



Review On the Issues of NO_x as Greenhouse Gases: An Ongoing Discussion . . .

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Abstract: Nitrogen oxides (NO_x = NO + NO₂) 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. In this paper, the issue of the impact of NO_x on the GHE is discussed, and it was analyzed and explained that NO_x are an indirect greenhouse gas (GHG). However, the impact of NO_x on the GHE is a complex process affected by different parameters (cooling and warming nature is possible). It has been estimated that NO_x emitted from stationary, ground-placed sources (such as boilers and furnaces) have little impact on the GHE compared to CO₂ and other direct GHGs. The contribution of NO_x in the GHE compared to the emission of all GHGs is less than 3%. NO_x sources from waste incineration and co-incineration plants were especially considered and analyzed. The co-incineration in smaller plants (capacity range of $1 \div 5$ MW) gives more benefits to the environment due to a decrease in the NO_x emission standards when the share of the waste increases.

Keywords: NO_x; greenhouse effect (GHE); indirect greenhouse gas; direct greenhouse gas



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1. Introduction

1.1. NO_x Environmental Impact

Nitrogen oxides (NO_x = NO + NO₂) are emitted from natural and man-made (anthropogenic) sources. One of the main anthropogenic sources of NO_x emissions is combustion processes realized in stationary chambers (such as boilers) and vehicle engines. The existence of NO_x in the atmosphere causes many environmental problems such as acid rain and photochemical smog. Both of these have a negative influence on human and animal health and cause disturbances in plants and vegetation [1,2]. However, there are some positive applications of nitrogen oxides. For example, nitric oxide (NO) is used in medicine as an inhalation agent (concentration dose in the range of 1–80 ppm) for children and adults suffering from circulatory and respiratory problems [3]. Furthermore, NO is also applied as an antimicrobial agent [4]. It should be explained that the toxicity of NO_x results from the fact that primarily emitted NO is converted to NO₂, which belongs to the group of highly toxic gases [3].

Currently, there is a debate in the scientific community concerning the impact of NO_x on the greenhouse effect (GHE). Some scientists unambiguously cite NO_x as a greenhouse gas (GHG), placing this compound beside direct GHGs such as CO_2 , CH_4 , N_2O , and hydrofluorocarbons (HFCs) (see Radoslaw Lajnert's graphics in Figure 1).

The opinions regarding the impact of NO_x on the GHE are unclear in the scientific community. There appear to be inconsistent views on whether NO_x influences the GHE, and on the nature of this influence. Despite the proliferation of relevant investigations, a range of different opinions can be observed, and some confusion exists within the scientific literature. Therefore, it is necessary to present a synthesis of existing opinions. This will

involve appropriate interpretation, consistent with the current knowledge in the field, of the role NO_x play in the GHE. From the different opinions presented in the scientific literature, some common characteristic views can be classified as follows:

- NO_x are GHGs and influence global warming;
- NO_x are not GHGs and do not influence the GHE;
- NO_x are indirect GHGs and influence global warming;
- NO_x are indirect GHGs and influence global cooling.



Figure 1. NO_x as defendants in court (permission obtained from the author, © Radoslaw Lajnert).

Thus, in this paper, the issue of NO_x impact on the GHE is discussed, and an investigation into the nature of this impact was conducted. Butterbach-Bahl et al. [5] in 2011 and Pinder et al. [6] in 2013 showed the complex analysis of nitrogen-species emission (including NO_x) on GHE. Instead of these analyses, the role of NO_x in GHE is still discussed. In the current paper, the role of CO in NO_x conversion is underscored, and the mechanism of warming and cooling effects is presented in terms of the role of NO_x in the GHE. New insights and investigation results related to the role of NO_x in the GHE and the reason for misunderstanding the role of NO_x in the GHE. The seriousness of this debate is especially important now when the world is faced with dramatic challenges related to global warming. (compare the document: "A Clean Planet for all. A European long-term strategic vision for a prosperous, modern, competitive and climate neutral economy" https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX: 52018DC0773&from=EN (accessed on 1 October 2022))

1.2. Methodology

Since this is a review paper with some aspects of analytical analysis, we would like to present some methodology in terms of the article collection method, data analysis, data completion, etc. in detail. A few scientific web browsers and databases were used, namely Google Scholar, Science Direct, and Scopus. The papers were searched using specific keywords such as "Greenhouse effect", "GHE", "Greenhouse gases", "GHG", "Global warming potential", and "GWP" with the combination of the word "NO_x". All collected papers were read and analyzed by the context of NO_x impact on the greenhouse effect. In some cases, the combination of the words "NO_x" and the listed keywords were searched using the corresponding function in .pdf files. The phrases including the mentioned words were marked and collected. After the search and analysis, the obtained information was collected and combined in the groups, creating the following sections of the manuscript.

