
- of the constituent NMVOCs.
   The default carbon content factors for NMVOCs emissions proposed above were selected based on data from four countries. Data on NMVOC emissions from the U.S. National Air Quality and
- 20 Emissions Trends Report data (EPA, 2002) include the following end-use categories: industrial releases (i.e., chemical and allied products, petroleum and related industries, metals processing, and other
- industrial processes) and product use (i.e., solvent use). For industrial NMVOC emissions, a carbon content of 85 percent by mass was assumed to reflect the carbon content of a typical volatile organic
- compound. Separately, the weighted average carbon content of U.S. NMVOC emissions from solvent evaporation was estimated to be 56 percent by mass. Similar analyses of solvent use emissions from
- Austria<sup>10</sup> and Hungary<sup>11</sup> lead to weighted average carbon contents of 60 to 66 and 76 to 80 percent by mass, respectively. The Netherlands<sup>12</sup> reported carbon contents (by mass) for solvents as follows: for
- 28 paint application 64 percent; degreasing and dry cleaning, 16 percent; chemical products, manufacture and processing, 63 percent;, and for other 69 percent. The Dutch percentages are based on NMVOC
- 30 profiles for each category and the mass of the NMVOC species.

## 3 Implications for GHG emission estimates

- 32 For some countries, indirect CO<sub>2</sub> from atmospheric oxidation of CH<sub>4</sub>, CO, and NMVOCs
- accounts for more than 1 percent of their total GWP-weighted emissions. To estimate indirect CO<sub>2</sub>, the default methodology described above was applied to four datasets of national GHG emissions.<sup>13</sup> These datasets include:
- National inventory reports submitted by Annex I Parties to the UNFCCC in 2006 and the most recent national communications submitted by non-Annex I Parties;<sup>14</sup>
- The compilation database of party submissions held by the UNFCCC Secretariat in Bonn, Germany;

<sup>&</sup>lt;sup>10</sup> Austria's national GHG inventory report for 2004.

http://unfccc.int/files/national\_reports/annex\_i\_ghg\_inventories/national\_inventories\_submissions/application/zip/au t\_2004\_nir\_15apr.zip/

<sup>&</sup>lt;sup>11</sup> Hungary's national GHG inventory report for 2004.

http://unfccc.int/files/national\_reports/annex\_i\_ghg\_inventories/national\_inventories\_submissions/application/zip/h un\_2004\_nir\_4jun.zip/

<sup>&</sup>lt;sup>12</sup> The Netherlands national GHG inventory report for 2004.

http://unfccc.int/files/national\_reports/annex\_i\_ghg\_inventories/national\_inventories\_submissions/application/zip/nl d\_2004\_nir\_1apr.zip/

 $<sup>\</sup>frac{13}{14}$  The data in each of these four datasets are not independent. Significant overlaps exist in the data sources used.

<sup>&</sup>lt;sup>14</sup> <u>http://unfccc.int/national\_reports/annex\_i\_ghg\_inventories/national\_inventories\_submissions/items/3734.php/</u>

- The World Resource Institute's Climate Analysis Indicator Tool (CAIT);<sup>15</sup> and
- 2 RIVM/TNO's EDGAR 3.2 database (Olivier, 2002).<sup>16</sup>
  - Because of the complexity of analyzing  $CO_2$  emissions from non-energy uses of fossil fuels,
- 4 indirect CO<sub>2</sub> estimates were made only using data for fugitive emissions from fossil fuel production activities (e.g., coal mining and petroleum and natural gas production). Globally and for most countries,
- 6 fugitive sources account for the majority of indirect  $CO_2$ , although for some countries indirect  $CO_2$  from industrial processes and solvent use may also be significant.

#### 8 3.1 Implications for global and international GHG emissions

Both the CAIT and EDGAR databases provide global estimates of all GHGs for all countries. Based on CAIT data, the inclusion of indirect  $CO_2$  from the atmospheric oxidation of  $CH_4$ , CO, and

- NMVOCs in GHG inventories would increase global anthropogenic emissions of all GHGs from all sources (excluding land-use, land-use change and forestry) by 0.7 and 0.5 percent in 1990 and 2000,
- respectively. Based on similarly defined EDGAR data, the inclusion of indirect  $CO_2$  would increase global GHG emissions by 0.6 percent in 2000.<sup>17</sup> Based on data reported by countries to the UNFCCC
- Secretariat, the inclusion of indirect  $CO_2$  would increase aggregate Annex I Party emissions by 0.6 and 0.4 percent in 1990 and 2004, respectively. For comparison purposes,  $CO_2$  emissions from all aviation
- activities account for between 1.5 and 2 percent of global GHG emissions from all sources (IPCC, 1999). 18 The decrease in emissions from indirect CO<sub>2</sub> globally and from Annex I Parties (down 23

percent) is the result of decreased fugitive emissions from coal mines and petroleum and natural gas activities. By omitting indirect CO<sub>2</sub>, global and Annex I GHG emission trends have been upwardly

biased. UNFCCC data from national inventory reports shows that aggregate GHG emissions from Annex

- I Parties has increased by 2.5 percent from 1990 to 2004. However, if emissions from indirect  $CO_2$  are included, then this value is revised downward to an increase of 2.3 percent. Therefore, using the current
- 24 IPCC guidelines and UNFCCC reporting framework produces an overestimation of the Annex I GHG emissions trend of 0.2 percentage points.

