# ORIGINAL ARTICLE

# A review of major non-power-related carbon dioxide stream compositions

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**Abstract** A critical component in the assessment of longterm risk from geologic sequestration of carbon dioxide (CO<sub>2</sub>) is the ability to predict mineralogical and geochemical changes within storage reservoirs as a result of rock-brine-CO2 reactions. Impurities and/or other constituents in CO<sub>2</sub> source streams selected for sequestration can affect both the chemical and physical (e.g., density, viscosity, interfacial tension) properties of CO<sub>2</sub> in the deep subsurface. The nature and concentrations of these impurities are a function of both the industrial source(s) of CO<sub>2</sub>, as well as the carbon capture technology used to extract the CO<sub>2</sub> and produce a concentrated stream for subsurface injection and geologic sequestration. Most work on CO<sub>2</sub> capture, utilization, and storage has been focused on large fossil-fuel-fired power plants. This article reviews the relative concentrations of CO2 and other constituents in exhaust gases from other major non-power-related industrial point sources. Assuming that carbon capture technology would remove most of the air (i.e., incondensable gases  $N_2$ ,  $O_2$ , and Ar) from the exhaust gases, the authors summarize the relative proportions of SO<sub>2</sub>, NO<sub>x</sub> and other remaining impurities expected to still be present in nonpower-related CO2 source streams that could be targeted for geologic sequestration. The summary is presented relative to the four largest non-power-related sources of CO<sub>2</sub>: (1) use of fossil fuels as carbon feedstock, (2) iron, steel, and metallurgical coke production, (3) lime and Portland cement production, and (4) natural gas processing and industrial heat/steam generation.

**Keywords** Carbon dioxide  $\cdot$  CO<sub>2</sub> source streams  $\cdot$  CO<sub>2</sub> impurities  $\cdot$  CO<sub>2</sub> sequestration

#### Introduction

Most studies concerning the potential for CO<sub>2</sub> capture, utilization, and storage (CCUS) have been focused on emissions from large-scale fossil-fuel-fired power plants. Other medium- to small-scale industrial non-power generating CO<sub>2</sub> emission sources have gained less attention. Their contribution to global CO<sub>2</sub> emissions is still substantial and in some cases their potential for CCUS may be economically viable (Hendricks et al. 2009; Laude and Ricci 2011; Poiencot and Brown 2011). However, much less is known about the potential impurities in emissions from these non-power-related industries that may affect the utility of CO<sub>2</sub> for CCUS.

This article summarizes available information on chemical impurities typically found in major non-power-related CO<sub>2</sub> source streams, and identifies some prototypical source stream compositions that should be considered when evaluating the performance of CCUS from these types of sources. The primary objective of this review is to identify important impurities/co-contaminants in major non-CO<sub>2</sub> source streams from industrial sources outside of electrical power generation that should be considered in assessing the long-term geologic storage of CO<sub>2</sub>.

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#### Background

Geologic sequestration of CO<sub>2</sub> is a promising technology for stabilizing atmospheric greenhouse gas concentrations by separating and capturing CO<sub>2</sub> from power-related and non-power-related sources, transporting it to a storage location and injecting it deep underground for long-term isolation from the atmosphere (IPCC 2005). While the predominant source of anthropogenic CO<sub>2</sub> emissions is the combustion of fossil fuels (coal, oil and natural gas) in electrical-power-generation plants (EPA 2013), industrial non-power-generating processes, such as cement production, metal production, and manufacturing also emit notable quantities of CO<sub>2</sub> (Table 1).

A critical component in the assessment of risk from these activities is the ability to predict geochemical changes (e.g., corrosion) within well-bore materials and other infrastructural elements as well as long-term mineralogical and geochemical changes within storage reservoirs due to rock-brine-CO<sub>2</sub> reactions. Sass et al. (2005) identified a large variety of potential impurities from a number of typical CO<sub>2</sub> sources. Impurities and/or other constituents selected for co-sequestration can affect both the chemical and physical (e.g., density, viscosity, interfacial tension) properties of CO2 and alter the geochemical and geomechanical properties of the reservoir rock, cap rock, and well bore materials (IEAGHG 2011; Koenen and Tambach 2011; Koenen et al. 2011; Renard et al. 2011; Wang et al. 2010; Xu et al. 2007; Knauss et al. 2005; Jacquemet et al. 2005; Li et al. 2005; Savage et al. 2004).

