Dualistic Nature of NOx Impact on Greenhouse Effect

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Nitrogen oxides (NO_x = NO + NO_2) emitted from a stationary combustion chamber (including waste to energy plants) or engines cause numerous undesirable environmental effects. These include negative influences on human and animal health, detrimental effects on plants and vegetation, acid rain, and smog. These negative influences are commonly accepted by the scientific community. However, the impact of NO_x on the greenhouse effect (GHE) is not generally accepted by the scientific community.

NOx greenhouse effect (GHE) indirect greenhouse gas direct greenhouse gas

1. Introduction

It has already been mentioned that global warming potential (GWP) can be negative or positive. Indeed, the warming and cooling effect of NO_x in the atmosphere is highlighted in the literature [1][2][3]. The nature of this effect depends on the mentioned parameters such as NO_x source, horizontal and vertical location, and the co-existence of other compounds. In the next section, an explanation of the cooling and/or warming nature of NO_x is provided.

2. Warming Nature

The presence of NO_x can influence global warming. The results of investigations suggest that the main process responsible for this effect is the impact of NO_x on the conversion of tropospheric ozone (O_3) [4], which is recognized as a GHG [5]. Depending on the concentration of NO_x in the atmosphere and the equilibrium between other compounds contained in the atmosphere, O_3 can either be created or destroyed. If the concentration of NO_x are higher than the range of 10–30 pptv (parts-per-trillion (volumetric), 10^{-12}), O_3 can be created in the atmosphere. Furthermore, the rate of O_3 creation because of the presence of NO_x depends on the latitudes and seasons [4]. Namely, it has been postulated that the presence of NO_x (NO/NO_2) influences the catalytic conversion of O_3, according to the following reactions ((2)–(5)) [6]:

$$OH + CO + O_2 \rightarrow CO_2 + HO_2 \quad (2)$$

$$HO_2 + NO \rightarrow NO_2 + OH \quad (3)$$

$$NO_2 + h\nu \rightarrow NO + O(^3P) \quad (4)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (5)$$

Summarizing reactions (2)–(5), the overall process reaction (6) is

$$CO + 2O_2 + h\nu \rightarrow CO_2 + O_3 \quad (6)$$

Thus, this proves and provides clear evidence that the presence of NO_x causes the creation of O_3 and CO_2 under sunlight irradiation. Hence, they influence global warming because of the creation of GHGs. The effect of the presence of NO_x on O_3 conversion in the atmosphere was confirmed by Renyi Zhang, Xuexi Tie, and Donald W. Bond [7].

Another phenomenon potentially influencing global warming due to the presence of NO_x is their impact on N_2O conversion [4][8]. Namely, NO_x emitted into the atmosphere can be converted into N_2O (a direct GHG) in the complex processes occurring in the soil. The simplified description of this complex mechanism of converting NO_x into N_2O is as follows: Emitted NO is transformed into NO_2, and next to nitrogen acids and other compounds in the form of aerosols. These compounds are then transferred into the soil by precipitation. Further transformation in the soil (such as by the denitrification process) leads to incidental emissions of N_2O from the soil to the atmosphere. It was estimated that the N_2O emissions from soil (as a consequence of NO_x transformation) are 1.2%–3.6% of the total N_2O emissions from other sources [4]. Nevertheless, understanding the soil N cycling processes is still being discussed [9].

3. Cooling Nature

It was previously mentioned that the presence of NO_x can lead (in some specific conditions) to global cooling. This is why the GWP values are sometimes negative. Furthermore, NO_x are sometimes termed as cooling gases [10][11][12][13]. It was proven that the presence of NO can influence the increase in the concentration of OH radicals in the atmosphere, and OH radicals contribute to destroying methane, according to the following reactions [12]:

$$HO_2 + NO \leftrightarrow OH + NO_2 \quad (7)$$

$$OH + CH_4 \leftrightarrow H_2O + CH_3 \quad (8)$$

Here, CH_4 belongs to the direct group of GHGs, thus destroying it causes a cooling effect. Moreover, CH_4 reduction results in a long-term reduction in tropospheric O_3, and a long-term reduction in stratospheric water vapor from the reduced oxidation of CH_4. Both of these phenomena are recognized as negative radiative forcing effects [14]. It should be explained that the cooling effect of NO_x depends on the impact of other compounds existing in the atmosphere. Namely, the presence of CO can contribute to a decrease in the concentration of OH radicals. Consequently, the cooling effect of NO_x can be inhibited, and the GWP for NO_x is positive (a warming effect). Furthermore, the decrease in the OH concentration inhibits CH_4 destruction (being a direct GHG). If the impact of NO_x is considered without reference to the CO contribution, it would only be assumed that the cooling effect of NO_x is from surface sources. The increase in the CO concentration in the atmosphere causes NO_x to convert from cooling gases to warming gases with a positive GWP [13]. One can have reasonable hope that the development of combustion technology by increasing the combustion efficiency and decreasing CO emissions will inhibit NO_x from having an effect as a warming gas.