Concerning the section " NO_x in waste incineration and co-incineration plants", the analysis includes the comparison of NO_x emission limits for power plants, incineration,

and co-incineration installations in terms of the plant capacity, type of fuel, and waste share. The emission standards were taken from the Polish legislative document "Regulation on emission standards for certain types of installations, fuel combustion sources, and waste incineration or co-incineration devices"—Journal of Laws 2020 item 1860 is consistent with the European Standards (Directive 2010/75/EU). The standards depend on the installation age, type of fuel, annual operation time of installation, and period/type of measurement (continuous, quasi-continuous, periodic measurement). The regulations include the following ranges of installation capacities (thermal power in fuel): ≤ 5 MW; >5 and <50 MW; ≥ 50 and ≤ 100 MW; >100 and ≤ 300 MW; >300 MW. Based on these ranges, four capacities were assumed (i.e., 15, 55, 105, and 305 MW). The analysis assumptions are presented in Table 1. To calculate the case when co-firing is realized, the mixing rule (Journal of Laws 2020 item 1860 and Directive 2010/75/EU) should be applied. The main part of this rule is based on the equation:

$$C = (V_{waste} \times C_{waste} + V_{proc} \times C_{proc}) / (V_{waste} + C_{proc})$$
(1)

where C is the total emission limit values for co-firing fuels with waste; V_{waste} is the waste gas volume resulting from the incineration of waste only determined from the waste with the lowest calorific value specified in the permit. C_{waste} is the emission limit values for waste incineration plants and co-firing. V_{proc} is the waste gas volume resulting from the plant process including the combustion of the authorized fuels normally used in the plant (wastes excluded). C_{proc} is the emission limit values specified for fuels in the case of co-incineration or the absence of such values in the legal acts, in other words, the actual values of the concentration of the substance in the waste gases during the operation of the combustion process (without waste incineration).

Case	Assumptions			
Coal combustion (100%)	LHV = 22 MJ/kg, new installation, continuous measurement (daily average values)			
Biomass combustion (100%)	LHV = 18 MJ/kg, new installation, continuous measurement (daily average values)			
RDF combustion (100%)	LHV = 15 MJ/kg, new installation, continuous measurement (daily average values)			
Coal/RDF co-firing (10% by energy)	LHV = 22 MJ/kg (coal) and LHV = 15 MJ/kg (RDF), RDF share of 10% (by energy), new installation, continuous measurement (daily average values), installation capacity (thermal power in fuel) of 1.5 MW, 15 MW, 105 MW, and 305 MW			
Biomass/RDF co-firing	LHV = 22 MJ/kg (coal) and LHV = 15 MJ/kg (RDF), RDF share of 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90% (by energy), new installation, continuous measurement (daily average values), installation capacity (thermal power in fuel) of 1.5 MW, 15 MW, 105 MW, and 305 MW			

Table 1. The assumptions during the calculation of NO_x emission standards in different cases.

1.3. NO_x: The Matter of Definition

To find the right direction in the debate over the role of NO_x in the GHE, the definition of NO_x should be reiterated: NO_x emissions are the sum of NO and NO₂ [7]. The classification of NO and NO₂ into one group (NO_x) is related to the phenomenon of NO conversion in the atmosphere into NO₂ in the presence of ozone (this is a simplified representation of a complex process). The time taken for NO to turn into NO₂ in atmospheric air conditions is a few minutes. Subsequently, NO₂ can be transformed into other nitrogen compounds within a period of hours to days [8]. It should be noted that in addition to NO and NO₂, N₂O can also be emitted from the combustion process. The highest emission of N₂O (from combustion processes) is observed in fluidized-bed combustors. The concentration in flue gas from these combustors can be in the range of 40–100 ppm [9]. Although N₂O belongs to the group of direct GHGs, it cannot be classified as NO_x. In addition, the term NO_y is also seen in the literature, which contains all reactive nitrogen compounds that exist in atmospheric air. Examples of NO_y are HNO₃, C₂H₃NO₅ (peroxyacetyl nitrate (PAN)), HONO, N₂O₅, HO₂NO₂, NO₃, and NO_x [8]. Because NO_x belong to NO_y, the remainder of the listed compounds are referred to as NO_z. Therefore, NO_x + NO_z = NO_y. The main conversion processes of NO_x into NO_z (NO_x \rightarrow NO_z) are NO₂ + NO₃ \rightarrow N₂O₅ and PAN formation, which account for 55% and 34% of the total NO_x \rightarrow NO_z, respectively. The opposite process (NO_z \rightarrow NO_x) is also possible, and the main process components of this are the reverse reactions N₂O₅ \rightarrow NO₂ + NO₃ and PAN decomposition [10].

2. The Role of NO_x in the Greenhouse Effect

It has been previously mentioned that different opinions exist within the scientific community about the role of NO_x in the GHE. This inconsistency existed in historical scientific papers as well as in currently published issues (i.e., in 2022). Some researchers directly include NO_x in GHGs or they suggest that NO_x are GHGs, but do not explain the nature of this impact [11–21]. Some researchers do not distinguish precisely between N₂O and NO_x, or they even include N₂O into NO_x [22–26], suggesting that NO_x are GHGs. Indeed, N₂O is created during the combustion process. Higher concentrations of N₂O can be found be in flue gas when the flame temperature is lower than 900 °C such as in fluidized-bed combustors [27]. Furthermore, N₂O is recognized as a by-product during NO formation [28]. However, it has already been explained that the inclusion of N₂O into NO_x is not a true assumption. Conversely, in some scientific articles, the impact of NO_x on the GHE is not highlighted, and only other environmental negative effects of NO_x are mentioned [29–31].