### 26 **3.2** Implications for national GHG emission accounts

- Although including indirect CO<sub>2</sub> reduces the growth in aggregate emissions across countries, the effect of their inclusion on individual country GHG inventory estimates varies depending on the level of fossil fuel production activities and the extent to which emissions control measures have been
- 30 implemented (e.g., coal mine methane capture and associated gas flaring instead of venting).

The increase in a country's total emissions from the inclusion of indirect  $CO_2$  varies from close to 32 zero to several percent. Table 1 presents emissions data for the 11 countries with the largest emissions

- from indirect  $CO_2$ , based on data each country submits under the UNFCCC.<sup>18</sup> Table 2 presents similar data that include indirect  $CO_2$  from industrial process and solvent use emissions of  $CH_4$ , CO, and
- NMVOCs as well as from fossil fuel fugitive sources. Table 2 only includes the subset of countries in Table 1 that reported CO and NMVOC emissions in their national submissions under the UNFCCC.
- Because Table 2 includes some indirect CO<sub>2</sub> sources that are likely to already be accounted for in national inventories along with emissions from feedstock and other non-energy uses of fossil fuels, the estimates
- in Table 2 are likely to be overestimates. The actual value of emissions from indirect  $CO_2$  for these
- 40 countries is likely between the estimates presented in these two tables.

<sup>&</sup>lt;sup>15</sup> Climate Analysis Indicators Tool (CAIT) version 4.0. (Washington, DC: World Resources Institute, 2007). Available at <u>http://cait.wri.org</u>

<sup>&</sup>lt;sup>16</sup> http://www.mnp.nl/edgar/model/v32ft2000edgar/edgv32ft-ghg/

<sup>&</sup>lt;sup>17</sup> All estimates made using GWP values from IPCC (1996) to be consistent with Kyoto Protocol accounting.

<sup>&</sup>lt;sup>18</sup> CH<sub>4</sub> emissions data reported in Saudi Arabia's national communication are unexpectedly low, given the extent of petroleum-related activities. Saudi Arabia is included in Table 1 based on estimates in CAIT and EDGAR, which are more than an order of magnitude larger (see Table 3).

All of the Annex I Parties in Table 1 exhibit decreasing emissions from indirect CO<sub>2</sub> from 1990 to 2004, except Canada. Although emissions from indirect CO<sub>2</sub> for Russia and Ukraine decreased, they did not decrease as much as each country's total emissions, as can be seen by the increasing fraction of

- 4 national total values from 1990 to 2004. All three of these countries would be disadvantaged by the inclusion of indirect CO<sub>2</sub> in their national GHG emission inventory accounts. For example, inclusion
- 6 would increase Canada's historical growth in emissions by 0.2 percentage points (i.e., from 26.6 to 26.8 percent from 1990 to 2004).
- 8 In contrast, including indirect  $CO_2$  in national GHG inventories would be beneficial to the other eight Parties presented in Table 1, as it would reduce the growth in their emissions over the period. For
- 10 example, the inclusion of indirect  $CO_2$  would reduce the growth in U.S. emissions by 0.2 percentage points (i.e., from 15.8 to 15.6 percent from 1990 to 2004).
- 12 Detailed background data for all emission estimates and indirect CO<sub>2</sub> estimates for all countries, for which data was available, are provided in Appendix 5 in the online supplementary materials for this 14 article.
- 16

# Table 1: Indirect CO2 from the atmospheric oxidation of CH4, CO, and NMVOC emissions from fossil fuel1818

	Frac	tion of <b>r</b>	ational	total	Absolu	Change			
Country/Party	1990	1994	1999	2004	1990	1994	1999	2004	(1990-2004)
<b>Russian Federation</b>	1.2%			1.5%	39 965			31 335	-22%
United States	0.6%			0.4%	34 821			28 280	-19%
China <sup>b</sup>		0.5%				19 866			
European Community	0.3%			0.2%	13 947			7 260	-48%
Ukraine	1.2%			1.7%	11 348			6 873	-39%
Canada	1.1%			1.2%	6 502			9 133	40%
Indonesia <sup>b</sup>		0.6%				5 605			
Venezuela <sup>b</sup>			2.6%				4,978		
Iran		1.0%				4 066			
India <sup>b</sup>		0.3%				3 4 4 0			
Poland <sup>c</sup>	0.5%			0.5%	2 4 3 1			2 146	-12%
Saudi Arabia <sup>b</sup>	0.1%				210				

<sup>a</sup> Data based on emissions reported in national inventory reports or national communications submitted under the

20 UNFCCC.

<sup>b</sup> National submissions and estimates in table exclude emissions of CO and NMVOCs.

<sup>c</sup> 1990 estimates from Poland exclude emissions of CO and NMVOCs.

24

Table 2: Indirect CO<sub>2</sub> from the atmospheric oxidation of CH<sub>4</sub>, CO, and NMVOC emissions from fossil fuel fugitives and industrial processes (percentage of national GHG emissions and Gg CO<sub>2</sub>)\*

Country/Party	1990	2004	1990	2004
Russian Federation	1.2%	1.5%	41 737	32 778
United States	0.9%	0.6%	56 394	44 888
European Community	0.6%	0.4%	25 877	20 952
Ukraine	1.5%	1.9%	14 125	7 755
Canada	1.4%	1.4%	8 190	10 921
Iran (1994)	1.7%		7 2	261
Poland		0.6%		2 301

\* Data based on emissions reported in national inventory reports or national communications submitted under the UNFCCC. Data only presented for countries reporting detailed CO and NMVOC emissions data in national

inventory reports or national communications.