The focus of this review is on anthropogenic  $CO_2$  emissions from non-power-related (non-electricity-generating) industrial sources and their co-contaminants that could be targeted for sequestration. These co-contaminants and their concentrations are a function of both the industrial source(s) of the  $CO_2$ , as well as the carbon capture/purification technology used to extract the  $CO_2$  (Walspurger and van Dijk 2012).

## Carbon dioxide recovery/capture

The first step in geologic sequestration of CO<sub>2</sub> is to separate the CO<sub>2</sub> from other exhaust gases and produce a concentrated stream of CO<sub>2</sub> that can be compressed into liquid form and readily transported to a geologic sequestration site. MacDowell et al. (2010) and Figueroa et al. (2008) provide good overviews of the leading options for large-scale CO<sub>2</sub> capture from large fixed-point emission-sources, such as power plants. Large air-fired power plants produce dilute CO<sub>2</sub> exhaust gases, with flue gas concentration from coal-fired power plants generally containing 3–13 % CO<sub>2</sub> by volume (Chapel et al. 1999). The most commonly used technology for low concentration CO<sub>2</sub>

**Table 1** Major sources of US CO<sub>2</sub> emissions in 2011 (after EPA 2013, Table 2.1)

Source/end-use sector	Relative proportion of CO <sub>2</sub> emissions in the US in 2011 [% (w)]
Fossil fuel combustion	94.0
Electricity generation	38.5
<ul> <li>Coal combustion (e.g., flue gas from coal-fired power plants)</li> </ul>	31.1 <sup>a</sup>
Transportation	30.2
Industrial (primarily associated with producing steam or heat for industrial processes)	13.8
Residential	5.86
Commercial (primarily associated with electricity consumption for lighting, heating, cooling, and operating appliances)	3.96
US territories <sup>b</sup>	0.89
Non-power use of fuels (e.g., scrap tires, carbon black, and synthetic rubber carbon emissions)	2.33
Iron and steel, and metallurgical coke production	1.15
Natural gas production	0.58
Cement production	0.55
Lime production	0.25
Incineration of waste	0.21
Other process uses of carbonates	0.16
Ammonia production	0.16
Cropland remaining cropland	0.14
Urea consumption for non-agricultural purposes	0.08
Petrochemical production	0.06
Aluminum production	0.06
Soda ash production and consumption	0.05
Titanium dioxide production	0.03
Carbon dioxide consumption	0.03
Ferroalloy production	0.03
Glass production	0.02
Zinc production	0.02
Phosphoric acid production	0.02
Wetlands remaining wetlands <sup>c</sup>	0.02
Lead production	0.01
Petroleum systems	0.01

Note that bolded rows identify the focus of this study



<sup>&</sup>lt;sup>a</sup> Lee et al. (2009a, b)

<sup>&</sup>lt;sup>b</sup> Fuel consumption by US territories (i.e., American Samoa, Guam, Puerto Rico, US Virgin Islands, Wake Island, and other US Pacific Islands)

<sup>&</sup>lt;sup>c</sup> CO<sub>2</sub> emissions from the removal of biomass and the decay of drained peat

capture is absorption with amine-based chemical solvents [e.g., monoethanolamine (MEA)], adapted from the gas processing industry (GCEP 2005; Herzog 1999). The process has been modified to incorporate inhibitors to resist solvent degradation and equipment corrosion when applied to CO<sub>2</sub> capture from flue gas (Yang et al. 2008). Additional modifications using different solvents, inhibitors, and/or use improved packing materials, continue to improve the efficiency of chemical absorption based CO<sub>2</sub> capture technology (Freeman et al. 2010; D'Alessandro et al. 2010; Goff and Rochelle 2006).

