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Analysis of the German Industry to Determine the Resource Potential of CO_2 Emissions for PtX Applications in 2017 and 2050

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Abstract: The production and use of crude oil-based materials, e.g., fossil fuels and bulk chemicals of organic origin, results in an increasing level of CO_2 emissions within the atmosphere. One way to reduce such CO_2 emissions is to substitute them with synthetic fuels and bulk chemicals. For the production of such CO_2 neutral materials, CO_2 from various sources can serve as a carbon source. Against this background, this paper analyses and quantifies CO_2 emissions released from German industry branches today (2017) and potentially in the future (2050) after a complete defossilization has been achieved. Thus, for the classification of CO_2 emissions from the respective industries in 2050, alternative techniques and manufacturing processes are analyzed that might lead to a reduction in energy- and process-related CO_2 emissions. Additionally, the individual production sites of the analyzed industries are determined at postcode level and a CO_2 potential on NUTS3 level has been developed. Based on this, two scenarios for future CO_2 emissions are developed. This shows that, in 2017, the analyzed German industrial sectors emitted almost 143 Mt CO_2. By 2050, the overall emissions can be decreased by about 77 Mt to 117 Mt CO_2 depending on the implementation level of alternative technologies.

Keywords: Power-to-X; carbon capture and utilization; resource efficiency; CO_2 emissions; defossilization

1. Introduction

The provision and use of synthetic fuels as well as synthetic bulk chemicals are increasingly attracting interest as a result of the debate about environmental concerns caused by the use of fossil, crude oil-based raw materials [1,2]. One way of providing synthetic and basically greenhouse gas (GHG) neutral fuels and bulk chemicals is the Power-to-Liquid (PtL) process. Based on such a thermo-chemical process, various materials such as diesel, kerosene, wax, or gasoline can be provided, e.g., by using Fischer–Tropsch synthesis. For such a synthesis, electrical energy, water, as well as a climate-neutral carbon source (e.g., CO_2 from ambient air or biogenic sources) are required as feedstock. This applies as well for various other Power-to-X (PtX) processes, e.g., the production of synthetic natural gas (SNG), synthetic methanol, etc.

Within such processes, water is decomposed into its components—hydrogen and oxygen—based on electrical energy in water electrolysis. Next, the provided hydrogen combined with a carbon-containing gas is transformed further into a synthesis gas to be used—with additional hydrogen—within further synthesis; the methanol- or the Fischer–Tropsch synthesis are two prominent examples. Based on Fischer–Tropsch synthesis, a so-called syncrude is provided to be further processed with conventional refinery processes into standardized transportation fuels and/or bulk chemicals.

CO_2, as the most important carbon source for such processes, can be obtained from numerous sources. These include, e.g., CO_2 from ambient air, from industry, and the energy sector as well as from the processing of biogenic/organic material. More fundamentally, CO_2 emissions from human activities can be categorized according to energy provision or non-energy-related material conversion. Besides this, the CO_2 emissions can be sub-categorized further according to their origin in biogenic or fossil provenance. Thus, only CO_2 emissions originating from the use of fossil fuel energy and the processing of natural material of fossil origin (e.g., limestone) increase the overall CO_2 inventory within the atmosphere. This fact is independent of the respective CO_2 emissions that are directly emitted into the atmosphere or used within a usage cascade (Figure 1). For the latter option, the absolute proportion of CO_2 within the atmosphere increases with a certain delay.

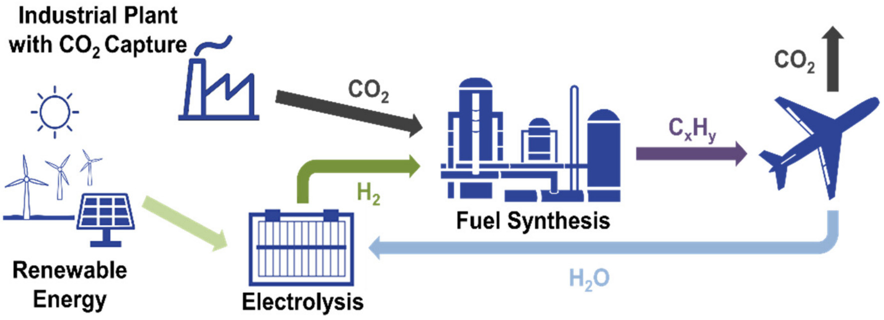

Figure 1. Use of fossil CO_2.

The use of CO_2 from processing sustainably provided biomass is essentially GHG neutral and results in an almost closed carbon circle (Figure 2). The utilization of CO_2 from direct air capture (DAC) reveals comparable behavior if renewable energies are used for the process.

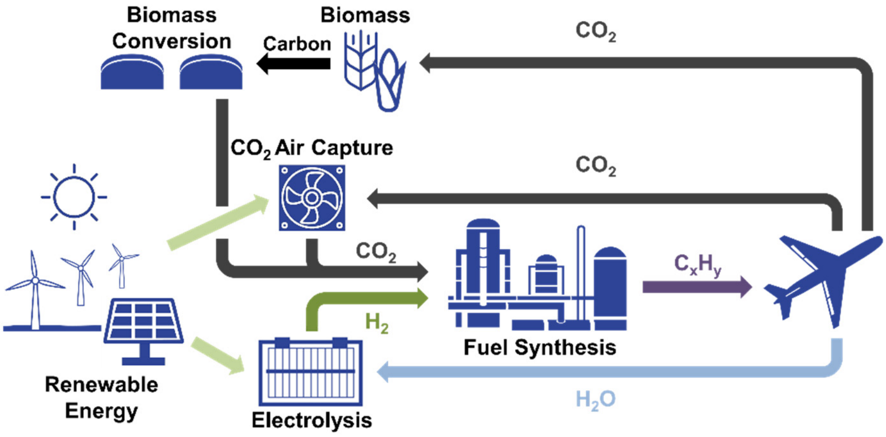

Figure 2. Use of biogenic CO_2 and CO_2 from DAC.

For a comprehensive analysis of the prospects and limitations of PtX-processes within a defossilized energy system in the years to come, it is necessary to understand to what extent CO_2 from which resources is available by taking technical constraints into consideration. Various studies have been carried out on the possible use of CO_2 for different applications [3–5]. However, these studies do not provide a complete analysis, because, e.g., not all industrial sectors are considered or no categorization according to process- and energy-related CO_2 emissions was applied. In this context, the goal of this paper is to identify and quantify various CO_2 sources available as a feedstock for the provision of PtX products today and in a preferably defossilized economy in 2050. This will be realized exemplarily for the German industrial sector.

2. Approach and Delimitation

One overarching goal of this work is to determine the amount of CO_2 emitted locally from industrial point sources within the year 2017 and in the future within a fully defossilized energy system (perspective 2050). The aim is to assess the amount of CO_2 available as a point source to be used as a raw material for subsequent synthesis processes. The focus is on the calculation of the total CO_2 emissions per site. This includes both fossil, i.e., climate-relevant, CO_2 and CO_2 resulting from the conversion of carbon from biogenic sources (i.e., sustainable sources).