6

4

2

#### **4** Uncertainties

8 The principal sources of uncertainty in the methods for estimating emissions from indirect CO<sub>2</sub> include the following:

- The uncertainty in estimated CH<sub>4</sub>, CO, and NMVOC emissions will vary significantly by source category. Discussion of uncertainties and default uncertainty values for individual source categories are provided in IPCC (2006).
- Carbon dioxide emissions from atmospheric oxidation of CH<sub>4</sub>, CO, and NMVOCs could be omitted 14 or double-counted if incorrect assumptions are made regarding the accounting of non-energy use and feedstock fossil carbon. Countries apply carbon storage factors to their data on non-energy uses of
- 16 fossil-fuel derived feedstocks to account for the fraction of carbon oxidized to CO<sub>2</sub> and emitted by industrial processing or during a product's use phase. The IPCC default values used by most countries 18 are based on expert judgment; actual values for many countries may significantly differ from these

defaults. There is no risk of double counting, however, with the estimation of  $CO_2$  from the oxidation of fugitive CH<sub>4</sub>, CO, or NMVOCs emissions from fossil fuels because the carbon in these fuels is not

captured in fossil fuel consumption statistics.

The actual carbon content of NMVOC emissions may differ from the default values recommended, although the chemical properties of volatile hydrocarbons limit the possible range of carbon content values (see Appendix 2 and 3 in the online supplementary materials for this article).

• The indirect CO<sub>2</sub> methodology is based on the assumption that methane is completely oxidized to CO<sub>2</sub> in the same year that it is emitted to the atmosphere. Methane's average atmospheric lifetime is

- approximately 12 years. Therefore, there is a time delay between the emission of methane and its oxidation to  $CO_2$ . In theory, the time-integration used to develop a GWP for this indirect  $CO_2$  would produce a value of less than one because it is in the form of a  $CH_4$  molecule for approximately the
- 30 first several years. However, the simplification of applying the standard  $CO_2$  GWP value is consistent with the approach already in use for emissions of  $CH_4$  from evaporative and combustion emissions

32 associated with other source categories such as fossil fuel combustion.

There are also uncertainties associated with the data used to estimate emissions from indirect  $CO_2$ in this paper. Table 3 presents national indirect  $CO_2$  estimates for the largest emitters using three of the

datasets described above. There is significant variation between the estimates from each database. Both

36 CAIT and EDGAR use default data and methods for many countries, which may explain their divergence from national submissions under the UNFCCC. Data in the UNFCCC database should exactly match that

- 38 reported in individual country national reports and communications; however, some countries use reporting formats that inhibit the importing of data by the UNFCCC Secretariat.
- 40

	CAIT <sup>a</sup>		<b>EDGAR</b> <sup>a</sup>				
<b>Country/Party</b>	1990	2000	2000	1990	1994	2000	2004
<b>Russian Federation</b>	51 975	25 575	48 413	39 965		29 886	31 335
United States	30 145	26 950	60 120	36 537		31 120	29 703
China	24 383	22 969	33 915		19 866		
European Community	15 623	9 926	17 990	14 023		9 282	7 294
Ukraine	22 432	12 637	6 632	11 348		6 938	6 873
Canada <sup>b</sup>	3 680	5 133	6 1 3 2	4 516		6 776	6 905
Indonesia	576	1 218	8 151		5 605		
Venezuela <sup>c</sup>	5 382	6 993	3 572				
Iran	2 946	7 425	7 790		4 066		
India	2 6 3 2	4 727	5 105		3 4 4 0		
Poland <sup>c</sup>	2 737	2 1 2 1	5 793				
Saudi Arabia <sup>c</sup>	3 785	6 142	7 559				

Table 3: Indirect CO<sub>2</sub> from the atmospheric oxidation of CH<sub>4</sub>, CO, and NMVOC emissions from fossil fuel fugitives using multiple databases (Gg CO<sub>2</sub>)

<sup>a</sup> Estimates do not include indirect CO<sub>2</sub> from CO and NMVOC emissions.

<sup>b</sup> The UNFCCC database does not include CO and NMVOC data for Canada.

<sup>c</sup> The UNFCCC database does not include data for these Parties. See Table 1 for data taken directly from national submissions.

8

24

4

#### 5 Arguments for and against including indirect CO<sub>2</sub> in GHG inventories

The IPCC recently published its 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC, 2006). These guidelines are likely to be the technical basis for determining compliance with any negotiated post-Kyoto emission reduction protocol.

The 2006 IPCC Guidelines does mention indirect CO<sub>2</sub> from the atmospheric oxidation of CH<sub>4</sub>,

14 CO, and NMVOCs (see Overview volume, p. 12) and provides partial methodological guidance (see Volume, section 7.2.1.5). However, it does not list indirect CO<sub>2</sub> as a source category for reporting

16 purposes (see Appendix 6 in the online supplementary materials for this article). Past versions of the IPCC guidelines did not consider indirect  $CO_2$  from the atmospheric oxidation of  $CH_4$ , CO, and NMVOC

18 emissions from non-fossil fuel combustion sources (see Appendix 1 in the online supplementary materials for this article).

20 The initial proposal for including indirect  $CO_2$  in GHG inventories was based on a conference paper by Gillenwater et al. (2002). A summary of the arguments for and against inclusion of indirect  $CO_2$ 

in GHG inventories, along with responses by the author, are provided in Table 4.