Many non-power-related industrial processes emit more concentrated CO<sub>2</sub>, which in some cases is routinely separated and captured as a by-product. Large quantities of CO<sub>2</sub> [typically at concentrations of 14–33 % (Worrell et al. 2001)] are produced by lime kilns, which calcine the limestone to produce calcium oxide (lime), and magnesium oxide from dolomite (calcium magnesium carbonate). Other industrial activities that produce large amounts of relatively concentrated CO<sub>2</sub> are refineries (e.g., gas sweetening plants), fertilizer (i.e., ammonia) production, the iron and steel industry, and the petrochemical industry (Farla et al. 1995). Fermentation related industries such as wineries, breweries, and biofuel production also generate relatively concentrated CO<sub>2</sub> streams. Farla et al. (1995) suggested that it might be possible to recover CO<sub>2</sub> from these more concentrated sources at a lower cost than from power plants.

# Major non-power industrial sources of CO<sub>2</sub> and associated impurities

A review of the major CO<sub>2</sub> sources and their specific associated impurities and relative concentrations follows. This review relies mostly on a compilation of air pollutant emission factors (AP-42) (Duprey 1968) as updated on the U.S. Environmental Protection Agency's (EPA) web site <a href="http://www.epa.gov/ttn/chief/ap42">http://www.epa.gov/ttn/chief/ap42</a>. For the purposes of this study, it is assumed that carbon capture technology applied to the exhaust gas emissions from these facilities removes most of the air (and its incondensable gases N<sub>2</sub>, O<sub>2</sub>, and Ar) to produce a concentrated CO<sub>2</sub> stream (IEAGHG 2004) with the same approximate ratio of other impurities (e.g., NO<sub>x</sub>, SO<sub>x</sub>) to CO<sub>2</sub> as the original exhaust emissions.

The focus of this article is on non-power-related industrial sources of CO<sub>2</sub> emissions. Many non-power-related industries use fossil fuels as carbon feedstocks for the manufacture of synthetic material and chemical products (such as plastics, fibers, synthetic rubber, paints, solvents, fertilizers, lubricants, and surfactants) or as an energy feedstock to produce steam or heat for industrial processes.

The authors concentrate on the top non-power-related industrial sources of CO<sub>2</sub>. As shown in Table 1, these include:

- Use of fossil fuels as carbon feedstock (e.g., scrap tires, carbon black, and synthetic rubber carbon emissions);
- Iron, steel, and metallurgical coke production,
- Lime and cement production (e.g., from kilns), and
- Natural gas processing and industrial heat/steam generation.

# Use of fossil fuels as carbon feedstock

Weiss et al. (2009) estimated that on average about 5 % of fossil fuels are used as feedstock in the chemical industry. Non-power use of fossil fuels for the production of chemicals and certain refinery products results in CO<sub>2</sub> emissions throughout the life cycle of industrial production, and during product use and subsequent waste treatment. This includes the first use of fossil fuels to create products such as lubricants, paraffin waxes, bitumen/asphalt, and solvents, and secondary uses or disposal of these products after first use (i.e., the combustion of waste oils such as used lubricants). For purposes of this review, the authors focused on three main industries: scrap tire, carbon black, and synthetic rubber.

#### Scrap tires

Two to three billion  $(2-3 \times 10^9)$  scrap tires are in landfills and stockpiles across the United States, with approximately one scrap tire per person generated every year (Reisman 1997). The synthetic rubber in scrap tires consists of about 90 % carbon (Freed et al. 2005).  $CO_2$  emissions primarily come from uncontrolled open burning and or controlled burning of the scrap tires as a source of fuel. For example, tire-derived fuels (TDF) are used in energy-intensive industries (such as cement kilns) as an energy feedstock and in this way present an opportunity for  $CO_2$  capture and utilization or storage.

An analysis performed on the rubber portion of passenger car tires indicated they are generally made of carbon, hydrogen, ash, oxygen, sulfur, and nitrogen (EPA 1992). Emissions from burning of scrap tires include a variety of organic and inorganic compounds, many of which may pose health risks. There is a limited amount of emission data available with which to estimate emission factors (EPA 1997). However, use of TDF is similar to the use of coal, with less moisture content, more carbon, about as much sulfur as medium-sulfur coal, and much less fuel-bound nitrogen (EPA 1997). Thus, dilute exhaust gas emissions are expected to be similar to those of flue gas from coal-fired power plants (Table 2).