Another phenomenon responsible for the cooling effect of NO_x is the formation of aerosols (dispersion of very fine liquid droplets) in the atmosphere. Increased aerosol formation and cloud reflectivity cause a decrease in sunlight radiation and enhance the cooling effect [4][10]. The main process responsible for aerosol formation is the conversion of SO_2 into H_2SO_4 formations, which condensate as very fine droplets (aerosols). The contribution of NO_x in this process relies on OH formation. It has already been explained that an increase in NO concentration causes an increase in OH radical concentration in the atmosphere. Moreover, the presence of OH radicals intensifies SO_2 conversion into aerosols, thus directly causing a cooling effect [10].

4. Summary

It has already been mentioned that the warming and cooling effects of NO_x in the atmosphere are possible due to the impact of different processes. The warming and cooling effects are summarized in **Table 1**. These effects were divided into three groups in terms of the influence area (i.e., air, water, soil, and vegetation aboveground). Some processes seem to be opposing. Thus, examples of these cases are described in a "cross-impact" column.

Table 1. The summary of the warming and cooling effect of NO_x in terms of the influence on the area.

Warming	Cooling	Cross Impact
	Air	
In the short-term, NO_x emissions contribute to warming by enhancing tropospheric O_3 concentrations (on a daily time scale), which are recognized as GHG [2][5].	NO_x enhances OH production. CH_4 (GHG) is oxidized in the presence of OH [2][14]. NO_x can lead to decreases in O_3 concentration on a decadal time scale because it causes an increase in OH radical concentration, which decreases CH_4 concentration, which decreases NO_2 formation, which decreases O_3 formation. [2][14]. The formation of fine particles called aerosols. Aerosols are powerful cooling agents, both directly by scattering or absorbing light, and indirectly by affecting the cloud formation, their lifetime, and brightness [2][10].	NO_x leads to O_3 decreasing (on a decadal time scale) or increasing (on a daily time scale) [2].
	Soil and vegetation aboveground	
Nitrogen is a substrate for N_2O production by nitrifying and denitrifying bacteria in soils. Thus, the	In some cases, inputs of Nr from atmospheric deposition enhance plant growth rates	Warming and cooling effects are possible. The effect of N on net C flux (both above and below ground

Warming	Cooling	Cross Impact
deposition of nitrogen (Nr) onto ecosystems can increase N_2O emissions and decrease the uptake of atmospheric CH_4 by soil microorganisms. Soil microbes that consume CH_4 often preferentially consume ammonium (NH_4^+), leading to reduced CH_4 consumption rates in the presence of abundant NH_4^+ [2]. Inhibition of photosynthesis and a reduction of atmospheric CO_2 sequestration by the plant biomass due to an increase of O_3 concentration in the atmosphere (impacted by NO_x). Reduction of aboveground C storage and reduction of belowground C assimilation and allocation [1][2] In some cases, the excess of N leads to the enhanced mortality of plants due to nutrient imbalances or acidification [2].	because of the fundamental constraint of N availability on plant productivity and CO_2 uptake into plant biomass. N additions to soil typically increase C capture and storage [2]. Foliar N may also increase the albedo of the canopy, enhancing the reflectivity of the Earth's surface, and hence contributing to cooling [2].	pools) differs among ecosystems [1][2].
	Water	
Nitrogen is a substrate for N_2O production by nitrifying and denitrifying bacteria in water bodies [2]. Denitrification occurring in water can emits N_2O [15]. Nitrous oxide (N_2O) can be emitted from wastewater treatment processes [15][16][17]. Both SO_2 and NO inhibited algal growth at a high level of CO_2 [18][19].	N- water can accelerate to grow algae growth. Nevertheless, the harmful (toxic, food-web altering, hypoxia-generating) algal blooms (HABs) have been linked to human nutrient (phosphorus (P) and nitrogen (N)) over enrichment [20] The serious problem is cyanobacterial bloom formation. Decreasing P and N loads can counteract the direct positive effect of warming temperatures on bloom proliferation [21][22]. Some algae species can sequestrate the CO_2 from the flue gas including SO_X and NO [23]. In the case of some species (green alga Chlorella sp.), the presence of NO_x can enhance algae growth [24]	NO_x and SO_x might be beneficial to the growth of microalgae as they can provide additional nutrients. However, this is true only when the culture pH is stably controlled and the NO_x/SO_x concentrations should be lower than the inhibitory level [25].

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