In the meantime, Working Group I of the IPCC completed work on its fourth scientific assessment report (AR4) (IPCC, 2007). The assessment report explicitly incorporates indirect  $CO_2$  in the

IPCC's analyses of radiative forcing and discussion of GWP values. In assessing the components of

26 radiative forcing, AR4 included forcings due to CO<sub>2</sub> from "fossil carbon from non-CO<sub>2</sub> gaseous compounds, which eventually increase CO<sub>2</sub> in the atmosphere (from CO, CH<sub>4</sub>, and NMVOC emissions)"

- 28 (IPCC, 2007) p.205. AR4 also addresses the issue of the GWP value for methane by stating: Following the approach taken by the [IPCC Second Assessment Report] and the [IPCC Third Assessment]
- 30 Report], the CO<sub>2</sub> produced from oxidation of CH<sub>4</sub>, CO and NMVOCs of fossil origin is not included in the GWP estimates since this carbon has been included in the national CO<sub>2</sub> inventories. This issue may need to
- be reconsidered as inventory guidelines are revised. (IPCC, 2007) p.214. Historically, these scientific assessments have formed a basis for the selection of GHGs and

34 sources for inclusion in IPCC methodology reports. Given the above findings by IPCC Working Group I authors, the inclusion of indirect CO<sub>2</sub> from the atmospheric oxidation of CH<sub>4</sub>, CO, and NMVOC

36 emissions in GHG national GHG inventory reports and IPCC guidelines reports is further justified.

#### 6 Conclusion

- 2 The atmosphere's  $CO_2$  burden is increased through the atmospheric oxidation of  $CH_4$ , CO, and
- NMVOC emissions from anthropogenic sources where the carbon in these gases originates in fossil fuels and other materials. A significant portion of these emissions from indirect CO<sub>2</sub> are excluded from national
- 4 and other materials. A significant portion of these emissions from indirect CO<sub>2</sub> are excluded from nat GHG emission inventories prepared using IPCC GHG inventory guidelines. The methodology for
- 6 estimating indirect  $CO_2$  is not burdensome on Parties to the UNFCCC, and uncertainties are equivalent to or less than those of other source categories included in inventories. The inclusion of indirect  $CO_2$  from
- 8 the atmospheric oxidation of CH<sub>4</sub>, CO, and NMVOCs in GHG inventories would increase global anthropogenic emissions of all GHGs from all sources (excluding land-use, land-use change and forestry)
- between 0.7 and 0.5 percent. However, the effect of inclusion on aggregate UNFCCC Annex I Party GHG emissions for would be to reduce the growth by 0.2 percentage points from 1990 to 2004. The effect on
- 12 the GHG emissions and emission trends of individual countries varies. In addition, indirect CO<sub>2</sub> is equally relevant for GHG inventories at other scales, such as global,
- 14 regional, organizational, and facility. Similarly, project-based methodologies, such as those used under the Clean Development Mechanism, may need revising to account for indirect CO<sub>2</sub>. Inclusion of indirect
- 16 CO<sub>2</sub> on calculated fugitive emission reductions from coal mines and petroleum and natural gas systems will increase the amount of credit these projects earn by 13 percent.
- 18

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- 24 Greenhouse Gas Inventories Programme and other lead authors, during the drafting of the 2006 IPCC Guidelines for National Greenhouse Gas Inventories. The author is solely responsible for all errors and
- 26 omissions.

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Table 4: Arguments against inclusion of indirect CO <sub>2</sub> from the atmospheric oxidation of CH <sub>4</sub> , CO, and NMVOCs in the 2006 IPCC Guidelines an
related reponses*

Argument against inclusion	Response
IPCC methodologies should not account for GHG	It is assumed that the CH <sub>4</sub> , CO, and NMVOCs emitted to the atmosphere is oxidized to CO <sub>2</sub> in the same
emissions before they actually occur.	year that it is emitted. This is a simplification in the case of CH <sub>4</sub> , because the atmospheric lifetime of
	CH <sub>4</sub> is on the order of 12 years. However, it is not a simplification for CO and NMVOCs because their
	atmospheric lifetime is significantly less than one year. The indirect CO <sub>2</sub> method does not set a new
	precedent. Many existing IPCC methods, such as for fossil fuel combustion, accept a time delay in actual
	emissions.
Uncertainties in the estimates of indirect $CO_2$ are too	The uncertainties in the major sources of indirect $CO_2$ are not large and are the same as that for fugitive
large.	emissions of CH <sub>4</sub> , which are already included in inventories. Overall, these uncertainties are less than
	those for many major agricultural categories. If indirect $CO_2$ is excluded for reasons of uncertainty, then
	several major sources of emissions and removals would also need to be excluded.
IPCC GWP values should instead be revised to	Implementing this suggestion would mean that different GWPs for both CO <sub>2</sub> and CH <sub>4</sub> would be needed
account for indirect $CO_2$ .	for particular source categories. The application of a given GWP value would depend on the origin of
	the carbon and the specific accounting practices for the emission source. IPCC Working Group I, which
	develops GWP values, has repeatedly rejected this option.
IPCC should create a separate research effort that	The existing guidance is science-based. No scientific or technical argument has been presented to justify
uses a "science-based approach" to address this issue.	the creation of a special ad-hoc body.
Countries are not provided a way to improve	The Guidelines explicitly state that estimates can be improved by improving the quality of the
estimates of indirect $CO_2$ or to reduce emissions.	underlying CH <sub>4</sub> , NMVOC, and CO emissions data. There is no difference in the guidance provided for
	indirect $CO_2$ from that provided for other source categories.
The additional requirement overly complicates the	The methods to estimate indirect $CO_2$ are simple and rely on data already reported in national
inventory.	inventories. Little or no additional effort is required by Parties to report indirect $CO_2$ .
Indirect $CO_2$ is already included in the oxidation	The oxidation factors used to estimate $CO_2$ from fossil fuel combustion only addresses carbon left
factor used for fossil fuel combustion emissions, and	behind as solids (e.g., ash and soot). Contrary to the reviewer's comment, the IPCC default oxidation
therefore is not included in the methodology for	factors do not include carbon emitted in the form of $CH_4$ , CO, or NMVOCs."
tossil fuel combustion as claimed.	
The IPCC should further investigate the fraction of	It is well recognized in the atmospheric chemistry literature that the fate of $CH_4$ , CO, and NMVOC is
$CH_4$ , CO, and NMIVOUs that actually oxidize to $CO_2$	complete oxidation to $CO_2$ . Such an investigation is unnecessary.
in the atmosphere.	
IPCC should not require countries to use emission	Data from other emission inventories are no different from data used to estimate emissions for other
estimates for other pollutants in their GHG	categories. All national statistics undergo some amount of statistical and mathematical manipulation.
inventories.	I here is no reason to treat data from emission inventories differently from other data sources.