Table 2 Relative concentrations of flue gas impurities in a separated CO<sub>2</sub> stream (modified from Lee et al. (2009a, b) and Sass et al. 2005)

Component	Relative proportions in flue gas [% (v)]	Relative proportions in separated CO <sub>2</sub> stream without wet flue gas desulfurization scrubber [% (w)] <sup>a</sup>	Relative proportions in separated CO <sub>2</sub> stream with wet flue gas desulfurization scrubber [% (w)] <sup>a</sup>	Relative proportions in separated $co_2$ stream with low $NO_x$ burners, selective catalytic reduction, and wet flue gas desulfurization scrubber $[\% (w)]^a$	Estimated concentrations in separated CO <sub>2</sub> stream, assuming amine adsorption [% (v)] <sup>(b)</sup>
CO <sub>2</sub>	13.5	97.45	99.8	99.8	93.2
$SO_2$	0.016	2.3	0.12575	0.12575	Trace
$SO_3$	0.00325	0.0295	0.01535	0.01535	Trace
$N_2$	74.7				0.17
$NO_2$	0.0025	0.00585	0.0046	0.00185	
$NO_x$	0.06				Trace
HCl	0.00525	0.0422	0.000575	0.000575	
$O_2$	4				0.01
$H_2O$	7.7				6.5
Hydrocarbons	Trace <sup>b</sup>				Trace <sup>b</sup>
Metals	Trace <sup>b</sup>				Trace <sup>b</sup>
Hg(2 +)	Trace	0.0000142	0.00000145	0.00000145	

<sup>&</sup>lt;sup>a</sup> Estimated values (except mercury) include both with and without salt formation

#### Carbon black

Carbon black is a fine black amorphous form of carbon, generally 10-500 nm in diameter. It is principally used as a reinforcing agent in rubber compounds such as tires, and as a black pigment in inks, surface coatings, paper, and plastics (Donnet and Bansal 1993). The tire industry consumes about 80 % of the total carbon black manufactured worldwide (Hisazumi 2006). About 90 % of the carbon black manufactured in the United States is produced using an oil furnace process (EPA 1983). Here, an aromatic liquid hydrocarbon feedstock is heated and injected continuously into the combustion zone of a natural gas-fired furnace, where it decomposes to elemental carbon in the form of carbon black. However, typical emissions from this process include particulate matter, CO, organics, NO<sub>x</sub>, sulfur compounds, polycyclic organic matter, and trace elements (EPA 1983). The principal source of emissions is from the main process vent, and emissions may vary considerably according to the grade of the carbon black being manufactured, and the chemical makeup of the feedstock (EPA 1983). Typical emission factors for carbon black manufacturing, using an oil furnace process, are shown in Table 3.

Hisazumi (2006) indicated the imperfect combustion of carbon black oil (or feedstock) converts half of the hydrocarbons into carbon black while the other half goes into the tail gas. Hisazumi (2006) also documented the typical composition of this tail gas as shown in Table 4.

**Table 3** Typical emission factors for carbon black manufacturing (after EPA 1983, Table 6.1–3)

Component	Emissions, kg/kg carbon black produced
$\overline{\text{CO}_2}$	1.9 <sup>a</sup> –5.25 <sup>b</sup>
CO	1400°
$H_2S$	30°
$SO_x$	25 (from flare) <sup>c</sup>
$NO_x$	0.28°
$CH_4$	25°
Non-methane VOC	50°

<sup>&</sup>lt;sup>a</sup> Neelis et al. (2005)

**Table 4** Typical composition of tail gas from carbon black manufacturing (from Hisazumi 2006)

Component	Emissions [% (v)]
$CO_2$	2.4–4.9 <sup>a</sup>
CO	10.2–11 <sup>a</sup>
$N_2$	36.2
$H_2$	8.0
CH <sub>4</sub>	0.2
H <sub>2</sub> O	43.0

<sup>&</sup>lt;sup>a</sup> TRW Systems Group (1970)

CO<sub>2</sub> capture technologies for the dilute exhaust gas from carbon black manufacturing are expected to resemble those used with flue gas (from coal, oil, or gas-fired power



<sup>&</sup>lt;sup>b</sup> After Sass et al. (2005)

<sup>&</sup>lt;sup>b</sup> IPCC (2006)

<sup>&</sup>lt;sup>c</sup> Average values from six sampling runs

plants) and would likely result in similar levels of impurities in CO<sub>2</sub> targeted for sequestration (Table 2).