The role of NO_x in the GHE should be explained. It is very important to distinguish between two crucial issues. The potential possibility of NO_x influencing the GHE is not equal to including these gases in direct GHGs. Very often in scientific articles, these two issues are confused, and this distinction is not clearly presented. It should be explained that NO_x ($NO_x = NO + NO_2$) do not directly influence radiative heat transfer (from the Sun to the Earth's surfaces) in the radiation spectra typical for direct GHGs (such as CO₂, CH_4 , and N_2O). The GHE is caused by the balance between radiative heat transfer from the Sun (average surface temperature of 6000 K, and wavelength of 0.2–4 μ m) to the Earth's surface and the radiative heat transfer from Earth (average surface temperature 255 K, and wavelength of 4–100 μ m) to space. The GHGs existing in the atmosphere (such as H₂O and CO_2) weakly absorb radiation of a 0.2–4 µm wavelength and strongly absorb radiation of $4-100 \mu$ m, thus the Earth's surface is warmed. Part of the energy received from sunlight irradiation is accumulated on the Earth's surface because of the impact of GHGs. This is because radiative heat transfer from the Sun is transferred by the atmosphere, whereas the radiative heat emitted from the Earth's surface is captured due to the impact of GHGs. This phenomenon is called the greenhouse effect. It causes increases and stabilization of the temperature on the Earth's surface during the day and night. A lack of atmosphere and a deficiency of the GHE would result in a decrease of the temperature on Earth to an average value of -18 °C, whereas the actual average temperature on Earth is +15 °C. The GHE created specific conditions, allowing our planet to be habitable and to develop life [32]. The direct GHGs are H₂O, CO₂, CH₄, N₂O, fluorine compounds (such as NF₃ and SF₆), and chlorine compounds (such as $CFCl_3$ and CF_2Cl_2) [32,33]. A more particular list of direct GHGs was presented by Fuglestvedt et al. [33]. At this stage, it is necessary to mention the term atmospheric window. There is a region containing a long-wave spectrum from approximately 8 µm to 12 µm known as the atmospheric window, where absorption by water and CO_2 is weak (see Figure 2). However, other GHGs such as CH_4 , N_2O , O_3 , $CFCl_3$, and CF_2Cl_2 have absorption bands in or near this range, and contribute to the trapping of long-wave radiation despite their relatively low concentrations [32].



Figure 2. Percentage of atmospheric absorption for radiation passing from the top of the atmosphere to the surface for different GHGs versus NO_x and the atmospheric window (based on John F. B. Mitchell [32]).

An analysis of the absorption band of NO (maximal peaks for a wavelength of 5.2 and 5.4 μ m) and NO₂ (maximal peaks for a wavelength of 6.1 and 6.25 μ m as well as for wavelengths of 3.4 and 3.5 μ m) [22,34,35] clearly shows that NO_x do not have an absorption band in the region of the atmospheric window. Thus, these gases cannot be included in direct GHGs. However, it does not mean that their impact on the GHE can be omitted. Finally, we reached the conclusion that GHGs can be divided into two groups: direct GHGs and indirect GHGs (as presented in Figure 3). In the case of indirect GHGs, their impact on the global climate is complex and can be connected to global warming and/or cooling. Sometimes, indirect GHGs are called reactive gases in the literature [36]. Thus, it should be stated that NO_x influence the global climate, and they belong to the group of indirect GHGs. Such an explanation can be found in some scientific literature [6,7,33,36–49]. Furthermore, in addition to NO_x, other gases are also included in the indirect GHGs group such as carbon monoxide (CO), volatile organic carbons (VOC), and sulfur dioxide (SO₂) [6,33,50].



Figure 3. The division of GHGs including direct and indirect GHGs.

3. Global Warming Potential

To estimate the impact of a particular substance on the GHE, the different climate metrics (coefficients) should be defined. One commonly used factor is global warming potential (GWP). According to the definition, "GWP is based on the time-integrated radiative forcing due to a pulse emission of a unit mass of gas. It can be quoted as an absolute GWP (AGWP) (in units of $Wm^{-2} kg^{-1}$ year), or as a dimensionless value by dividing the AGWP by the AGWP of a reference gas, normally CO₂" [33]. Furthermore, "the relative (dimensionless) GWP signifies the cumulative radiative forcing relative to emission of the same mass of CO₂ within defined time horizons" [38]. The time horizon is an important factor influencing the GWP value. Usually, the time horizon is defined as 100 years (commonly used in climate politics). However, in scientific analysis, three