Within the scope of this work, industrial point sources are examined which, according to the European classification system NACE, mainly belong to Section C—Manufacturing [6]. Installations exclusively classified in other sections, e.g., Section D—Electricity supply [...], or Section E—Waste management [...], are not included here, as the focus is on classic manufacturing industries. Furthermore, CO_2 from, e.g., the electricity supply by coal-fired power plants will not remain in a future defossilized energy system. CO_2 emitting installations in the Sections D and E are, e.g., power plants, waste incineration plants, or sewage treatment plants. Exceptional cases are power plants directly linked to the respective industrial plant; i.e., CO_2 emissions from explicitly designated industrial power plants or heating plants are taken into account if they are part of an integrated industrial site. In contrast, CO_2 caused by electricity obtained from the national grid is not taken into consideration below because it is not emitted at the specific spot.

The manufacturing industry covers a wide range of different sectors. In order to identify the relevant point sources and their location, the CO_2 intensive sectors of the German industry are assessed first. For the estimation of the respective amount of CO_2 emitted per site today and in the future (i.e., within a fully defossilized world), it is necessary to analyze the origin of the various CO_2 sources within the respective production processes to evaluate possible CO_2 savings by application of new or emerging technologies and/or other measures. The general approach applied here for the determination of the resource potential is given in Figure 3.

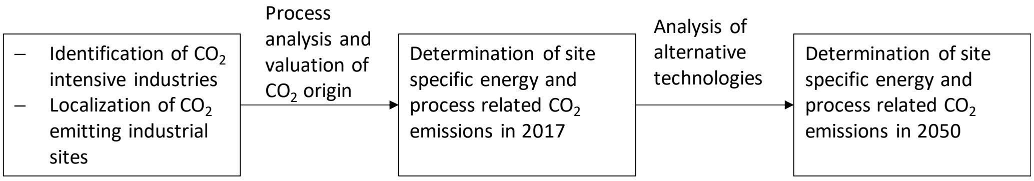

Figure 3. General approach.

CO_2 emitted by industry can be divided into process-related and energy-related emissions. The former are emerged during the production process by converting input and/or auxiliary materials essential for the properties of the manufactured products; i.e., these CO_2 emissions do not result directly from the use of energy (e.g., solid fuels such as coal) as it is the case for the latter category. This classification is made because it can be assumed that, based on the research conducted to date, substitution possibilities for climatic sound energy-related CO_2 emissions can be more easily and more effectively implemented (e.g., "renewable" fuels, "renewable" electricity) than alternative process technologies allowing to reduce process-related CO_2 emissions substantially by guaranteeing the same product characteristics. To determine these potentials, it is first analyzed which industrial processes emit process-related CO_2. Subsequently, it is assessed in which process and respective conversion step these emissions result.

In order to assess the development of CO_2 emissions in the respective sectors up to the year 2050 (i.e., a fully defossilized world), an extensive analysis of alternative technologies has been carried out, which may contribute to a reduction of both energy-related and especially process-related CO_2 emissions. For this purpose, various studies have been assessed, providing possible technologies to substitute or avoid CO_2 emissions in the medium to long term within the respective industrial production processes. Based on the determination of site-specific energy-related and process-related

CO_2 emissions in 2017 and the implementation of such alternative technologies, two scenarios are developed for each sector assessing the possible changes in CO_2 emissions related to the target year 2050.

2.1. Data Basis

In order to identify CO_2 intensive industries, the 2017 VET—Report of the German Emissions Trading Authority (DEHSt) was analyzed [7]. This report gives an overview of the total greenhouse gas (GHG) emissions for each sector. These GHG emissions serve as a first classification of relevant industries indicating, e.g., that industries with the greatest proportion of the overall emissions in 2017 have been refineries and the chemical industry (43.2 Mt CO_2 eq.), the iron and steel production (37.8 Mt CO_2 eq.), and the mineral industry (36.3 Mt CO_2 eq.). Additionally, the paper and pulp industry emitted about 5.5 Mt CO_2 eq. and the non-ferrous industry 2.6 Mt CO_2 eq. These industries are subdivided into the sectors presented in Table 1.

Table 1. Process-related CO_2 emitting industrial sectors.

Industry	Sector	Process-Related CO_2 emissions
Mineral Industry	Cement	Clinker burning
	Limestone	Application and burning of limestone
	Glass	Smelting of carbonate-containing raw materials
	Ceramic	Burning of raw materials containing carbonates and fossil components
	Soda application	Application of Na_2CO_3 in various processes (besides glass [1])
Metallurgy	Iron and Steel	Application of reduction agent, electrode burn-up, application of slag formers
	Primary aluminum	Anode burn off, anode manufacturing
	Secondary zinc	Application of reduction agent
	Lead	Application of reduction agent
	Copper	-
	Silicon	Application of reduction agent
Chemical industry	Ammonia	Steam reforming of fossil hydrocarbons
	Carbon black	Furnace Black Process
	Petrochemistry/refinery	Flare losses
	Soda production	Application of calcium carbonates/Solvay-process
	Bulk organic chemicals	-
Pulp and Paper	Recycling paper	-
	Fresh paper	-
	Cardboard	-

[1] CO_2 Emissions from soda application in glass manufacture are allocated to the glass sector.

Data basis overall CO_2 emissions. The location and amount of CO_2 emissions of the various production sites within the respective sectors are mainly obtained from the following two databases.

- The thru register (formerly Pollutant Release and Transfer Register) [8] is appropriate for identifying emitters with an annual CO_2 freight of more than 100 kt/year. This register contains pollutant and waste data from 5398 facilities in Germany [8]. It gives information about, inter alia, the company name, postal code, coordinates of the emitting site, type of pollutant or waste as well as the released amount. However, only the emissions of the respective plants exceeding a certain pollutant-specific limit value are listed. This limit is 100 kt/year for CO_2 (Annex II, E-PRTR Regulation [9]. For an installation to be included in the register, it is sufficient that a limit value of one pollutant or waste is exceeded. However, only the value of the exceeded pollutant is indicated. Values not exceeding this limit are not listed within that entry. A further criterion for the reporting obligation is defined by the size of the plant. This means that, e.g., plants for the production of cement clinker are only required to report if their production capacity exceeds 500 t/d (Annex I, E-PRTR Regulation [10]. In general, the emissions are listed for a plant site as a whole and the production processes within the site are indicated, without an explicit listing of the individual units.
- The register of installations of the DEHSt [11] can be used as the data source for determining the plants below the limit of 100 kt/year. Here, the lower limit of the site assessment is defined by annual CO_2 emissions of at least 40 kt/year. The reason is that the register of installations also lists

> many emitters with relatively small amounts of CO_2 assumed here to be inappropriate as a carbon source for medium to large scale PtX synthesis plants. This register lists installations obligated to emission trading [12]. It provides information about, inter alia, the name of the installation, the postcode, the allocated emissions of previous trading periods, etc., and the annually reported GHG emissions. In this register different units of an integrated plant may be listed individually.