Synthetic rubber

Synthetic rubber is an artificial elastomer with the mechanical (or material) property that allows it to undergo much more elastic deformation than most materials and still return to its previous size without permanent deformation. Synthetic rubber is generally made from the polymerization of a variety of monomers including styrene and butadiene. These and other monomers can be mixed in various proportions with other impurities or additives to achieve a wide range of physical, mechanical, and chemical properties.

There are two types of polymerization reactions used to produce styrene-butadiene copolymers—the emulsion type and the solution type (EPA 1982). During these processes, the condenser tail gases [non-condensable gases (e.g., N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub>) and volatile organic compound (VOC) vapors (mostly styrene and butadiene)] are vented to the atmosphere. The estimated emission factor for VOCs from the emulsion latex process is 8.45 g/kg of copolymer produced (EPA 1982). An estimated 2–3.5 kg of CO<sub>2</sub> is released to the air for every 1 kg of plastic produced (Harding et al. 2007). A similar level of CO<sub>2</sub> release is assumed for the manufacture of synthetic rubber. The San Joaquin Valley Air Pollution Control District found only VOCs in area and point source emissions for rubber and rubber products manufacturing (San Joaquin Valley Air Pollution Control District 2010). They reported zero emissions for  $NO_x$ , CO, and SO<sub>x</sub>.

Based on this study, the authors of this report have been unable to find relative proportions of impurities in a potential  $CO_2$  source stream for carbon sequestration from the manufacture or use of synthetic rubber<sup>1</sup> other than as a TDF (See Table 2).

Iron, steel, and metallurgical coke production

Iron and steel production is an energy-intensive activity that generates process-related emissions of CO<sub>2</sub>, CH<sub>4</sub>, and other gasses. Process emissions occur at each step of the production process. Metallurgical coke is an important component of this process. Coke is used to produce iron or pig iron from raw iron ore, and is produced both onsite at "integrated" iron and steel plants and offsite at "merchant" coke plants (EPA 2008).

Iron and steel production

Steel production at an integrated iron and steel plant is accomplished using several interrelated processes. The major operations are as follows: (1) coke production; (2) sinter production; (3) iron production; (4) raw steel production; (5) ladle metallurgy; (6) continuous casting; (7) hot and cold rolling; (8) finished product preparation (EPA 2012).

EPA (2012) indicated the vast majority of greenhouse gases (i.e., CO<sub>2</sub>) from steel production is emitted from blast furnace stove stacks where the combustion gases from the stoves are discharged. A small amount of emissions may also occur from flares, leaks in the ductwork for conveying the gas, and from blast furnace emergency venting. Emissions of CO<sub>2</sub> are also generated from the combustion of natural gas using flame suppression to reduce emissions of particulate matter. EPA (2012) estimated that the relative composition of blast furnace gas contains about 60 % nitrogen, 28 % CO, and 12 % CO<sub>2</sub>. Carbon capture technology applied to this dilute CO<sub>2</sub> exhaust stream would likely produce similar impurity estimates to those of flue gas (Table 2).

#### Metallurgical coke production

Metallurgical coke is used in iron and steel industry processes (primarily in blast furnaces) to reduce iron ore to iron. Metallurgical coke is produced by destructive distillation of coal in coke ovens, in an oxygen-free atmosphere (–coked–) until most volatile components are removed. Most coke plants are co-located with iron and steel production facilities, and the demand for coke generally corresponds with the production of iron and steel. An estimate of the relative proportions of concentrated (post carbon capture) combustion stack gases from coke production is provided in Table 5 (from EPA 2008).

# Lime and cement production

Lime and cement production are key sources of  $CO_2$  emissions, due to combustion-related emissions from lime kilns and in cement production, but also due to process-related emissions resulting from the release of  $CO_2$  during the calcination of limestone (Hanle et al. 2004).

#### Lime production

Lime is produced through calcination of limestone, dolomite or other natural materials. The center of lime production is the lime kiln, and the most prevalent type of kiln is the rotary kiln, accounting for about 90 % of all lime production in the United States (EPA 1998b). CO<sub>2</sub>, CO,



 $<sup>^1</sup>$  The carbon content of synthetic rubber is estimated at 90 % for tire synthetic rubber and 85 % for non-tire synthetic rubber. Approximately 2.5 lb per passenger tire and 10 lb per commercial tire are assumed to be abraded from the tires during use and considered to be 100 % emitted (presumably as pure  $CO_2$ ).