<sup>&</sup>lt;sup>19</sup> Personal communication between Michael Gillenwater and Gregg Marland (Oak Ridge National Laboratories), July 2004.

If indirect CO <sub>2</sub> from CO and NMVOCs is included in	The carbon in these halogenated compounds typically comes from fossil fuel feedstocks (e.g., natural
inventories, then indirect CO <sub>2</sub> from other pollutants	gas), and therefore may already be included in national emission estimates from non-energy and
such as HFC, HCFCs, and CFCs should also be	feedstock uses of fossil fuels. If the atmospheric lifetime of the compound is shorter than 100 years (the
included.	basis for the GWP time integration) then they should be included. However, the resulting emissions from
	indirect CO <sub>2</sub> from these compounds are likely to be exceedingly small. For example, indirect CO <sub>2</sub> from
	HFC-134a emissions is less than 0.0005% of global emissions.
IPCC methodologies should only include direct GHG	Inventories already implicitly include indirect CO <sub>2</sub> from fossil fuel combustion. Indirect N <sub>2</sub> O emissions
emissions. All indirect GHG emissions should be	for agricultural soil management are also a major source category in the IPCC Guidelines. Limiting the
excluded from the IPCC Guidelines.	Guidelines to direct sources would entail a major change, the recalculation of every countries fossil fuel
	combustion emission estimates, and the deletion of a major agriculture source category.

\* This table summarizes information in IPCC deliberation and review tracking documents during the drafting of the 2006 IPCC Guidelines for National Greenhouse Gas Inventories.

## Appendix 1: Language in the Revised 1996 IPCC Guidelines

2

The following excepts are taken from pages Overview.7-8 of the IPCC Reference Manual (Volume 1) (IPCC/UNEP/OECD/IEA, 1997).

The Reference Approach provides an upper bound to CO<sub>2</sub> emissions inferred from the country's supply of fossil fuels by identifying the carbon content, subtracting from it the carbon stored in non-energy products and products made from fuels used as raw material, adjusting for carbon which remains unburnt and multiplying by 44/12. It is an upper bound because some of the carbon will be emitted in forms other than CO<sub>2</sub>, in part because fuel combustion is not always complete but also because fuels may leak or evaporate. Consequently the CO<sub>2</sub> emissions figure obtained from the Reference Approach will include carbon emitted

as CH<sub>4</sub>, CO or NMVOC. At the same time the Guidelines encourage countries to estimate separate inventories for these gases and when this is done these gases are reported twice, in their emitted form and as CO<sub>2</sub>. It is in this sense that they are "double counted".

- 16 Use of the Reference Approach carries with it two consequences which should be carefully noted. Because the Reference Approach uses fossil fuel supply statistics as a basis for determining the carbon supply
- Not all carbon based emissions from fossil fuel are reported twice. The Reference Approach CO<sub>2</sub> estimate will not include emissions from combustion or release of fossil fuels for which the corresponding quantities (activity data) are not included in national production or import figures. Notable examples of activities which lead to emissions not included are the venting of natural gases from coal mining and handling and oil and gas production. Emissions from the flaring of natural gases are also excluded. As a result, when emissions from these activities are included in the relevant inventories using the fugitive emissions methodologies recommended in the Guidelines no "double counting" occurs.
- When a national CO<sub>2</sub> inventory is constructed from emissions estimated for each source category using
   emission factors derived from measurements on combustion plant, care should be taken to include the CO<sub>2</sub>
- equivalent of other fossil carbon based emissions from the source category. In this manner, the resulting total CO<sub>2</sub> emissions can be compared with the result of the CO<sub>2</sub> Reference Approach as part of the
- total CO<sub>2</sub> emissions can be compared with the result of the CO<sub>2</sub> Reference Approach as part of the inventory verification stage. If, however, CO<sub>2</sub> emission factors, derived from the carbon content of the fuel, are used then no addition of the CO<sub>2</sub> equivalent of carbon gases is required.