For the site-specific analysis of the plants, the data from the register of installations is agglomerated and compared with the data from thru. This comparison shows that the majority of the CO_2 emissions recorded in the register of installations corresponds to the overall CO_2 emissions in thru. In the iron and steel, chemical, and refinery industries, this analysis revealed some discrepancies between thru data and the register of installations data. This is, for example, true for the following exemplary case: A specific electro steel plant emitted about 141 kt CO_2 in 2017 according to the register of installations. The register lists four different units within the integrated steel plant (i.e., the melting shop and steel casting in molds, the rolling mill, and two different heat-treating furnaces). The entry of this plant in thru includes the main activity of *iron and steel production* as well as the secondary activities of *incineration plants* > 50 MW and *hot rolling of ferrous metals* > 20 t/h. These activities correspond approximately to the units described above, which means that it is to be expected that the limit value of 100 kt/year CO_2, and thus the reporting obligation for thru, was exceeded. However, there are no entries for CO_2 or other GHG emissions.

To create a sound data basis, the values from both databases—if available—were therefore compared. In the case that the CO_2 emissions of a plant are below the limit value, but other GHG emissions (e.g., N_2O) are listed, these were deducted from the entries in the register of installations using the corresponding global warming potential (GWP) factor according to the 5th IPCC Assessment Report [13].

Nevertheless, in most cases, the values of the two databases correspond. However, the case exemplarily discussed above show that an exact determination of the CO_2 emissions at a certain spot might be difficult. If a plant is only listed in the register of installations and no differentiated GHG entries are made within the thru register, it is assumed that the respective amount of CO_2 eq. is approximately similar to the amount of CO_2.

Data basis process-related CO_2 emissions. The National Inventory Report on the German Greenhouse Gas Inventory [14] is used as a data basis for the identification of relevant process-related CO_2 emissions within the industrial sectors assessed here. In this inventory, CO_2 emissions are classified into the categories energy, industrial processes and agriculture. Within the category addressing industrial processes, the mineral, chemical, and metal producing sectors show process-related CO_2 emissions. An overview of these industries is given in Table 1. The different sectors of the mineral industry emit process-related CO_2 mainly from processing carbonate-containing raw minerals. In the metallurgy and chemical industries, process-related CO_2 is also emitted in the majority of the processes, apart from the copper production and to some extent the production of bulk chemicals. The pulp and paper industry only emits energy-related CO_2.

2.2. Site-Specific CO_2 Emissions

Due to the inhomogeneous data availability, specific approaches have been developed for each sector to quantify the CO_2 emissions in a site-specific manner. These approaches are outlined in the methodology of the respective industries. This is true for the iron and steel, cement, lime/quicklime, glass and ceramics, as well as aluminum industries, which were subjected to a more detailed analysis. An overview of the respective determination factors for the site-specific process-related CO_2 emissions can be obtained from Table 2. The total site-specific CO_2 emission is obtained from thru and the register of installations as described above.

Table 2. Approach for the determination of process-related share in total site-specific CO_2 emissions.

Sector	Determination of Process-Related CO_2 Emission
Cement	Proportion of 61% process-related and 39% energy-related
Limestone/quicklime	Proportion of 65% process-related and 35% energy-related
Glass	Proportions specific to each type of glass (glass specific ratios see Section 3.4.2)
Ceramic	Proportions specific to each type of ceramic (ceramic specific ratios see Section 3.4.2)
Iron and Steel	Specific EF for Oxygen steel route: 1.75 t CO_2/t steel and Electro steel route: 0.03 t CO_2/t steel
Primary aluminum	Application of specific EF of 1.37 t CO_2/t aluminum to production figures based on own calculations of each site
Ammonia	Proportion of 72% process-related and 28% energy-related

The sectors zinc, lead, carbon black, petrochemistry/refinery, and soda production also show process-related emissions (Table 1). However, it was not possible to determine the site-specific energy and process-related CO_2 emissions due to no or insufficient data. The site-specific results of these sectors show the total CO_2 emissions only.

To determine the process- and energy-related CO_2 emissions of the cement, lime/quicklime, and glass and ceramic sectors, the proportions of process-related and energy-related emissions (Table 2) were applied to the total emissions of the individual sites. The determination of the proportions is explained in the methodology of the respective sector.

The process-related CO_2 emissions of the iron and steel industry were determined from steel production figures in 2016 using emission factors based on own calculations and assumptions. The site-specific production figures obtained from the German steel association [15] are only available until 2016. The calculation of the emissions factors is presented in detail in the methodology of the iron and steel industry section.

The process-related emission factor for primary aluminum given in Table 2 was applied to site-specific production figures, which are based on own calculations. The approach for the determination of these production figures is given in the methodology of the aluminum section.

Ammonia production also emits process-related CO_2. Based on the specific process and energy-related emission factors, the proportions shown in Table 2 were determined and applied to the absolute CO_2 emissions of the respective sites.

2.3. Scenarios

The two scenarios are based on the assumption that the production of goods remains constant until 2050. The basis for the calculation of the results in 2050 is therefore the real emitted amounts of CO_2 per site in 2017 changing according to the assumptions and conditions assumed within the respective scenarios. The analysis for these various CO_2 sources and their potential development focuses on a spatially resolved quantification. Depending on the distribution of energy and process-related emissions in each sector, the two scenarios outlined below are developed.

Scenario RFS (renewable fuel supply): the calculation of future CO_2 emissions in the scenario RFS is based on the assumption that fossil fuel energy is replaced by methane produced from renewable sources of energy. A differentiation of whether the fuel is, e.g., biomethane or synthetically produced methane has not been realized. In order to calculate the effects of the substitution on the site-specific CO_2 emissions, the CO_2 emissions from the use of this "renewable" methane are calculated using the specific emission factor of methane and the respective amount of energy provided so far by the substituted fossil fuels. The proportional emission reduction is then applied to the CO_2 emissions of each site to determine the remaining emissions for 2050. The specific emission factors used for the calculation are given in Table 3 [14]. The share of fossil fuels in the different sectors is given in the respective sections.

Table 3. Specific CO_2 emissions factors of fossil fuels.

