Carbon Disulfide (CS_2) Mechanisms in Formation of Atmospheric Carbon Dioxide (CO_2) Formation from Unconventional Shale Gas Extraction and Processing Operations and Global Climate Change

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ABSTRACT: Carbon disulfide (CS_2) has been historically associated with the production of rayon, cellophane, and carbon tetrachloride. This study identifies multiple mechanisms by which CS_2 contributes to the formation of CO_2 in the atmosphere. CS_2 and other associated sulfide compounds were found by this study to be present in emissions from unconventional shale gas extraction and processing (E&P) operations. The breakdown products of CS_2; carbonyl sulfide (COS), carbon monoxide (CO), and sulfur dioxide (SO_2) are indirect greenhouse gases (GHGs) that contribute to CO_2 levels in the atmosphere. The heat-trapping nature of CO_2 has been found to increase the surface temperature, resulting in regional and global climate change. The purpose of this study is to identify five mechanisms by which CS_2 and the breakdown products of CS_2 contribute to atmospheric concentrations of CO_2. The five mechanisms of CO_2 formation are as follows:

1. Chemical Interaction of CS_2 and hydrogen sulfide (H_2S) present in natural gas at high temperatures, resulting in CO_2 formation;
2. Combustion of CS_2 in the presence of oxygen producing SO_2 and CO_2;
3. Photolysis of CS_2 leading to the formation of COS, CO, and SO_2, which are indirect contributors to CO_2 formation;
4. One-step hydrolysis of CS_2, producing reactive intermediates and ultimately forming H_2S and CO_2;
5. Two-step hydrolysis of CS_2 forming the reactive COS intermediate that reacts with an additional water molecule, ultimately forming H_2S and CO_2.

CS_2 and COS additionally are implicated in the formation of SO_2 in the stratosphere and/or troposphere. SO_2 is an indirect contributor to CO_2 formation and is implicated in global climate change.

KEYWORDS: global climate change, carbon disulfide, GHG, carbon dioxide

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Introduction

Carbon disulfide (CS_2) is a chemical intermediate best known for its historical use in the production of rayon, cellophane, and carbon tetrachloride.[1–3] Industrial emissions of CS_2 to the atmosphere have declined as textile manufacturing has shifted from the US to Asia, and the use of CS_2 in carbon tetrachloride production has been phased out.[4] With energy extraction expanding across the US, emission of CS_2 may be on the rise and its contribution in formation of greenhouse gas (GHGs) is underreported.

CS_2 is a component of sour natural gas and occurs naturally in the environment from the degradation of organic material, including geologic deposits of oil and natural gas; it is a waste gas emitted from the processing of sour natural gas.[5,6] In natural gas extraction, CS_2 is used as a paraffin solvent for sulfur, phosphorous, selenium, bromine, resins, and rubber.[7] It is also a component of mercaptan, an odorant added to natural gas.[8] Mercaptans may also be removed from a gas stream by oxidation to disulfides, which are then easily separated from the gas stream by absorption.[9] It can be produced from the interaction of natural gas with hydrogen sulfide at high temperatures. CS_2 is also known to be released in fossil fuel combustion, including natural gas combustion. During the extraction of natural gas, venting and flow-back operations release large amounts of gases, including CS_2, directly to the atmosphere.[10,11]

Recent ambient air monitoring studies have identified CS_2 and other associated sulfide compounds present in emissions emanating from natural gas exploration and production (E&P).[12–15] As CS_2 is present in many geologic formations and aspects of energy extraction, residential communities experiencing the trend of "urban drilling" – ie, extraction and processing of natural gas in populated urban communities – may be exposed to higher concentrations of CS_2 in ambient air when compared to other residential areas not experiencing extraction and processing.[16]

CS_2 is categorized as a non-methane volatile organic compound (NMVOC) and classified, along with carbonyl sulfide, as a hazardous air pollutant (HAP) according to the Clean Air Act Amendment of 1990 (CAAA). NMVOCs are a category of chemicals commonly used as solvents in industrial processes with the ability to vaporize at room temperature.[17] NMVOCs may be classified as a direct or indirect GHG, and can be involved in indirect radiative reactions that form CO_2.[14] NMVOCs indirectly contribute to global climate change by producing GHGs, such as CO_2, through reactions with other compounds, through their own chemical transformation influencing atmospheric lifetime of other GHGs, and by affecting the absorptive characteristics of the atmosphere such as cloud formation.[18,19] In an indirect radiative reaction, a chemical breaks down in the atmosphere producing a GHG, or interacts with other chemicals in the atmosphere changing atmospheric concentrations of GHGs. The size of the indirect effect is dependent upon when and where the gas is emitted.[20,21] CO_2 is a GHG that is transparent to incoming solar radiation but with the capacity to easily absorb and trap infrared radiation. This allows heat to be retained at the Earth's surface, contributing to ground-level ozone and global climate change.[22] Ground-level ozone can damage crops and human health, and can lead to reduced crop production.[23,24]

This study is the first to identify five direct and/or indirect mechanisms by which CS_2 contributes CO_2 to the atmosphere and exhibits its capacity as a GHG and contributor to global climate change. This study is also one of the first to identify the presence of CS_2 and other sulfide compounds in emissions from unconventional shale gas E&P operations.