**Table 5** Emission factors and relative proportions of combustion stack emissions from coke production (after EPA 2008, Table 4–27)

Component	Emissions (kg/Mg)	Relative proportion [% (w)]
Extractable organic matter	0.012	0.00247
CO	0.34	0.07010
CO <sub>2</sub> (BFG)	482	99.37313
$NO_x$	0.82	0.16906
$SO_x$ (DCOG)	1.47	0.30307
HCl (DCOG)	0.013	0.00268
Total organic compounds	0.19	0.03917
Methane (CH <sub>4</sub> )	0.1	0.02062
Ethane	0.005	0.00103
Acetone	0.0295	0.00608
VOC	0.047	0.00969
Benzene	0.0075	0.00155
Toluene	0.0033	0.00068
Chloromethane	0.0032	0.00066
Benzoic acid	4.14E - 05	0.00001
Bis(2-ethylhexyl)phthalate	3.40E - 06	0.00000
Diethyl phtalate	9.90E-06	0.00000
2,4-Dimethylphenol	4.17E-06	0.00000
Phenol	2.56E-06	0.00000

BFG Blast furnace gas, DCOG desulfurized coke oven gas, VOC volatile organic compound

 $SO_2$ , and  $NO_x$  are all produced in lime kilns (EPA 1998b). Emissions are influenced by the content of the fuel used to heat the kiln, content and mineralogic form of the feed material, quality of the lime produced, type of kiln used, and type of pollution control equipment used (EPA 1998b). An estimate of the relative proportions of these gases expected in a concentrated (post-carbon capture)  $CO_2$  source stream is provided in Table 6 (from EPA 1998b).

The primary air toxics present in the exhaust gases from lime kilns are metals such as arsenic, cadmium, chromium, and nickel, and HCl.<sup>2</sup>

An example of lime kiln exhaust gas emission concentrations comes from EPA testing of a lime kiln in Alabaster, Alabama, in 1998 (EPA 2000), Table 7. Note these data would be concentrations/relative proportions prior to carbon capture.

#### Cement production

Portland cement accounts for 95 % of the hydraulic cement production in the United States (EPA 1995a). Portland

<sup>&</sup>lt;sup>2</sup> EPA. "Fact Sheet Final Rule to Reduce Toxic Air Emissions From Lime Manufacturing Plants"; www.epa.gov/ttn/atw/lime/limefs8-19-03.pdf (accessed January 6, 2014).



**Table 6** Emission Factors and relative proportions of gases from lime manufacturing (after EPA 1998b, Table 11.17-5)

Component	Emission factor (kg/Mg)	Relative percent [% (w)]
$SO_2$	2.7	0.17
$SO_3$	0.11	0.01
$NO_x$	1.7	0.11
CO	3.2	0.20
$CO_2$	1600	99.52

cement consists of a mixture of calcium silicates, aluminates, and aluminoferrites. More than 30 raw materials have been used in the manufacture of Portland cement, the most notable of which is limestone. These materials are chemically combined through pyroprocessing and subjected to subsequent mechanical processing operations.

NO<sub>x</sub>, SO<sub>2</sub>, CO, and CO<sub>2</sub> are the primary gaseous emissions in the manufacture of Portland cement (EPA 1995a). Small quantities of VOC, ammonia (NH<sub>3</sub>), chlorine, and HCl may also be emitted (EPA 1995a). Emissions may also include products of incomplete combustion that are considered to be hazardous. Because some facilities burn waste fuels, particularly spent solvents in the kiln, these systems may also emit small quantities of additional hazardous organic pollutants. Also, raw material feeds and fuels typically contain trace amounts of heavy metals that may be emitted as a particulate or vapor (EPA 1995a).

In addition, calcium oxide (CaO) is produced from concrete plants and has been shown capable of being stored with sequestered  $CO_2$  (Stolaroff et al. 2005). CaO reacts with  $CO_2$  to create  $CaCO_3$ , which has proven to be a stable compound that can be stored safely underground. In the presence of water, CaO also reacts relatively quickly with  $CO_2$  so it is not difficult to create this compound. This is also an option for steel plants because high levels of CaO are present in steel slag.