Fuel	Specific Emission Factor (t CO_2/TJ)	Reduction Compared to Natural Gas (%)
Natural gas	55.9	-
Hard coal	93.9	40.5
Lignite	108.2	48.3
Lignite briquettes	99.3	43.7
Petroleum coke	94.8	41.0
Heavy fuel oil	79.6	29.8
Light fuel oil	74.0	24.5
Blast furnace and converter gas	252.9	77.9
Municipal waste	91.5	38.9
Scrap tires	88.4	36.8
Used plastics	80.9	30.9

Scenario ATRES (alternative technologies and renewable energy supply): this scenario assumes the implementation of alternative production technologies and the substitution of fossil fuels by renewable fuels and/or electricity. Thus, this scenario describes a more drastic change of the considered processes. The studies, Climate-neutral industry [16], Energy consumption and CO_2 emissions of industrial process technologies—saving potentials, barriers and instruments [17] and Greenhouse gas neutral Germany 2050 [18], are used as a basis for the technology analysis. For the estimation of the remaining CO_2 emissions, the results of these investigations are adapted into the scenario ATRES. If electricity is used instead of fuels to provide energy, it is assumed that it is produced GHG neutral, i.e., from renewable energies. A description of the adapted technologies is given in the respective sections of the different sectors.

3. Mineral Industry

Below, the industry sector producing cement, limestone/quicklime, glass, and ceramic is analyzed in detail.

3.1. Cement

Cement is a heterogeneous composition of different pure materials. The specific composition of each type of cement depends on the required properties for different areas of application (e.g., durability or sulfate resistance). One of the main components in almost every type of cement is cement clinker (between 5 and 100%, DIN EN 197-1). In addition to clinker, cement may also consist of granulated slag, pozzolana, fly ash, silica dust, plaster, and burnt oil shale.

3.1.1. Process Description

Cement production is based on three steps. First, various raw materials (e.g., clay and limestone) are extracted from the ground and crushed. Then, further components (if necessary with, e.g., quartz sand and iron ore) are added, the mixture is homogenized, dried, grinded, and burned in kilns. The thermally treated material is again homogenized, grinded, and intermingled with additives to meet the required standards.

The process step of clinker production emits the largest quantities of CO_2 throughout the overall process chain of cement production. These CO_2 emissions can be divided into energy-related and process-related emissions. The latter are released during the burning of the input material at high temperatures (gas temperature up to 2000 °C) within a rotary or shaft kiln. During the chemical transformation resulting from this thermal treatment, CO_2 is released from the carbonate, known as “deacidification” (Equation (1)).

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2. \tag{1}$$

This reaction takes place in presence of SiO_2, Al_2O_3, and Fe_2O_3 at temperatures above 550 °C and strongly increases above 900 °C.

The provision of heat for the kiln contributes to the majority of energy-related CO_2 emissions in the cement industry. The average specific thermal energy consumption was 2824 MJ/t cement in 2017. This amounts to a total need of 96.9 PJ in Germany. Approximately one third of this energy is provided by burning fossil fuels and two thirds by burning refuse-derived fuels, such as scrap tires or waste.

Additionally, electricity is needed as auxiliary energy for the electric driven devices (e.g., grinders, exhaust gas treatment) resulting in 110 kWh/t cement or a total of 3.77 TWh in 2017 [19].

3.1.2. Methodology

The CO_2 emissions from the production of cement originate from burning fuel for heat provision, electricity demand for auxiliary energy supply and process-related emissions from processing the material itself. The share of the process- and energy-related CO_2 emissions from the kilns and furnaces varies depending on the mixture of the input material (fuels, clay, limestone, etc.). Nevertheless, the variations are relatively small. Therefore, it is assumed that the share of the process- and energy-related CO_2 is similar for each cement production site. To determine the process-related share of CO_2 related to the overall CO_2 emissions for the emission data received from thru, the total emissions for the year 2017 of approx. 21.9 Mt CO_2 are recalculated [20] to exclude the possibility that larger quantities of CO_2 are integrated into the emission data of thru that are not process- or energy-related. The overall process emissions in 2017 sum up to 13.4 Mt CO_2 according to [21]. The difference of 8.4 Mt CO_2 is assumed to be emitted by fuel burning (i.e., energy-related). The quantities of input fuel for heat supply, broken down by fuel, are published annually [19]. On the basis of these quantities, the total amount of energy-related emissions is calculated using the specific CO_2 emissions per TJ of fuel [14,21].

The calculated data for the CO_2 emissions from burning fuel deviate by approximately 126 kt (2017) being less than 0.6% compared to the overall emissions of 21.9 Mt (2017). Another uncertainty lies in the specific emission factor of the refuse-derived fuels used for the energy-related emission calculations, as they are based on average values. The calculated share of process-related emission is about 61% being similar to the given share of 60% by [19]. Thus, the CO_2 emissions from each cement producing facility is multiplied with the raw material related share of 61% to obtain the process-related CO_2 amount.

3.1.3. Scenarios

Scenario RFS: for the scenario RFS it is assumed that the heat provision is still based on fuels. The share of refuse-derived fuels remains constant while fossil fuels are substituted by methane from renewable sources. The amount of energy provided by each fossil fuel is obtained from [19]. Lignite (20.5 PJ/year) and hard coal (8.2 PJ/year) have the greatest share within the overall heat provision based on fossil fuel energy. A complete list of substituted energy by fuel is given in Table 4. The resulting CO_2 emissions in 2050 for scenario RFS are calculated assuming that the sole use of "renewable" methane as fuel enables almost the complete avoidance of energy-based CO_2 emissions from fossil origin (fossil carbon in the refuse-derived fuels remains). This results in the fact that mainly process-related fossil and energy-based biogenic CO_2 remain on site.

Table 4. Thermal heat demand cement sector in 2017.

Total thermal heat demand	96,900 TJ
Thereof:	
Refuse-derived fuels	63,100 TJ
Hard coal	8200 TJ
Lignite	20,500 TJ
Petroleum coke	3500 TJ
Heavy fuel oil	500 TJ
Light fuel oil	700 TJ
Natural gas and other gases	500 TJ

Scenario ATRES: for the scenario ATRES, it is assumed that the overall heat provision is covered by electricity based on an approach called LEILAC process [16]. It contains an indirectly heated steel tank as the calciner. It is assumed that, in 2050, the electricity provided completely GHG-free will be obtained from the public grid. The present-day technology readiness level (TRL) is given as 4 to 5 and the earliest possible large-scale application is assumed for the years between 2030 and 2035 [16].

3.2. Limestone and Quicklime

Limestone consists of more than 90% $CaCO_3$ and a small percentage of $MgCO_3$, whereas dolomite is a mixture of about 55% $CaCO_3$ and 45% $MgCO_3$. The German lime industry, however, is dominated by limestone processing [22]. A special case within this section is the production of refined sugar, for which lime is also processed to quicklime, resulting in energy-related and process-related emissions. For this reason, emissions from the sugar industry's lime kilns are also considered.

3.2.1. Process Description

The processing of limestone starts with the extraction of raw material typically in open-pit mines located close to the lime plant. Besides certain chalk deposits in Northern Germany, the majority of limestone is quarried by the use of explosives. Apart from lime, dolomite is also mined in a few quarries and further processed at several locations. After blasting, the material is crushed, washed and screened. Then it is fed into kilns for calcination or processed (e.g., lime putty) without burning for other purposes, such as aggregates for the cement or steel industry.