Materials and Methods

A literature review was performed examining previous work related to occupational exposure to CS_2 and any mechanism by which CS_2 contributes to CO_2 atmospheric concentrations and to CS_2 use or presence in emissions from natural gas extraction or processing operations.

Key words searched included CS_2, CS_2 and CO_2, CS_2 occupational exposure, natural gas E&P emissions, and CS_2 mechanism of CO_2 formation. Databases searched included MEDLINE, TOXLINE, Scopus, Science Direct, TOXNET, and PubMed. Although many articles were found identifying CS_2 exposure in occupational settings, they were mostly published prior to 1980. Recent publications on ambient air monitoring in regions experiencing energy extraction analyzed air samples collected for CS_2, but failed to identify the potential CS_2 has as a GHG and contributor to global climate change. No article to date was found identifying all five potential mechanisms by which CS_2 might form CO_2 in the atmosphere or the potential for COS and SO_2 to be contributors to CO_2 formation.

Results

The five potential mechanisms by which CS_2 may form CO_2 either directly or indirectly and contribute to GHG atmospheric concentrations are described in this paper (Fig. 1).

Mechanism 1 – Chemical interaction. The interaction of CS_2 and natural gas with hydrogen sulfide (H_2S) at high temperatures can form CO_2.[25]

$$CS_2 + H_2S \rightarrow CO_2$$

In the document *Report to Congress on Hydrogen Sulfide Air Emissions Associated with the Extraction of Oil and Gas*, gas processing operations were identified as potential sources of H_2S releases. Impurities present in natural gas (produced water, H_2S, and CO_2) are removed prior to the gas being compressed and shipped in pipelines. This removal process is often performed at pad sites located in residential areas where extraction occurs and may be a source of H_2S.[26]

Mechanism 2 – Combustion. Combustion of CS_2 in the presence of oxygen produces CO_2 and SO_2.

$$CS_2 + 3O_2 \rightarrow 2SO_2 + CO_2$$

CS_2 is highly flammable and can ignite easily. When exposed to spark or friction, it is known to easily combust. Contact with steam pipes or even light bulbs have been known to initiate the combustion of CS_2.[27–31]

Mechanism 3 – Photolysis. Photolysis of CS_2 leads to the formation of carbonyl sulfide (COS), CO, and SO_2.

$$CS_2 + (\text{light}) \rightarrow COS + CO + SO_2$$

CS_2 may have an indirect effect on global climate change through the main transformation product COS. CO is only a weak direct GHG but has important indirect effects on global climate change. CO reacts with hydroxyl (OH) radicals in the atmosphere, reducing their abundance. As OH radicals help the atmospheric lifetimes of strong GHGs such as methane, CO may indirectly increase the global climate change potential of these gases from OH radical scourging.[32–34]

The half-life of CS_2 in the atmosphere from photolysis is estimated to be 1 week, whereas that of COS is estimated at 2 years, which provides the opportunity for long-range chemical transport and atmospheric conversions.[35,36]

Chin reported an additional indirect source of CS_2 present in sulfur recovery operations in the oil industry, which is oxidized COS in the atmosphere.[6]

Mechanism 4 – One-step hydrolysis. Shangguan identified two mechanisms of hydrolysis of CS_2. In the one-step hydrolysis mechanism, CS_2 directly reacts with the hydrogen atoms in two molecules of water, producing CO_2 and H_2S.[37–39]