#### Appendix 2: Sources of CO<sub>2</sub> from the atmospheric oxidation of CH<sub>4</sub>, CO, and NMVOCs

$ \begin{array}{ c c c c c c } \hline Source Category \\ (IPCC reporting format) \end{array} & \begin{array}{ c c c c c } \hline Gases & Emitted^{(a)} \\ \hline \vec{H} & O & \overleftarrow{E} & O \\ \hline \vec{H} & O & \overleftarrow{E} & O \\ \hline \vec{H} & O & \overleftarrow{E} & O \\ \hline \vec{H} & \vec$		Gases Emitted <sup>(a)</sup>		Fossil	Addition to				
		Explanation							
1. Energy									
A. Fuel Combustion Activities <sup>(b)</sup>	x	х	x	Yes	No	Fuel combustion emission estimates calculated with use of carbon content factors include emissions of $CO_2$ from atmospheric oxidation of $CH_4$ , CO and NMVOC.			
B. Fugitive Emissions from Fuels									
1. Solid Fuels									
a. Coal Mining	х		х	Yes	Yes	The carbon in fugitive emissions of CH <sub>4</sub> and NMVOCs is fossil in origin but the indirect CO <sub>2</sub>			
2. Oil and Natural Gas						from the atmospheric oxidation of this carbon is not included in emissions estimates from any			
a. Oil	х	х	х	Yes	Yes	other source category.			
b. Natural Gas	х		х	Yes	Yes				
c. Venting	х		х	Yes	Yes				
d. Flaring	х	х	x	Yes	No	Fuel combustion emission estimates with use of carbon content factors include emissions of CO <sub>2</sub> from atmospheric oxidation of CH <sub>4</sub> , CO and NMVOC.			
2 Industrial Processes and Product Use									
B: Chemical Industry	х	Х	х	Yes	(d)	The carbon in emissions of CH <sub>4</sub> and NMVOCs from chemical and metallurgical processes is			
C: Metal Industry		x	x	Yes	(d)	likely to be of fossil in origin. The $CO_2$ from the atmospheric oxidation of this carbon may or may not be included in emissions estimates from these source categories or from non-energy uses of fossil fuels.			
D: Non-Energy Use of Fuels									
1: Lubricant Use			х	Yes	(d)				
2: Asphalt Paving of Roads and Roofs	х		х	Yes	(d)	The carbon in emissions of CH <sub>4</sub> and NMVOCs occurring from the use of non-energy products			
3: Paraffin Waxes Use			х	Yes	(d)	is of fossil origin and does lead to CO <sub>2</sub> emissions. The oxidation during use factors used to			
4: Solvents and other Petroleum Product Use			х	Yes	(d)	estimate emissions from these source categories in most cases will include CO <sub>2</sub> emissions.			
4. Waste <sup>(c)</sup>									
A. Solid Waste Treatment and disposal	Х	Х	х	No	-	The vast majority of the carbon in CH4 CO and NMVOC emissions is of biogenic origin			
B. Wastewater Treatment and discharge	х	Х	х	No	-	The vast majority of the carbon in C114, CO, and WWVOC christions is of biogenic origin.			
C. Incineration and open burning of waste <sup>(b)</sup>	x	x	x	Yes	No	The carbon in CH <sub>4</sub> , CO, and NMVOC emissions is of both biogenic and fossil origin. Estimates of CO <sub>2</sub> emissions from the fossil carbon portion of waste materials include the emissions of CO <sub>2</sub> from atmospheric oxidation of CH <sub>4</sub> , CO and NMVOCs when carbon content factors are used.			
<sup>(a)</sup> Only gases listed are those relevant to the estima <sup>(b)</sup> Assumes that CO <sub>2</sub> emissions are estimated using <sup>(c)</sup> Emissions assumed to be biogenic in origin.	ution of <b>(</b> 3 data on	$CO_2 em$ the car	issions fr bon cont	om atmospher ent of fuels or	ic oxidation of CH <sub>4</sub> , waste materials, not	CO and NMVOCs. direct measurement.			

(d) CO<sub>2</sub> emissions from atmospheric oxidation of CH<sub>4</sub>, CO and NMVOCs may or may not be accounted for by oxidized during use factor under non-energy use of fuels.

			ENER	ENERGY							IPPU		AFOLU	WASTE		
			Stationary Combustion Transport								se			and		
CAS number	NMVOC Species	Carbon content	Commercial and Residential	Energy Production	Combustion in Industry	Road Transport (DERV)	Road Transport (Evaporation)	Road Transport (PETROL)	Other Transportation and Machinery, Off Road	Other Transp & Mach (Other Transport) (5)	Extraction & Distribution of Fossil Fuels	Industrial Process	Solvent Use	Nature (Forests)	Waste Treatment i Disposal	Total
107-98-2	2-propanol	0.533										$\checkmark$	$\checkmark$		$\checkmark$	$\checkmark$
67-64-1	Acetone	0.620	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$	$\checkmark$		$\checkmark$	$\checkmark$
74-86-2	Acetylene	0.923	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$				$\checkmark$
71-43-2	Benzene	0.923	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$			$\checkmark$	$\checkmark$
106-97-8	Butane	0.827	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$	$\checkmark$
74-84-0	Ethane	0.799	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$			$\checkmark$	$\checkmark$
64-17-5	Ethanol	0.521	$\checkmark$		$\checkmark$							$\checkmark$	~		$\checkmark$	$\checkmark$
74-85-1	Ethylene	0.856	$\checkmark$	$\checkmark$	$\checkmark$	~		~	~	✓	$\checkmark$	$\checkmark$				$\checkmark$
110-54-3	Hexane	0.835	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	✓		$\checkmark$	$\checkmark$
75-28-5	Isobutane	0.827	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	~	$\checkmark$	$\checkmark$	✓	$\checkmark$	$\checkmark$			$\checkmark$	$\checkmark$
78-78-4	Isopentane	0.832	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	~	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$					$\checkmark$
108-38-3	m-xylene	0.905	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$			$\checkmark$
95-47-6	o-xylene	0.905	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$			$\checkmark$
109-66-0	Pentane	0.832	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	~	$\checkmark$	$\checkmark$	✓	$\checkmark$	$\checkmark$	$\checkmark$			$\checkmark$
74-98-6	Propane	0.817	$\checkmark$	$\checkmark$	$\checkmark$			$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$	$\checkmark$
115-07-01	Propylen	0.621	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$			$\checkmark$	$\checkmark$
106-42-3	p-xylene	0.905	$\checkmark$			$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$			$\checkmark$
108-88-3	Toluene	0.913	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	✓			$\checkmark$
Unspeciated mixtu	ures of m-, o- and p-xylene	0.905	$\checkmark$		$\checkmark$					$\checkmark$		$\checkmark$	$\checkmark$		$\checkmark$	
Total			$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$	$\checkmark$