Process-related CO_2 is emitted during the processing of limestone or dolomite during the calcination in kilns. This process takes place at temperatures between 900 and 1200 °C for limestone and between 500 and 750 °C for dolomite. At these temperatures, calcium and magnesium carbonates are thermally destroyed by emitting CO_2 originally bound within the mineral according to Equation (2) for calcium carbonate and to Equation (3) for magnesium carbonate.

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2. \tag{2}$$

$$CaCO_3{\cdot}MgCO_3 + \text{heat} \rightarrow CaO{\cdot}MgO + 2\,CO_2. \tag{3}$$

After the kiln, quicklime is stored and can be hydrated to form calcium and magnesium hydroxide, which is used, e.g., in mortar. There are also various applications for the direct use of quicklime, such as desulphurization of raw steel or as a fertilizer [23].

The production of refined sugar also depends on limestone and quicklime. It is used for the purification of the raw sugar juice after the extraction process. Therefore, the sugar industry operates its own lime kilns, most of which are located onsite of the sugar refineries [23].

3.2.2. Methodology

The emissions from the limestone industry result from fuel burning and the calcination process. The share of 35% energy and 65% process-related CO_2 emissions according to [24] is applied to the site-specific data. This share is also used for the determination of the CO_2 emissions from the sugar industry since the input feed of fuel and limestone is more or less the same. Most CO_2 recombines in the limed juice and forms $CaCO_3$ to be sold to agriculture for pH adjustment of farmland. The share of 35 to 65% of energy-related and process-related emissions is still applicable since the CO_2 used in the purification process ($CaCO_3$ is formed) is separated from the entire exhaust gas stream [23] and, therefore, assumed to be not included in the site-specific emission data.

3.3. Scenarios

CO_2 in this sector is emitted mainly from the processing of the raw materials dolomite and limestone. Furthermore, the product properties of the processed raw material are the reason for their use for a wide variety of applications. Additionally, no information on possible adequate substituents is available.

Scenario RFS: against this background, within scenario RFS, process-related emissions stay constant and energy-related emissions are caused solely by the use of "renewable" methane for heat supply. The reduction of energy-related emissions is calculated via the reduction factor obtained by substituting various fossil fuels (coal, mineral oil) with methane. The fuel mix of the lime/quicklime industry in 2012 is given by [25] and dominated by fossil solid fuels (51%) and by natural gas (34%) (Table 5). The former is assumed to consist of half lignite and half hard coal.

Table 5. Fuel mix of the limestone/quicklime sector in 2012.

Fuel	Share in Total Fuel Demand
Natural gas	34%
Fossil solid fuels	51%
Oil	5%
Waste	8%
Biomass	2%

Scenario ATRES: the scenario ATRES is based on an electrified heat supply comparable to the LEILAC-process described in Section 3.1.3.

3.4. Ceramics and Glass

There are numerous different types of glass and ceramics available on the market. Nevertheless, production processes are similar. Therefore, the analysis is presented in one section.

3.4.1. Process Description

Raw materials used for glass production are silica sand, limestone caustic soda, and several additives for purification, dyeing, or melting point reduction. The first process step is the batch preparation and mixture with recycled material, which is then fed into the melting process. Afterwards, the melt is formed, conditioned as well as cured and dried. The final steps are cutting, milling, and packaging. The majority of process-related and energy-related CO_2 emissions of the overall process occur during the melting process [17]. The sources of process-related emissions are the used carbonates $CaCO_3$, Na_2CO_3, $MgCO_3$, and $BaCO_3$. During the melting, CO_2 is driven out of these carbonates, similar to the clinker and quicklime production [14]. The process-related energy for the kilns is mainly provided by natural gas.

The process of ceramic production is similar to that of glass production. However, the basic production path for all ceramics is characterized by the extraction and preparation of silicates and oxidic raw materials, followed by shaping, drying, surface finishing and the subsequent burning process. If necessary, further finishing treatment follows as the last processing step. The drying and burning process consumes most of the overall energy demand. The process-related emissions also occur during the burning process and result from both the carbonate and fossil components of the raw material. Porosification agents, such as sawdust, also contribute partly to the overall emissions [14].

3.4.2. Methodology

A distribution of processes is used to identify the share of process-related emissions in the total emissions of each plant. The applied values of the glass industry are listed in Table 6 and those of the ceramic industry in Table 7 [17]. Thus for the site-specific determination, the percentages of process-related CO_2 per sector (Tables 6 and 7, right column) are multiplied by the absolute CO_2 emissions of the corresponding sites. Although the absolute values are given in CO_2 eq., this is negligible as only the share is applied. As described below, the production category of plants with CO_2 emissions of less than 40 kt/year has not been accurately recorded. This share is therefore undefined.

Table 6. Emission distribution glass industry 2007.

Category	**Direct Process-Related Emissions (Mt CO_2 eq.)**	**Indirect Emissions (Electricity) (Mt CO_2 eq.)**	**Direct Energy-Related Emissions (Mt CO_2 eq.)**	**Share of Process-Related CO_2 eq. in Direct Emissions (%)**
Container glass	0.19	1.12	1.51	11
Flat glass	0.31	1.04	1.12	22
Glass fiber	0.03	0.31	0.27	10
Other glass	0.06	0.4	0.3	17

Table 7. Emission distribution ceramic industry 2007.

Category	**Direct Process-Related Emissions (Mt CO_2 eq.)**	**Indirect Emissions (Electricity) (Mt CO_2 eq.)**	**Direct Energy-Related Emissions (Mt CO_2 eq.)**	**Share of Process-Related CO_2 eq. in Direct Emissions (%)**
Bricks	1.54	0.48	1.29	54
Refractory ceramic	0.55	0.19	0.36	60
Tiles, plates, others	0.38	0.19	0.40	49
Tableware	0.19	0.06	0.10	66
Sanitary ceramics	0.10	0.01	0.07	59
Technical ceramics and others	0.89	0.14	0.17	84

The share of process-related CO_2 in total emissions of undefined production facilities (no information on the type of glass or ceramics production provided) is calculated with the weighted mean of the different categories. The total output per category is obtained from [14]. The weighted mean of process-related CO_2 relative to the overall CO_2 assigned to the glass facilities is 15% and that of the ceramic industry is 55%.

The available list of glass producing plants sums up to a total of 74 records and that of the ceramic production facilities to 133 plus 7 plants manufacturing mineral wool. However, these lists lack data that is essential for a comprehensive analysis including the location and product category. Therefore, these parameters are partly obtained from [11] and completed by manual search.

3.4.3. Scenarios

Since the CO_2 emissions are directly linked to the used raw materials, a potential reduction might only be possible by substituting the whole production process and/or by using other basis materials without carbonates. For the latter no realistic substitutions are visible. Thus, only the reduction of energy-related emissions is analyzed so far [17,26,27]. This analysis shows that it is possible to obtain the required process heat by furnaces powered by electricity as it is already implemented for furnaces with smaller capacities (<100 t/d).