Emission factors from Portland cement kilns and their relative proportions expected in a concentrated (post-carbon capture)  ${\rm CO_2}$  source stream are summarized in Table 8.

Natural gas processing and steam/heat production

The natural gas industry generates  $CO_2$  both during its production and its use as an energy source. Natural gas production encompasses field production, processing, transmission, and distribution. The majority of non-combustion  $CO_2$  emissions come from acid gas removal units within the processing plants (EPA 2013). The majority of combustion-related  $CO_2$  emissions (outside of the electrical generation industry) come from its use as an energy source for industrial steam and heat generation.

**Table 7** Concentrations and relative proportions of gases from a lime kiln in Alabaster, Alabama (after EPA 2000)

Component	Maximum concentration	Minimum concentration	Average concentration	Units	Relative proportion [% (v)]
$O_2$			10	% by volume (assumed)	23.5379
$CO_2$			20	% by volume (assumed)	47.0758
Moisture	21.1	20	20.467	% by volume	29.3447
Total PCDD			ND	ng/dscm	
Total PCDF			ND	ng/dscm	
HCl	1.33	0.968	1.11	ppmvd	0.0261
Ammonia (as NH <sub>4</sub> )	0.433	0.257	0.326	ppmvd	0.0077
Aluminum (Al)			ND	ppmvd	
Calcium (Ca)			0.13	ppmvd	0.0031
Magnesium (Mg)			0.042	ppmvd	0.0010
Potassium (K)			0.045	ppmvd	0.0011
Sodium (Na)			0.115	ppmvd	0.0027

PCDD Polychlorinated dibenzo-p-dioxins and PCDF polychlorinated dibenzofurans

**Table 8** Summary of emission factors and relative proportions for portland cement kilns (from EPA 1995a)

1	/	
Component	Max. emissions (kg/Mg)	Relative proportion [% (w)]
Total organic carbon	0.09	0.00810
CO	1.8	0.16208
CO <sub>2</sub>	1100	99.04792
$NO_x$	3.7	0.33316
$SO_2$	4.9	0.44121
HCl	0.073	0.00657
Acetone	0.00019	0.00002
Benzene	0.008	0.00072
Toluene	0.0001	0.00001
Chloromethane	0.00019	0.00002
Benzoic acid	1.80E-03	0.00016
Bis(2-ethylhexyl)phthalate	4.80E-05	0.00000
Phenol	5.50E-05	0.00000
Hg	1.10E-04	0.00001

## Natural gas processing

Raw natural gas is usually passed through field separators at the wellhead to remove hydrocarbon condensate and water. Natural gas contains a number of impurities, principally CO<sub>2</sub> and H<sub>2</sub>S, that must be removed before a number of separable commodities can be utilized. This is called "sweetening" the gas. The typical concentrations of CO<sub>2</sub> remaining in the processed natural gas delivered to the United States commercial pipeline grid is typically less than 3 % by volume (Baker and Lokhandwala 2008). Major emission sources in natural gas processing come from compressor engines, acid gas wastes, fugitive emissions from leaking equipment, and glycol dehydrator vent

**Table 9** Emission factors and relative proportions from natural gas combustion (from EPA 1998a, Table 1.4–2 unless otherwise indicated)

Component	Maximum emissions (kg/10 <sup>6</sup> m <sup>3)</sup>	Relative proportion [% (w)]
CO <sub>2</sub>	1.92 E+6	99.7
CO	1.57 E+3	0.0814
N <sub>2</sub> O (Uncontrolled)	1.82 E+1	0.00183
$SO_2$	9.60 E+0	0.0005
$NO_x^a$ (Uncontrolled)	4.48 E+3	0.233
CH <sub>4</sub>	3.68 E+1	0.00191
VOC	8.80 E+1	0.00457
TOC	1.76 E+2	0.00914
Lead	8.00 E-3	0.00000

<sup>&</sup>lt;sup>a</sup> For large wall-fired boilers, taken from EPA (1998a), Table 1.4-1

streams (if present). Most plants employ elevated smokeless flares or tail gas incinerators for complete combustion of all waste gas constituents, including virtually 100 % conversion of the  $\rm H_2S$  to  $\rm SO_2$ . Thus, the major pollutant is  $\rm SO_2$ . The emission factor for  $\rm SO_2$  from gas sweetening plants is 26.98 kg/10³ m³ gas produced, while those for CO and NO\_x are negligible (EPA 1995b). Due to the high level of impurities and low levels of CO\_2, it is unlikely that natural gas processing plants would be targeted for carbon capture and sequestration, at least in the near future.