#### Appendix 3: Examples of NMVOC species from the different source categories

Reference: Data in table complied from various references by Kristina Saarinen, Finnish Environment Institute.

- DO NOT CITE OR QUOTE WITHOUT PERMISSION OF AUTHOR -

# Appendix 4: Carbon content of various materials (percent carbon by mass, $P_c$ ) and percent of total solvent NMVOC emissions (by mass, $P_u$ )

	P <sub>C</sub>	P <sub>U</sub>		P <sub>C</sub> P <sub>U</sub>		P <sub>C</sub>	P <sub>U</sub>
Methane	75.0	-					
Carbon monoxide	42.9	-					
United States			Austria		Hungary <sup>19</sup>		
Solvent NMVOCs <sup>1</sup>			Solvent NMVOCs		Solvent NMVOCs		
Methylene chloride	14	2					
Perchloroethylene	14	1					
Trichloroethane	18	1					
Trichloroethylene	18	1	Residuals	25			
Methyl alcohol	38	1	Methanol	38			
Ethylene glycol	39	1					
Propylene glycol solvents <sup>2</sup>	47	1	Glycols	50			
Ester solvents <sup>3</sup>	49	1					
Ethyl alcohol	52	24	Alcohols	52			
Butanediol derivatives <sup>4</sup>	53	7					
Ester acetate <sup>5</sup>	55	19	Ester	59			
Other ethylene oxide solvents <sup>6</sup>	55	<1			Glue, etc.	57	-
Propyl acetate	59	2			Waste base paint	57	-
Isopropyl alcohol	60	10					
Propyl alcohol	60	2	Alcohols / propanols	60			
E-series ether solvents <sup>7</sup>	61	<1					
Acetone	62	2	Acetone	62			
Butyl acetate	62	<1					
Other propylene oxide-derived solvents <sup>8</sup>	62	<1					
Furfural solvents <sup>9</sup>	63	2					
Other chlorinated solvents <sup>10</sup>	64	<1					
Ether solvents <sup>11</sup>	65	1	Ether	65			
Other alcohol solvents <sup>12</sup>	65	2					
Methyl ethyl ketone	67	1	Ketones	67			
Tetrahydrofuran solvents <sup>13</sup>	67	1	Aldehydes	67			

Methyl isobutyl ketone	72	1					
Other ketone solvents <sup>14</sup>	72	2			Other paint, lack, etc.	80	-
Special napthas <sup>15</sup>	84	12	Solvent naphta	86	Solvent based paint	81.4	-
D-Limonene solvents <sup>16</sup>	88	<1	Cyclic hydrocarbons	86	Solvent	81.6	-
Pinene solvents <sup>17</sup>	88	1	Paraffins	86			
Toluene	91	<1	Aromates	91			
Xylene	91	<1					
Benzene	92	<1					
Solvent weighted average <sup>18</sup>	56.3		60 to 66		76 to 80		

Reference: P<sub>u</sub> values taken from national inventory reports submitted in 2004.

<http://unfccc.int/national reports/annex i ghg inventories/national inventories submissions/items/3473.php/>

P<sub>c</sub> values as noted below.

1) Except where noted, values from CRC Handbook of Chemistry and Physics. CRC Press, 1995.

2) Assumed to be "propylene glycol"

3) Assumed to be DuPont "Dibasic Ester Solvent" <a href="http://pubs.acs.org/pin/dupont/dup222p6.html">http://pubs.acs.org/pin/dupont/dup222p6.html</a>

4) "The Physical and Theoretical Chemistry Laboratory Oxford University Chemical and Other Safety Information," assumed to be 1,3-butanediol, <a href="http://physchem.ox.ac.uk/MSDS/BU/1,3-butanediol.html">http://physchem.ox.ac.uk/MSDS/BU/1,3-butanediol.html</a>

5) Assumed to be "ethyl acetate"

6) Assumed to be "ethylene oxide"

7) Assumed to be "ethylene glycol n-butyl ether" (trade name "Dowanol EB), www.dow.com/dowanol/nam/products/eb.htm

8) Assumed to be "propylene oxide"

9) "The Physical and Theoretical Chemistry Laboratory Oxford University Chemical and Other Safety Information," assumed to be "furfural" (2-furaldehyde), <a href="http://physchem.ox.ac.uk/MSDS/FU/furfural.html">http://physchem.ox.ac.uk/MSDS/FU/furfural.html</a>

10) Assumed to be "chlorobenzene"