different time horizons are suggested: 20, 100, and 500 years [33]. Thus, assuming such definitions, the GWP for CO_2 equals one. It should be stated that GWP can take a positive "+" or negative "-" value. A positive value indicates the considered compound influences global warming, while a negative value indicates an influence on global cooling. There are other factors for estimating the impact of gases on global warming such as the radiative forcing index (RFI) and global temperature change potential (GTP). However, GWP is the most popular and commonly used metric in climate politics, despite its limitations [33,39]. Precise determination of GWP for NO_x (as an overall value for all emission sources) is very difficult because in these gases, the GWP strongly depends on the type of source: grounded (surface), airborne, transportation, or from immobile sources. Furthermore, GWP can be affected by geographical location and time horizons [33,45]. Moreover, the GWP for NO_x varies substantially, according to the literature. For example, G. Lammel and H. Graßl [38] estimated that the GWP for NO_x from surface sources (time horizons of 20 and 100 years) were in the range of $\text{GWP}_{20} = 30-33$, and $\text{GWP}_{100} = 7-10$. Johnson and Derwent determined [50] GWP₁₀₀ = 5 for surface Northern Hemisphere sources, GWP₁₀₀ = -10 for surface Southern Hemisphere sources, and $GWP_{100} = 456$ for aircraft sources. The time horizon and source location strongly influence the GWP value. A. Skowron, D.S. Lee, and R.R. De León [39] presented the evaluated GWP for NO_x emitted from aircraft. They determined that the mean global values of GWP for time periods of 20, 100, and 500 years were $GWP_{20} = 322$, $GWP_{100} = 59$, and $GWP_{500} = 17$, respectively. Researchers noticed that different values of GWP were obtained for the Northern and Southern Hemispheres and particular regions in the world. The highest value of GWP_{20} (542) was an estimate for the area over Brazil. Such a potentially strong effect on the sensitive global climate was caused by the presence of O_3 and CH_4 . Researchers have concluded that GWP has limitations, and the influence of NO_x-O₃-CH₄ should be considered. They also noticed that in aircraft sources of NO_x , a more precise estimation of global climate change was obtained when radiative forcing (RF), with a unit of mW m⁻² Tg(N)⁻¹, was used as a climate metric. The descriptive difference between RF and GWP is that "while RF indicates the climate effect between past and present points in time, GWP gives the perspective for future impact on current emissions" [39]. The values of GWP and other climate metrics were presented by J.S. Fuglestvedt et al. [33]. Here, the researchers presented an advanced analysis of the impact of emissions on global warming. They considered different substances (direct and indirect GHGs) for different time horizons, types of emitters, and horizontal and vertical locations. Interestingly, NO_x —GWP₁₀₀ for surface sources was in a large range of values (from -28 to +1.6), and the average global value was -11.

4. Dualistic Nature of NO_x Impact on the Greenhouse Effect

It has already been mentioned that GWP can be negative or positive. Indeed, the warming and cooling effect of NO_x in the atmosphere is highlighted in the literature [5,6,40]. 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.

4.1. 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 (O₃) [38], which is recognized as a GHG [32]. Depending on the concentration of NO_x in the atmosphere and the equilibrium between other compounds contained in the atmosphere, O₃ 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}), O₃ can be created in the atmosphere. Furthermore, the rate of O₃ creation because of the presence of NO_x depends on the latitudes and seasons [38]. Namely, it has been postulated that

the presence of NO_x (NO/NO₂) influences the catalytic conversion of O₃, according to the following reactions ((2)–(5)) [36]:

$$OH + CO + O_2 \rightarrow CO_2 + HO_2 \tag{2}$$

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

$$NO_2 + h\nu \to NO + O(^3P) \tag{4}$$

$$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$$
(5)

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

$$CO + 2O_2 + h\nu \rightarrow CO_2 + O_3 \tag{6}$$

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 O₃ conversion in the atmosphere was confirmed by Renyi Zhang, Xuexi Tie, and Donald W. Bond [51].

Another phenomenon potentially influencing global warming due to the presence of NO_x is their impact on N_2O conversion [38,52]. 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 [38]. Nevertheless, understanding the soil N cycling processes is still being discussed [53].

4.2. 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 [7,45,50,54]. 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 [50]:

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

$$OH + CH_4 \leftrightarrow H_2O + CH_3 \tag{8}$$

Here, CH₄ belongs to the direct group of GHGs, thus destroying it causes a cooling effect. Moreover, CH₄ 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 CH₄. Both of these phenomena are recognized as negative radiative forcing effects [39]. 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 CH₄ 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 to convert from cooling gases to warming gases with a positive GWP [54]. We 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 [7,38]. The main process responsible for aerosol formation is the conversion of SO₂ into H₂SO₄ 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 SO₂ conversion into aerosols, thus directly causing a cooling effect [7].

4.3. 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 2. 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 2. 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 [6,32].	 NO_x enhances OH production. CH₄ (GHG) is oxidized in the presence of OH [6,39]. NO_x can lead to decreases in O₃ concentration on a decadal time scale because it causes an increase in OH radical concentration, which decreases CH₄ concentration, which decreases NO₂ formation, which decreases O₃ formation. [6,39]. 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 [6,7]. 	NO _x leads to O ₃ decreasing (on a decadal time scale) or increasing (on a daily time scale) [6].
5	Soil and vegetation aboveground	
Nitrogen is a substrate for N ₂ O production by nitrifying and denitrifying bacteria in soils. Thus, the deposition of nitrogen (Nr) onto ecosystems can increase N ₂ O 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 ⁺ [6]. 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 [5,6] In some cases, the excess of N leads to the enhanced mortality of plants due to nutrient imbalances or acidification [6].	In some cases, inputs of Nr from atmospheric deposition enhance plant growth rates 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 [6]. Foliar N may also increase the albedo of the canopy, enhancing the reflectivity of the Earth's surface, and hence contributing to cooling [6].	Warming and cooling effects are possible. The effect of N on net C flux (both above and below ground pools) differs among ecosystems [5,6].