Scenario RFS: for scenario RFS, the heat supply is covered by "renewable" methane. This results in the same amount of CO_2 as the reference amount in 2017 because natural gas is already the main fuel used in these industries (>97%) [17].

Scenario ATRES: scenario ATRES assumes a 100% substitution of fossil or rather natural gas fired furnaces with electric furnaces.

3.5. Summary

Below, the overall emissions of the mineral industry are summed up for today (2017) and the future (perspective 2050).

3.5.1. Cement

Results: in 2017, 36 cement clinker producing facilities are under operation in Germany, of which two facilities produce oil shale clinker and white clinker, respectively, together with grey clinker at one site. Therefore, only 34 facilities are listed in the Supplementary Material.

The overall CO_2 emissions in 2017 were 22,062 kt, of which approx. 13,400 kt are process-related and 8660 kt are energy-related (Figure 4). The site-specific CO_2 emissions show a wide range. The lowest emissions of a production site amount to approx. 180 kt CO_2 and the largest emitter released almost 1.7 Mt CO_2 in 2017. Within the mineral sector, cement production sites show the highest CO_2 emissions with an average of 630 kt CO_2 per site in 2017.

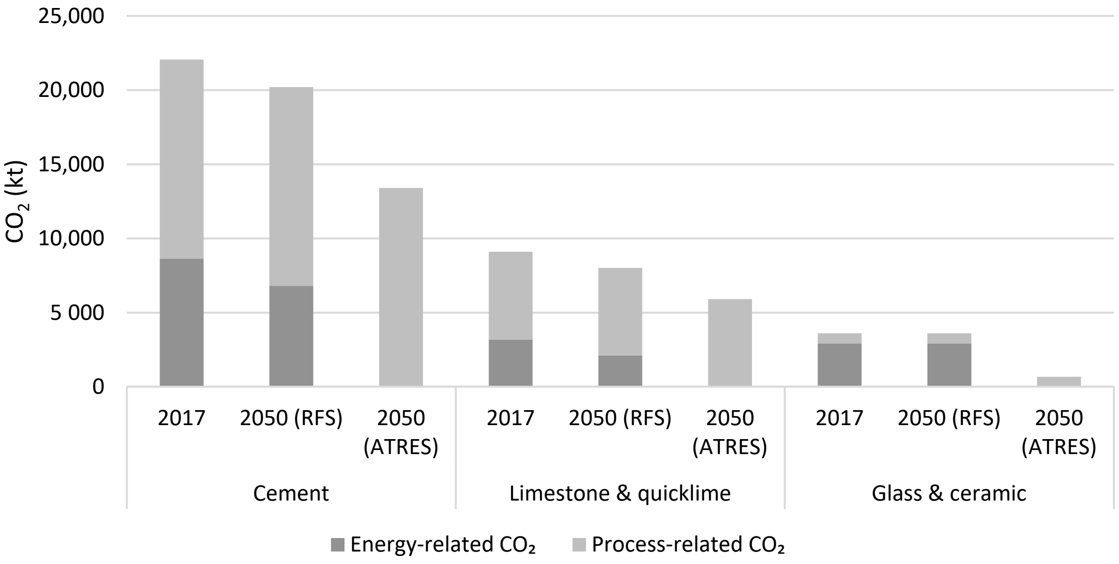

Figure 4. Energy- and process-related CO_2 of the mineral industry in 2017 and 2050 (RFS and ATRES).

The site-related emissions in 2017 and their locations are presented in Figure 5. An agglomeration of cement plants is found in the region between Paderborn and Erwitte in the north-east of North Rhine-Westphalia and in the south of Germany. This is due to the local deposits of the required raw materials lime, dolomite, and lime marl. In north Germany, production facilities with corresponding deposits can only be found in the Hannover area and north of Hamburg. An overview of the various production sites is listed in the Supplementary Material.

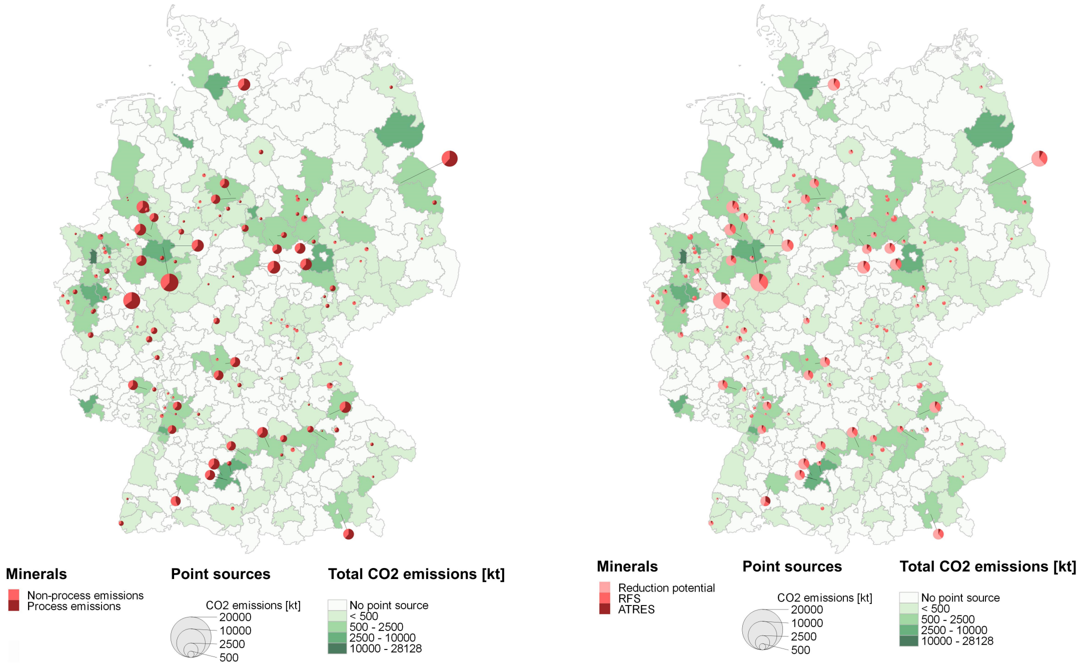

Figure 5. Distribution of CO_2 potential from the mineral industry in 2017 (**left**) and 2050 (**right**, scenario RFS and ATRES).

If “renewable” methane substitutes the share of fossil fuels used in 2017 by 2050, the total CO_2 emissions are reduced to 20,211 kt/year in scenario RFS (Figure 4) and if the process heat is only provided by electricity from renewable sources (Scenario ATRES) only process-related emissions remain (Table 8), which is a reduction of approx. 40% compared to 2017. The remaining CO_2 emissions in scenario RFS are slightly lower than the emissions in 2017 as the specific CO_2 emissions from methane combustion are lower compared to e.g., lignite or refuse-derived fuels (Table 3). The distribution of CO_2 emissions in the scenarios RFS and ATRES (2050) is shown in Figure 5. The absolute number of CO_2 emitting cement plants remains the same compared to 2017. The average CO_2 emissions of the sites decrease by approx. 6% (scenario RFS) and 37% (scenario ATRES), respectively, compared to 2017.