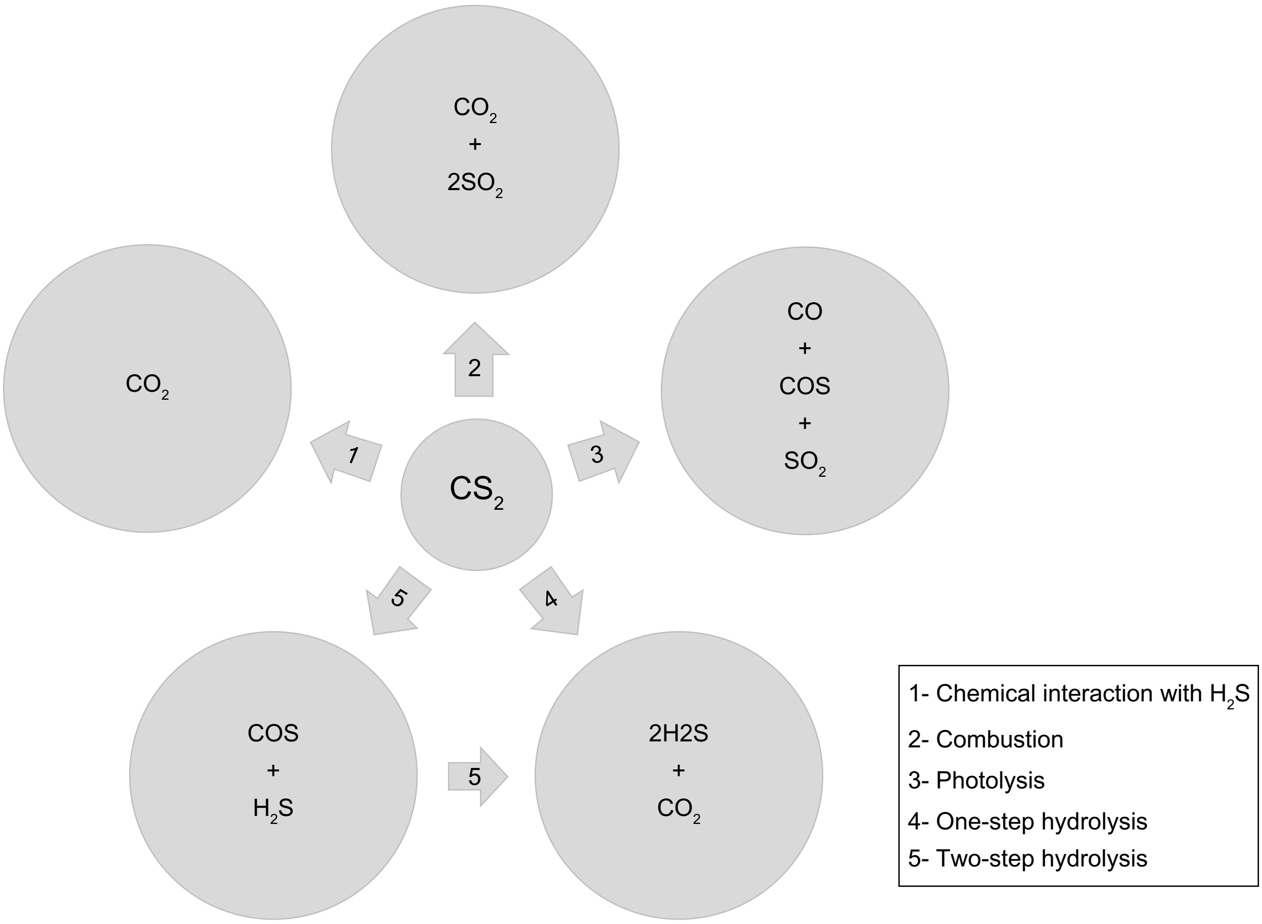

Figure 1. Five mechanisms of CO_2 formation from CS_2.

$$CS_2 + 2H_2O \rightarrow CO_2 + H_2S$$

Mechanism 5 – Two-step hydrolysis. In a two-step hydrolysis mechanism, CS_2 reacts with a hydrogen atom in a water molecule, leading to reactive intermediate COS. COS then reacts with an additional water molecule to form CO_2 and H_2S.

$$CS_2 + H_2O \rightarrow COS + H_2S$$

$$COS + H_2O \rightarrow CO_2 + H_2S$$

Research has shown that hydrolysis of CS_2 can occur at room temperature at a slow rate.[40]

A previous study by the authors identified CS_2 and 12 other sulfide compounds present in ambient air in residential communities in the Barnett Shale geologic formation where natural gas E&P operations were being carried out.[41] CS_2 concentrations and the detection frequency were found to vary with distance from the natural gas emission source. Values ranged from 0.3 to 200 parts per billion by volume (ppbv) based on a 24-hour air monitoring period, and from 1.5 to 980 ppbv based on a 1-hour monitoring period. The results presented in Table 1.