Warming	Cooling	Cross Impact
	Water	
Nitrogen is a substrate for N ₂ O production by nitrifying and denitrifying bacteria in water bodies [6]. Denitrification occurring in water can emits N ₂ O [46]. Nitrous oxide (N ₂ O) can be emitted from wastewater treatment processes [46,55,56]. Both SO ₂ and NO inhibited algal growth at a high level of CO ₂ [57,58].	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 [59] The serious problem is cyanobacterial bloom formation. Decreasing P and N loads can counteract the direct positive effect of warming temperatures on bloom proliferation [34,60]. Some algae species can sequestrate the CO ₂ from the flue gas including SO _X and NO [61]. In the case of some species (green alga Chlorella sp.), the presence of NO ₂ can enhance algae growth [62]	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 [63].

Table 2. Cont.

5. Simplified Evaluation of NO_x (Surface Sources) Impact on GHE

Generally, unequivocal determination of the global impact of NO_x on the GHE (cooling or warming) is very difficult. This is because of the mentioned differences in the GWP value and dualistic behavior of NO_x as cooling or/and warming gases [33,40,41]. It was mentioned that the impact of NO_x on climate change depends on many factors such as latitude, horizontal and vertical localization, the contribution of other gases (mainly CO, CH_4 , and SO_2), conditions in the atmosphere (such as wind and sunlight irradiation), the processes occurring in the soil, and time horizons [7,33,38,39]. A. Skowron, David S. Lee, and Ruben R. De Leon [39] noticed that the same amount of emitted NO_x can cause different responses in terms of the GHE, depending on the emitter localization (aircraft in this case). Additionally, J.S. Fuglestvedt et al. concluded that "GWPs are not a useful tool for calculating the complete suite of aircraft effects" [33]. Particulate analysis of this issue has been presented by A. Skowron, David S. Lee, and Ruben R. De Leon [39]. It is commonly accepted that the emissions of NO_x from aircraft (especially in the North Pacific and North Atlantic ocean zones) have a much stronger influence on global warming than the emissions of NO_x from surface sources [33,39,50]. A. Skowron, David S. Lee, and Ruben R. De Leon [39] concluded that the global GWP_{100} from NO_x emitted from aircraft (based on 0.035 Tg(N)/yr incremental aircraft NO_x emissions) equaled 59. However, depending on the region, this factor has a large range of values (25–110). The complexity of this scientific analysis is caused by the already mentioned conditions in the atmosphere [64] and the aircraft parameters (such as weight, engine type, and combustion conditions) [64,65]. Moreover, NO_x emissions from aircraft depend on the flight phase. For example, during landing and take-off periods (idle/taxi, approach, climb out, and takeoff), the highest NO_x emissions were observed during the climb-out phase [66]. Thus, the presented analysis here did not include NO_x emissions from aircraft because this has been covered by other researchers.

Presented below is a simplified analysis, the aim of which is to estimate the impact of NO_x emissions from stationary, surface sources on the GHE compared to the impact on the GHE from other direct GHGs. It is assumed that NO_x emissions are from stationary, surface sources localized at central latitudes with a time horizon of 100 years. G. Lammel and H. Graßl [38] estimated a GWP₂₀ = 30–33 and GWP₁₀₀ = 7–10 for NO_x as the global average value. However, in other references, the values of GWP for surface sources are extremely varied including positive and negative. For example, positive values in the range of GWP₂₀ = 43–130 for sources localized in tropical regions, and positive/negative values in the range of GWP₂₀ = -43 to +23. From all of the analyzed values of GWP₁₀₀ for surface sources, the highest global GWP₁₀₀ is 10. Thus, this value is assumed as the most pessimistic. The other assumed variant is GWP₁₀₀ = 1.6. This value seems to be most realistic because it was

estimated for central latitudes [33] and the highest NO_x emissions are observed for such regions [67]. Nevertheless, it should be noted that for surface sources, the global GWP₁₀₀ = -11 [33]. Moreover, it is assumed that the contribution of emitted CO₂ from fossil fuel usage and industrial processes in the GHE is 65% compared to the impact of all direct GHGs [68]. Based on this assumption, the impact of NO_x on the GHE compared to CO₂ can be described by the coefficient %GHG_{NO_x} (9).

$$\% GHG_{NO_x} = NO_{x-eq,CO2} / (NO_{x-eq,CO2} + CO_2) \times 100\%$$
(9)

Furthermore, the impact of NO_x on the GHE compared to all direct GHGs (%(total)GHG_{NO_x} is