Table 8. CO_2 potential from the German industry in 2017 and 2050.

Sector	Total Emissions 2017 (kt)	Process-Related Emissions 2017 (kt)	Total Emissions Scenario RFS (kt)	Total Emissions Scenario ATRES (kt)
Cement	22,062	13,406	20,211	13,406
Limestone/quicklime	9103	5916	8015	5916
Glass and ceramic	3602	678	3602	678
Steel mills	54,882	47,975	18,617	1271
Separate rolling and casting mills	1638	-	1303	-
Primary aluminum	1002	799	1002	Not determined
Aluminum foundries	472	-	453	-
Zinc	128	Not determined	121	-
Lead	151	Not determined	142	-
Cooper and silica	551	-	521	-
Soda	604	Not determined	604	Not determined
Carbon black	608	Not determined	608	Not determined
Petrochemistry/refineries and bulk chemicals	32,582	-	Not determined	-
Ammonia	5921	3969	3696	-
Pulp and Paper	9466	-	7778	4100

Discussion: when determining the process-related and fuel-related CO_2 proportions for the cement sector, a verified but flat-rate proportion for the respective emissions is assumed. However, it can be presumed that the fuel composition and, thus, also the resulting CO_2 emissions vary from plant to plant. As a result, the real proportions may differ for each plant location. Furthermore, a comprehensive plant-specific list of the fuels used is not available Germany-wide. The determination of process-related and energy-related CO_2 from the oil shale plant and white clinker plant was not possible, which leads to an incomplete presentation, as only the absolute emissions of this site are listed.

There are several different approaches to the reduction of process-related CO_2 emissions within the cement industry. The gradual substitution of clinker in multi-component cement, as well as the development of alternative binders, are the two most promising approaches subject to currently ongoing research activities [28]. Concrete made by the application of new binder systems varies fundamentally from concrete made by the use of cement. Most of the alternative new binders are still in a research stage or pilot scale and require further investigation to achieve an appreciable substitution potential of Portland cement. Because of the lack of long-term tests on the behavior of concrete produced from these binders, they were not considered here. However, some new binder systems may be produced on a large scale by 2050 and, thus, lead to a further reduction of CO_2 emissions in the cement sector.

3.5.2. Limestone and Quicklime

Results: limestone and quicklime were produced at 49 sites in 2017, of which 18 plants produced quicklime for the sugar industry. One plant is allocated to the iron and steel industry and three plants have been excluded because they are about to be closed or have been closed already. The overall emissions amount to 9100 kt CO_2, of which about 3200 kt are energy-related and 5900 kt are process-related in 2017 (Figure 4). Limestone and quicklime production requires roughly the same raw materials as clinker production. Therefore, the plants are located in the same regions as the cement plants (Figure 5). However, the capacity and the associated CO_2 emissions are, on average, lower in the lime industry compared to the cement industry. The range of CO_2 emissions per site is between almost 40 kt CO_2 and about 1.3 Mt CO_2 (2017), representing average site-specific emissions of 152 kt CO_2 (2017). An overview of the various production sites is given in the Supplementary Material.

The emissions in 2050 for both scenarios are presented in Table 8 and Figure 5. Process-related CO_2 remains at about 5900 kt for both scenarios. Overall emissions are reduced by 12% (scenario RFS) and 35% (scenario ATRES) compared to 2017. The slight decrease in emissions in the scenario RFS is due to the substitution of mainly fossil solid fuels (lignite and hard coal) by "renewable" methane characterized by a lower specific emission factor. Since "renewable" electricity is used for heat provision in scenario ATRES only process-related CO_2 remain (Figure 4).

Discussion: the direct CO_2 emissions from the manufacture of quicklime result from the process-related proportion and use of fuels. However, it cannot be ruled out that additional fuel-related emissions may also occur at some of the plants, e.g., due to the drying of ground limestone. It is therefore possible that the 35% proportion of energy-related emissions used in the potential analysis is exceeded.

The production of quicklime in the sugar industry has a seasonal availability since the production of sugar is directly linked to the sugar beet harvest.

Regarding the CO_2 emitted by the burning of lime for the production of, e.g., mortar, a natural reduction of CO_2 occurs when quicklime is used in the construction industry, especially in mortar and plaster. The setting of mortar and plaster removes CO_2 from the ambient air and leads to carbonation. The maximum degree of carbonation of mortar is between 80 and 92%. For such a high degree of carbonation, however, ideal conditions are required, such as the ambient temperature, thickness and composition of the walls in which the mortar is embedded [29]. This does not change the total CO_2 emissions from this industrial sector. However, this special case represents a natural CO_2 sink.

3.5.3. Ceramics and Glass

Results: five out of 133 ceramic production sites emit more than 40 kt of CO_2 (2017); the same applies for six out of seven mineral wool producing plants. Glass is produced at 74 sites, of which 35 plants emit more than 40 kt/year. Figure 4 shows the overall emissions of about 3600 kt CO_2, of which about 700 kt are process-related and 2900 kt are energy-related in 2017. The location and respective amounts of CO_2 are shown in Figure 5. A complete list of these sites is given in the Supplementary Material. The distribution of the ceramics and glass production sites is parallel to that of cement and limestone production. However, this is less pronounced. The site-specific CO_2 emissions are significantly lower than in the other mineral sectors assessed here. The given range varies between 40 kt and 245 kt CO_2 in 2017 with an average of 80 kt.

The prospective emissions in 2050 are presented in Table 8 as well as in Figure 4. It can be seen that the CO_2 reduction potential in scenario ATRES is about 82%, which can be explained by the increased share of energy-related CO_2 emissions in this sector compared to cement and limestone facilities. The remaining site-specific CO_2 in 2050 are presented for both scenarios in Figure 5.

Discussion: by determining the limit value of 40 kt/year, 130 plants in the ceramics industry and around 40 plants in the glass industry are not considered in the site location analysis. However, the shares of these plants in the process-related emissions of these sectors are approx. 85% and almost 17%, respectively. Although the share of 85% is quite high, the respective emissions of more than 100 plants are less than 10 kt CO_2/year, respectively. A certain uncertainty of the results is caused by the fact that the process- and energy-related shares originate from 2007 when determining the weighted averages, which are applied to the total CO_2 emissions in 2017. These shares may have changed since 2007, but this cannot be verified since no recent data are available. In addition, only 96% of total production in 2017 can be allocated to the production of bricks (80%), refractory ceramics (10%) and tiles (6%). Accordingly, 4% are assumed for the remaining three production areas.

4. Iron and Steel Industry

Below, the production of iron and steel via the oxygen steel and electric arc furnace route are discussed in detail, as well as the processing of ferrous metals. In Germany, two different production processes for crude steel are currently applied. Approximately one third of the production is electrical steel and two thirds are oxygen steel, which is produced in electric arc furnaces and integrated mills, respectively [15]. Usually, oxygen steel is mainly made out of iron ore and scrap metal.