11) "The Physical and Theoretical Chemistry Laboratory Oxford University Chemical and Other Safety Information," assumed to be "diethyl ether, <a href="http://ptcl.chem.ox.ac.uk/MSDS/DI/diethyl\_ether.html">http://ptcl.chem.ox.ac.uk/MSDS/DI/diethyl\_ether.html</a>

12) Assumed to be "butyl alcohol"

13) "The Physical and Theoretical Chemistry Laboratory Oxford University Chemical and Other Safety Information,", assumed to be "tetrahydrofuran" (THF) (1,4-Epoxybutane), <a href="http://ptcl.chem.ox.ac.uk/MSDS/TE/tetrahydrofuran.html">http://ptcl.chem.ox.ac.uk/MSDS/TE/tetrahydrofuran.html</a>

14) "The Physical and Theoretical Chemistry Laboratory Oxford University Chemical and Other Safety Information,", assumed to be methyl isobutyl ketone (MIBK), <a href="http://physchem.ox.ac.uk/MSDS/ME/methyl\_isobutyl\_ketone.html">http://physchem.ox.ac.uk/MSDS/ME/methyl\_isobutyl\_ketone.html</a>

15) Assumed to be "hexane"

16) "The Physical and Theoretical Chemistry Laboratory Oxford University Chemical and Other Safety Information," Assumed to be "limonene" (1-methyl-4-(1-methylethyl)cyclohexene), <a href="http://physchem.ox.ac.uk/MSDS/LI/limonene.html">http://physchem.ox.ac.uk/MSDS/LI/limonene.html</a>

17) Assumed to be "alpha pinene" (bicylc(3.1.1)hept-2-ene,2,6,6-trimethyl),

<http://www.iff.com/Ingredients.nsf/0/D8DADD753B3B483780256990005DC01F>

18) USA value is for 1998, Austria and Hungary values vary from year to year based on mix of solvent chemicals used.

19) Values apply only to the solvent portion of each material. The solvent content of each material assumed was: solvent based paint 50%, water based paint 5-6%, other paint 25%, glue 8%, and solvent 100%.

# Appendix 5: Raw data calculation spreadsheets

2

[Attach Excel spreadsheet files]

4

#### Appendix 6: Language on Indirect CO<sub>2</sub> in 2006 IPCC Guidelines

2

Excerpt from Overview Volume, in section 5, Specific Developments in the 2006 IPCC Guidelines

4 (p.12).

#### Relevant to all volumes

CO<sub>2</sub> resulting from the emissions of other gases: The 2006 IPCC Guidelines estimate carbon emissions in terms of the species which are emitted. Most of the carbon emitted as these non-CO<sub>2</sub> species eventually oxidises to CO<sub>2</sub> in the atmosphere; and this amount can be estimated from the emissions estimates of the non-CO<sub>2</sub> gases. In some cases the emissions of these non-CO<sub>2</sub> gases contain very small amounts of carbon compared to the CO<sub>2</sub> estimate and it may be more accurate to base the CO<sub>2</sub> estimate on the total carbon. See Volume 1 Section 7.2.1.5 for an approach to estimating these inputs of CO<sub>2</sub> to the atmosphere. Examples are fossil fuel combustion (where the emission factor is derived from the carbon content of the fuel) and a few IPPU sectors where the carbon mass balance can be estimated much better than individual gases.

6

#### 8 Excerpt from Volume 1 of the 2006 IPCC Guidelines (IPCC, 2006).

#### 7.2.1.5 CARBON EMITTED IN GASES OTHER THAN CO<sub>2</sub>

The 2006 Guidelines estimate carbon emissions in terms of the species which are emitted. Most of the carbon emitted in the form of non-CO<sub>2</sub> species eventually oxidises to  $CO_2$  in the atmosphere and this amount can be estimated from the emissions estimates of the non-CO<sub>2</sub> gases. Box 7.2 provides an approach for making this calculation.

In some cases the emissions of these non- $CO_2$  gases contain very small amounts of carbon compared to the  $CO_2$  estimate and it may be more accurate to base the  $CO_2$  estimate on the total carbon. Examples are fossil fuel combustion (where the emission factor is derived from the carbon content of the fuel) and a few IPPU categories where the carbon mass balance can be estimated much better than individual gases.

Box 7.2

CALCULATING CO2 INPUTS TO THE ATMOSPHERE FROM EMISSIONS OF CARBON-CONTAINING COMPOUNDS

Methane, carbon monoxide (CO) or NMVOC emissions will eventually be oxidised to  $CO_2$  in the atmosphere. These  $CO_2$  inputs could be included in national inventories. They can be calculated from emissions of methane, CO and NMVOCs. The basic calculation principles are:

From CH4:	Inputs <sub>CO2</sub>	=	Emissions <sub>CH4</sub>	٠	44/1	6
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From CO: Inputs<sub>CO2</sub> = Emissions<sub>CO</sub> • 44/28

From NMVOC: Inputs<sub>CO2</sub> = Emissions<sub>NMVOC</sub> • C • 44/12

Where C is the fraction carbon in NMVOC by mass (default = 0.6)

The carbon content in NMVOCs will vary depending on the source. Therefore, an inventory based on the speciation of the NMVOC compounds gives more accurate results.

In making these estimates inventory compilers should assess each category to ensure that this carbon is not already covered by the assumptions and approximations made in estimating CO<sub>2</sub> emissions. Relevant examples include carbon from;

- · Fugitive emissions from energy use,
- Carbon from Non-CO<sub>2</sub> gases from IPPU,
- AFOLU emissions where non-CO2 gases have been explicitly deducted.