The $NO_{x-eq.CO2}$ parameter is the sum of the emitted NO_x (Gt/year) multiplied by GWP_{100} for NO_x. In other words, NO_{x-eq.CO2} is the emission of NO_x as an equivalent of CO₂ (regarding the GHE) at an assumed time horizon. It can be seen from Table 2 that the participation of NO_x in the GHE regarding CO₂ impact and the most pessimistic scenario does not exceed 5%. In the case of the most realistic scenario ($NO_x GWP_{100} = 1.6$), this value does not exceed 1%. If the total direct GHGs emissions are considered (meaning the emission of $CO_2/0.65$), the NO_x contribution to the GHE does not exceed 2.8% and 0.5% for the most pessimistic ($GWP_{100} = 10$) and the most realistic ($GWP_{100} = 1.6$) scenarios, respectively. Although the presented analysis is simplified, it allows for an estimation of the impact of NO_x from surface sources on the GHE. Thus, even a pessimistic scenario assumes this impact is not large compared to CO_2 and other direct GHGs. Moreover, assuming the values of NO_x emissions from a combustion of 0.038 GtN/year, provided by W. Battye, V.P. Aneja, and W.H. Schlesinger [69], the impact of NO_x on the GHE is weaker. This is consistent with the conclusions of Lee et al. [70]. Furthermore, they noticed that NO_x emissions, O_3 as well as particulate matter, and SO_x , which are not the major concern in climate change and perspectives, are threatening the air quality and premature deaths (<75 years). Considering the emission of NO_x from coal-fired units (power plants and combined heat and power (CHP) plants only), the participation of NO_x in the GHE is lower. It is known that the maximal NO_x emission per capacity from such units is $1.8 \text{ kg NO}_x/\text{MW}$ when cold type start (i.e., start time >48 h since plant shutdown) is considered [71]. The capacity of coal-fired units in 2019 was estimated at 2087 GW/year [72]. Thus, the total NO_x emissions from such sources is 0.00376 GtNO_x/year. The estimated installed capacity of coal-fired units was compared with the estimation presented by Tong and co-workers [73] According to their estimation, a combined installed capacity of biomass- and fossil-fuelburning power plants operating worldwide in 2010 was 3570 GW. Nevertheless, the global NO_x emissions (in 2010) from these sources was 0.0252 GtNO_x/year. However, comparing these values with the data presented in Table 3, it is clear that the maximal impact of NO_x emitted from solid fuel-fired sources is less than 1% compared with direct GHGs. Finally, Miyazaki and co-workers [74] reported that anthropogenic NO_x emissions dropped by at least 15% globally and 18 to 25% regionally in April and May 2020 due to the pandemic influence. Similar observations were presented by Doumbia and co-workers [75]. According to their estimations, NO_x emissions exhibited large decreases (13–42%) during the strictest shutdown period (i.e., in April 2020).

	CO ₂ Emission Data from [12,76]	NO _x Emission	Data from	Calculated as GtCO ₂ /Year	Calculated as GtNO _x /Year	GWP100 = 10	Contribution of NO _x in the GHE Compared to CO ₂ Emissions from Fossil Fuels Usage and Industrial Processes, %	Contribution of NO _x in the GHE Compared to the Emission of all GHGs, %	
Year	GtC/Year	GtN/Year		GtCO ₂ /Year	GtNO _x /Year	NO _x -eq.CO ₂ , GtCO ₂ /Year	% (Calculated from Equation (9))	%(Total), (Calculated from Equation (10))	
2000	6.733	0.0256	[72]	24.7	0.084	0.8	3.3	2.2	
2005	8.042	0.0454	[77]	29.5	0.149	1.5	4.8	3.2	
2006	8.336	0.0191	[78]	30.6	0.063	0.6	2.0	1.3	
2009	8.697	0.0209	[78]	31.9	0.069	0.7	2.1	1.4	
2014	9.855	0.0475	[79]	36.1	0.156	1.6	4.1	2.7	

Table 3. Estimation of the participation of NO_x emitted from surface sources in the GHE compared to CO₂ and other direct GHGs. Pessimistic scenario (GWP₁₀₀ = 10).

[72] This data includes the roles of fossil fuel combustion, biomass burning, and soil emissions, [12,76] This data includes the combustion of gaseous, liquid, and solid fuels, cement production, and gas flaring.

6. NO_x in Waste Incineration and Co-Incineration Plants

Thermal processing of waste, especially combustion, can generate NO_x emissions. The combustion of MSW and RDF in incineration and co-incineration plants generates NO_x inside a furnace. The underlying role of incineration and co-incineration plants in the issue of NO_x emissions can be explained by the emerging concerns that the high nitrogen content (usually) in municipal waste can influence the enhanced NO_x emissions. In fact, N-fuel directly impacts NO_x emissions. Nevertheless, nowadays, these plants are equipped with an advanced flue gas cleaning system.

The consideration of NO_x emissions from the WtE plant is preliminarily considered as the issue of nitrogen content in burned fuels. It is known that the nitrogen content in solid fuel directly impacts NO_x emissions. The low N content in biomass (especially for wood and woody biomass) is a big advantage due to decreased NO_x and ammonia (HN₃) emissions [80]. The nitrogen in woody biomass (mean value, dry-ash-free, daf state) is 0.4 wt%, whereas the nitrogen content in waste is usually higher and can reach a value of more than 2.3 wt% [81]. Considering the particular components of MSW, a higher nitrogen content was observed in plastics (polyurethane N = 6 wt%, db), biomass residues (garden trimmings N = 3.4 wt% db), and food wastes (N = 2.6 wt% db) [82]. The nitrogen content varies in the waste sources in terms of regions, countries, and season. For example, Sajid and colleagues [83] reported that nitrogen content in waste from China in the period of 2015–2021 varied between 0.37 and 2.11 wt% depending on the region.