The U.S. Environmental Protection Agency's Urban Air Toxcs Monitoring Program (NMP) comprising 52 sites around the US reported only CS_2 as a monitored sulfide compound comparable to the values in this study. CS_2 atmospheric concentrations based on a 24-hour air monitoring period showed a minimum level for CS_2 of 0.005 ppbv and a maximum of 0.193 ppbv. Sampling period was for up to 12 consecutive months.[42] CS_2 is denser than air (2.62 vapor density when compared to air = 1) and can settle close to the ground in ground-level breathing zones.[43]

Discussion

The potential contribution of CS_2 to atmospheric CO_2 and GHG levels warrant further examination due to its unique qualities as a NMVOC and HAP. COS, CO, SO_2, breakdown products of CS_2, and indirect greenhouse gases additionally contribute to CO_2 formation in the atmosphere. The transparency of CO_2 to incoming solar radiation allows it to trap and absorb infrared radiation at the Earth's surface. This, in turn, gives rise to ground-level ozone formation, which is a major factor in climate change.

Many urban cities experiencing natural gas E&P are designated as nonattainment areas with air quality below National Ambient Air Quality Standards (NAAQS). Iden-

Table 1. CS_2 and associated sulfide compounds in natural gas emissions 24- and 1-hour minimum and maximum concentrations in parts per billion by volume (ppbv). fgdgggdgfgdggsdfgdgdgsddgddgsdfg

CHEMICAL (PPBV)	MIN. 24 HOURS	MAX. 24 HOURS	MIN. 1 HOUR	MAX. 1 HOUR
Carbon disulfide	0.7	103.0	3.4	504.6
Carbonyl sulfide	0.3	36.7	1.5	180.0
Dimethyl disulfide	0.3	200.0	1.5	980.0
Methyl ethyl disulfide	0.3	145.0	1.5	710.0
Methyl propyl disulfide	0.3	41.6	1.5	204.0
Diethyl disulfide	0.3	32.7	1.5	160.2
Ethyl, methylethyl disulfide	0.3	46.7	1.5	228.8
Dimethyl trisulfide	1.2	46.3	5.9	226.8
Ethyl *n*-propyl disulfide	0.3	25.2	1.5	123.5
Diethyl trisulfide	0.3	8.2	1.5	40.3
Methyl *n*-butyl disulfide	0.3	15.5	1.5	76.0
Propyl *n*-butyl disulfide	0.3	14.6	1.5	71.5
Dipropyl disulfide	0.3	23.1	1.5	113.2

tification of airborne chemicals contributing to CO_2 levels as well as the sources of those emissions is critical in order to manage air quality and achieve NAAQS compliance. The quantification of emissions from chemical manufacturing facilities producing CS_2 in the US may be easy due to the major source reporting requirements. Quantification of CS_2 emissions from natural gas E&P operations is more difficult due to the lack of required emission reporting and the vast number of well sites. Additionally, each pad site may have multiple sources of CS_2 emission. As CS_2 escapes into the atmosphere, to quantify secondary atmospheric conversion becomes a challenge. While CS_2 is a direct contributor to atmospheric CO_2 levels, it is also an indirect contributor and is responsible for intermediates that may also produce CO_2 in the atmosphere.

Currently, there is a profound lack of information and quantification of CS_2 emissions from natural gas E&P operations. At facilities where combustion takes place, CS_2 may be counted overall in VOC emissions. Quantification of CS_2 or speciation of sulfide compounds is not currently required. Additionally, these data are self-reported and may be more qualitative rather than quantitative. Although CS_2 and COS are HAPs, capable of adversely impacting health, this chemical has been considered to be primarily an occupational exposure agent. Current peer-reviewed nonoccupational health studies are lacking and outside the scope of this paper.

This study provides additional knowledge to the atmospheric puzzle, but more questions remain. Future studies are needed to examine and quantify the direct and indirect contribution of CS_2 and intermediates of CS_2 to atmospheric CO_2 formation and GHG levels. Quantification of direct source CS_2 emissions from natural gas E&P operations is also required to better understand how CS_2 originating from energy extraction may contribute to local and regional CO_2, GHG, and HAP levels. With additional knowledge, we can prepare proper mitigation strategies for this previously unidentified and underreported chemical that contributes to CO_2 concentrations in the atmospheric and contributes to global climate change.

Author Contributions

Conceived and designed the experiments: ALR, JTP. Analyzed the data: ALR, JTP. Wrote the first draft of the manuscript: ALR, JTP. Contributed to the writing of the manuscript: ALR, JTP. Agree with manuscript results and conclusions: ALR, JTP. Jointly developed the structure and arguments for the paper: ALR, JTP. Made critical revisions and approved final version: ALR, JTP. Both authors reviewed and approved of the final manuscript.

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