Natural gas combustion for production of process steam and heat

Natural gas is one of the major fuels used to produce industrial process steam and heat. Natural gas contains a high percentage (generally <85 %) of CH<sub>4</sub> and varying amounts



**Table 10** Summary of relative proportions (%[w]) of major impurities in post carbon capture CO<sub>2</sub> source streams from major non-power emitters of CO<sub>2</sub>

Component	Carbon black manufacturing, tire-derived fuel, and iron/steel production emissions <sup>a</sup> (%)	Coke production combustion stack emissions (%)	Lime kiln emissions (%)	Portland cement kiln emissions (%)	Natural gas combustion emissions (%)
$CO_2$	97.50000	99.40000	99.52000	99.00000	99.70000
CO		0.07010	0.20000	0.16200	0.08140
$N_2O$					0.00183
$NO_2$	0.00585				
$NO_x$		0.16900	0.11000	0.33300	0.23300
HCl	0.04220	0.00268		0.00657	
$SO_2$	2.30000		0.17000	0.44100	0.00050
$SO_3$	0.02950		0.01000		
$SO_x$		0.30300			
$CH_4$		0.02060			0.00191
VOC		0.00969			0.00457
TOC				0.00810	0.00914
Lead					0.00000
Mercury (Hg[2 +])	0.00001			0.00001	

<sup>a</sup> Assumes CO<sub>2</sub> capture technologies would produce similar proportions of impurities to those produced from flue gas (from coal, oil, or gas-fired power plants)

of ethane, propane, butane, and inert gasses (typically N<sub>2</sub>, CO<sub>2</sub>, and helium) (EPA 1998a). There are three major types of boilers used for natural gas combustion for industrial purposes: watertube, firetube, and cast iron. The emissions from natural gas-fired boilers and furnaces include NO<sub>x</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, VOCs, trace amounts of SO<sub>2</sub>, and particulate matter (EPA 1998a). A number of control techniques (both during and after combustion) are used to reduce these emissions (particularly NO<sub>x</sub>). Emission factors for natural gas combustion, are summarized in Table 9.

# Discussion

The concentrations of CO<sub>2</sub> and co-contaminants in source streams that could be targeted for geologic sequestration are a function of both the industrial source(s) of the CO<sub>2</sub>, as well as the carbon capture technology used to extract the CO<sub>2</sub>. This article summarizes the relative concentrations of CO<sub>2</sub> and other constituents in exhaust gases from major non-power-related industrial sources of CO<sub>2</sub>, based on reviews of available information from both published and unpublished literature. Consistent information on stack emissions was difficult to find for most industries, so the authors relied heavily on a compilation of air pollutant emission factors (AP-42) taken from EPA's Clearinghouse for Inventories & Emissions Factors (Duprey 1968). It was also assumed that carbon capture technology applied to these industrial exhaust gases streams would remove most of the air components (N2, O<sub>2</sub>, and Ar) to produce a concentrated CO<sub>2</sub> stream with the same approximate ratio of other impurities (e.g.,  $NO_x$ ,  $SO_x$ ) to  $CO_2$  as the original exhaust emissions. This is similar to the approach used by the International Energy Agency's (IEA) Greenhouse Gas Research and Development program that found the most important impurities expected in co-captured  $CO_2$  were  $H_2S$  and  $SO_2$ , and listed  $NO_x$  and CO as other significant impurities (IEAGHG 2004).

Table 10 summarizes the relative proportions of the major impurities assumed to be present in post-carbon capture  $CO_2$  source streams from major non-power-related industries contributing to  $CO_2$  emissions that could be targeted for geologic sequestration. This summary suggests that carbon capture from most sources (except from cement production) would produce similar concentrations, not too different from that of food-grade  $CO_2$  with concentrations exceeding 99 weight percent.

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