The NO_x in MSW incinerators is mainly produced by fuel NO_x and thermal NO_x, accounting for about 80% and 20%, respectively [84]. Behind the fuel properties, the formation of NO_x depends on the different processes and technological parameters, mainly the furnace type, the temperature in the combustion zone, air distribution, oxygen excess, turbulence, and residence time of gaseous compounds in the combustion and post-combustion zone [82]. It is accepted that the design of the furnaces can achieve gas temperatures that fit the conditions of selective non-catalytic reduction by ammonia or urea to remove about 50% of the NO_x formed initially [85]. The nitrogen concentration in stack emissions of MSW incinerations was observed in the range of $90-150 \text{ mg/m}^3$ and $65-145 \text{ mg/m}^3$ $(11\% O_2, STP)$ for FBC and grate furnaces, respectively [82]. Nevertheless, the concentration of NO_x formed in the combustor, measured before the flue gas cleaning system can be much higher (i.e., up to 950 mg/m³ (11% O_2 STP)). The highest in-chamber NO_x concentration was observed during coal and waste blends (i.e., $470-950 \text{ mg/m}^3$ for meat and bone meal + coal and $220-550 \text{ mg/m}^3$ for paper and plastic waste + coal) [82]. There are various ways to reduce NO_x emissions from incineration plants. The most important techniques are divided in two ways, namely primary and secondary measures [37]. The primary measures include every technique realized inside the combustion chamber such

as air and/or fuel staging and/or special additives such as iron-containing additives. The secondary measures included every method realized with additional and independent apparatus outside the combustion chamber. Within these secondary measures, the following methods are included: selective catalytic reduction, SCR, selective non-catalytic reduction SNCR, non-thermal plasma, O₃ application, adsorption, and absorption processes, and photocatalytic processes [37,86,87]. Note that SNCR can be included in primary or secondary measures depending on where the process is realized (i.e., where a NH₃-containing additive is injected). The efficiency of NO_x removal depends on the applied method. For example, by applying air staging, NO_x emissions can typically be reduced by 30–60%, whereas during the application of SCR and SNCR techniques, efficiency at a level of 50–85% can be achieved [82]. Yang and colleagues [84] reported that during the optimal conditions of coupling technologies (i.e., flue gas recirculation and SNCR), the total NO_x removal efficiency reached over 76% for the grate furnace incinerator.

The regulations governing flue gas emissions were becoming more stringent and varied. Depending on the country, the emission limits for NO_x are in the range of 131.7–522.6 mg/m³ (11% O₂, STP) [88]. The regulations of the emissions can help to estimate the maximal possible emission of NO_x to the atmosphere from incineration and WtE plants. It is assumed that the emission of NO_x from particular plants can reach a level up to the regulation limit. In fact, the emission of gaseous pollutants and particulates from these plants is usually lower than the limits. Moreover, it should be explained that despite the EU regulations and standards (Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions), other documents introduce additional requirements for the emission. Namely, best available techniques are more strict (i.e., 120 mg/m³ 11% O₂ STP) compared to the EU standards (i.e., 200 mg/m³ 11% O₂ STP).

The analysis presented below includes the different scenarios in terms of waste ratio during co-combustion as well as the capacity of incineration or co-incineration plants. EU Directives as well as BAT regulations were taken into account. It was assumed that both the EU Directives and BAT regulations should be fulfilled, thus in every case, the most restrictive (EU or BAT) value was used in the analysis.

The results of the calculations of standards are presented in Tables 4 and 5. All values are presented as mg referred to as $11\% O_2$ (STP). It should be mentioned that the presented values are the required concentrations that cannot be exceeded (as daily averaged values). These requirements should be fulfilled (executed) by the combustion/incineration/coincineration plant. In other words, the acts of law define the standard values and the values that cannot be exceeded. For example, in the case of coal combustion and installations in the range of 1 to 5 MW, the standard value is 267 mg/m^3 (11% O₂ STP), but the required value (it cannot be exceeded) for continuous measurement is 400 mg/m³ (11% O_2 STP) as the 150% of standard value. The most restrictive standards are observed for the co-incineration of biomass and RDF for large plants. In the case of a 305 MW plant and 10% co-firing, the required value is 75 mg/m^3 . Table 5 represents the calculations of the value for the co-firing of biomass and RDF in the share range of 0–100% (by energy). These results are also presented (required values only) in Figure 4. For installations with a fuel capacity of 1.5 MW (standard range $1 \div 5$ MW), the NO_X standard decreases with the increase in waste share in the fuel mixture. Thus, the addition of waste to the mixture reduces the permissible emission of NO_X to the environment. The opposite tendency was observed for the installations of a capacity higher than 50 MW. Namely, the increase in waste share caused the increase in NO_x standards. Thus, in the case of larger installations, the addition of waste caused less restrictive limits of NO_x emissions. In the case of medium-capacity installations (i.e., 15 MW), the addition of waste to the fuel mixture does not significantly change the emission limit. Consequently, the decrease in NO_x emissions (due to legislation impact) will be suspected when co-incineration is realized in smaller plants. In other words, retrofitting the existing plant into a co-incineration plant will generate the necessity to apply a more advanced cleaning system of exhaust gas in terms of NO_x emissions. It should be mentioned that the emission limit does not represent the real value of NO_x emissions. Usually, the real NO_x emissions are much less than the emission limits due to the existence of a high-efficient flue gas cleaning system.

Table 4. The results of the emission standards estimation for NO_x (mg/m³, 11% O₂, STP), the cases of individual combustion, and co-firing of 10% (by energy) share.

	Emission Standard (Executed)								
Case	1.5 MW	15 MW	55 MW	105 MW	305 MW				
Coal combustion (100%)	400 (req.) (base 267)	300 (req.) (base 200)	220 (req.) (base 200)	146 (req.) (base 133)	110 (req.) (base 100)				
Biomass combustion (100%)	294 (req.) (base 267)	220 (req.) (base 200)	184 (req.) (base 167)	146 (req.) (base 133)	110 (req.) (base 100)				
RDF combustion (100%)	200	200	200	200	200				
Biomass/RDF (10%) co-firing	264	201	169	138	107				
Coal/RDF (10%) co-firing	265	202	202	138	106				

Req—required value that cannot be exceeded, base—base value according to the emission standard.

Table 5. The results of the emission standards estimation for NO_x (mg/m³, 11% O₂, STP), the cases of individual combustion and co-firing, RDF share 0%–100% (by energy).

				RI	OF Share (% by Ene	rgy)				
Capacity	0%	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
1.5 MW	294 (req.) 267 (base)	264	260	256	251	245	239	231	222	212	200
15 MW	220 (req.) 200 (base)	200.8	201.5	202.0	202.5	202.6	202.7	202.5	202.0	201.2	200
55 MW	184 (req.) 167 (base)	169	172	175	178	181	185	188	192	196	200
105 MW	146 (req.) 133 (base)	138	143	148	154	160	167	174	182	190	200
305 MW	110 (req.) 100 (base)	107	114	121	130	139	149	160	172	185	200

Req—required value that cannot be exceeded, base—base value according to the emission standard.



Figure 4. The impact of the installation capacity and share of RDF on the NO_x emission limits (required values based on the EU Directives and BAT regulations).

7. Conclusions

The negative impact of emitted NO_x on environmental issues (such as human and animal health and disturbance to plants and vegetation) is known and accepted by the scientific community. However, the discussion of the impact of NO_x on global warming continues. Furthermore, some irrationality is still observed in the scientific literature. It should be stated that NO_x belong to the group of indirect GHGs and they influence climate change. Nevertheless, the impact can be warming and cooling, depending on the particular conditions. This double-effect of NO_x on the global climate (positive and negative radiative forcing response) is described in the literature. However, this knowledge should be expressed in the scientific community. It should be noted that the impact of NO_x on global warming is not unequivocal. It depends on different parameters such as the location of the NO_x source, time, concentration of other compounds in the atmosphere (such as CO and CH_4), and prevailing atmospheric conditions. Thus, the same level of NO_x emissions might lead to different regional climate impacts. An accurate estimation of the impact of NO_x on global warming is very difficult. However, the estimated maximal impact of surface sources is less than 3.2% compared with direct GHGs. Finally, it is commonly accepted that the emissions of NO_x from aircraft have much more influence on global warming than the emissions of NO_x from surface sources. The retrofitting of a small firing plant (i.e., up to 50 MW_{th} in fuel) into a co-incineration plant (after numerous requirements) will lead to lower NO_x emissions due to legislative impacts (i.e., more restrictive emission limits compared to the combustion of primary solid fuels e.g., biomass). The co-incineration in smaller plants (capacity range of $1 \div 5$ MW) gives more benefits to the environment due to a decrease in the NO_x emission standards when the share of waste increases. In such installations, the NO_x emission standard in the case of coal combustion is 267 mg/m^3 (11%) O_2 STP), whereas the emission standards for RDF share (% by energy) of 50% and 90% are 245 mg/m^3 and 212 mg/m^3 , respectively.

Our research has a beneficial value to the scientific community because our paper collected and clarified opinions regarding the impact of NO_x on the GHE. Thus, from a practical point of view, this paper can be useful for scientists as well as for policymakers.

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Nomenclature

AGWP	Absolute global warming potential
С	Total emission limit values for co-firing fuels with waste
Cwaste	Emission limit values for waste incineration plants and co-firing
FBC	Fluidized-bed combustor
GHE	Greenhouse effect anthropogenic) sources
GHG	Greenhouse gas
GWP	Global warming potential
hai	Energy of photon (photochemical reactions) as the multiplication of Planck constant,
nν	h and photon's frequency, ν
MSW	Municipal solid waste
pptv	Parts-per-trillion (volumetric)
RDF	Refuse-derived fuel
SCR	Selective catalytic reduction
SNCR	Selective non-catalytic reduction
STP	Standard temperature and pressure
V _{proc}	Waste gas volume resulting from the plant process including the combustion of the
	authorized fuels normally used in the plant (waste excluded)
V _{waste}	Waste gas volume resulting from the incineration of waste only determined from the
	waste with the lowest calorific value specified in the permit
WtE	Waste-to-energy

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