4.1. Steel Mills

4.1.1. Oxygen Steel Mills

The reduction process in blast furnaces is preceded by the extraction of the ore and its processing. The crude steel from the converter is further processed into intermediate and final products in rolling mills. This is achieved by hot forming, which emits inter alia CO_2 from burning process gas or natural gas.

Process Description

At integrated mills, grinded iron ore (fines) is first sintered or pelletized for agglomeration. Fines are obtained from ore dressing necessary to remove gangue from the ore. These fines are mixed with aggregates (e.g., coke breeze and a mixture of shales and lime as slack formers in the blast furnace) and then sintered at temperatures between 900 and 1200 °C, which leads to caking. The sintered iron ore is further processed in blast furnaces to remove oxygen and remaining gangue.

In the production of pig iron in blast furnaces reducing agents are needed to reduce the iron oxide. The main reducing agent used in the blast furnace process is coke. The carbon contained within the coke is (partly) oxidized during this process and discharged as CO and CO_2 together with other gases (so-called blast furnace gas). The reduction process comprises indirect reduction via CO at temperatures between 450 and 1000 °C (Equation (4)) and direct reduction via carbon at temperatures above 1000 °C (Equation (5)).

$$Fe_3O_4 + 4\,CO \rightarrow 4\,CO_2 + 3\,Fe. \tag{4}$$

$$Fe_2O_3 + 3\,C \rightarrow 4\,CO_2 + 3\,Fe. \tag{5}$$

The pig iron is further processed in the oxygen steel converter. Here, the iron is first desulfurized and then decarburized together with steel scrap (for cooling) and other additives in the converter by blowing in oxygen, further reducing the carbon content. On average, a carbon content of approx. 0.15% remains in the crude steel. The gaseous emissions containing e.g., CO and CO_2 escaping from the converter are called converter gas. It is used together with the blast furnace gas as an energy carrier. Thus, some of these so-called coupling gases are used as fuel in the hot blast stoves of the blast furnace plant. Other applications include coke oven under-grate firing, process firing in sinter and rolled steel production, and electricity generation in industrial power plants.

Methodology

The process-related CO_2 emissions from integrated steel mills are mainly caused by the use of the reduction agent (mainly coke) and limestone. The blast furnace gas from the reduction process mainly consisting of CO and CO_2 is used for heat supply (CO reacts to CO_2) in different sections of the steel mill as well as for electricity production within the attached industrial power plants. The respective locations where the gases are used are indicated as emission sources [14], but only emissions from hot-blast stoves are listed as process-related emissions from the steel industry. The remaining emissions are attributed to the energy sector. Since all of these processes are located within the integrated steel mill or close by (industrial power plants are located nearby; since 2016 no gas was used in public power plants anymore) and originate from the reduction agent (process-related), it is assumed that all CO_2 emissions are emitted at the location of the respective steel mill. For the determination of the specific process-related emission factor of the reduction agents, the emissions of the different sources given in [14] are added up and divided by the total pig iron production [30]. The use of coke as a reduction agent leads to an emission factor of about 1.67 t CO_2/t pig iron.

Limestone is used in sintering plants and blast furnaces; burnt lime is used as a slag generator in electric steel production and in the converter of the oxygen steelworks. Quicklime is mainly obtained from the lime industry. Therefore, the respective emissions are attributed to the lime industry. There is one steel mill that covers its own demand for quicklime leading to emissions of 153 kt CO_2 in 2017 [14]. The quicklime plant is located at the steel mill at Eisenhüttenstadt and these CO_2 emissions are allocated to the limestone and quicklime sector, and thus not included in the overall emissions of that mill. The approach for determining the emission factor is similar to that for emissions from reducing agents. The emissions from the usage of limestone from 2015 to 2017 [14] are added up and divided by the respective amount of produced pig iron [30]. The arithmetic mean leads to a specific emission factor of 76 kg CO_2/t pig iron. The combined emission factor used for the determination of process-related CO_2 emissions amount to approx. 1.75 t CO_2/t pig iron.

Plant-specific and thus site-specific pig iron production figures are not available. To take into account the amount of scrap metal used in the converter, the proportion of pig iron used in the production of crude steel in 2016 has been calculated. This is due to the fact that the proportion of scrap added in the converter does not cause significant CO_2 emissions compared to pig iron produced in the blast furnace. This share amounts to 91.5% pig iron and is offset against the specific crude steel production of each factory for the determination of the respective CO_2 emissions.

The data used for the determination of process-related CO_2 emissions from the iron and steel industry is obtained from [15]. The values of the integrated steel mills are multiplied with the combined emission factor of 1.75 t CO_2/t pig iron of oxygen steel. When determining the CO_2 emissions from the converter of steel plants not operating their own blast furnace (oxygen steelworks), thus purchasing pig iron from other sites, a specific emission factor of 0.2 t/t crude steel was assumed. The total CO_2 emissions of each plant were obtained from the 2017 data. It is assumed that the specific production figures from 2016 also apply to 2017, with corresponding process-related emissions.

4.1.2. Electro Steel Plants

An alternative process for the production of pig iron is the electro steel route and will be discussed in the following subsections.

Process Description

Various input materials can be processed in electric arc furnaces. In Germany, all electro steel plants use scrap as input material besides one plant in Hamburg, which also uses direct reduced iron or rather iron sponge as input [31]. Alternatively, the input feed can also contain liquid or solid pig iron. Further input materials are e.g., quicklime and foaming coal as slag formers and reduction agents. Iron sponge is produced in shaft furnaces and uses a mixture of H_2 and CO as reduction gas to extract the oxygen from the iron ore (Equations (6) and (7)). The input material is melted by the electric energy applied through the electrodes. During this process, the electrodes are continuously consumed (Equation (8)). After reaching the required temperature and chemical composition, the hot melt is filled in a steel ladle for treatment in the secondary metallurgical process being similar to integrated steel mills and consists of, e.g., decarburization, alloying, and homogenization. The melt is then casted and solidified through continuous or block casting.

$$\mathrm{Fe_2O_3} + 3\,\mathrm{CO} \rightarrow 3\,\mathrm{CO_2} + 2\,\mathrm{Fe}. \tag{6}$$

$$\mathrm{Fe_2O_3} + 3\,\mathrm{H_2} \rightarrow 3\,\mathrm{H_2O} + 2\,\mathrm{Fe}. \tag{7}$$

$$\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2}. \tag{8}$$

Methodology

The process-related CO_2 emissions resulting from this process are caused by the combustion of the graphite electrodes and the oxidation reaction of the foaming coal. The electrodes consist of graphite burned with a ratio of 2.06 kg/t during the process. The specific emission factor for electric steel production is 7.1 kg CO_2/t steel [14]. The usage of injection/foaming coal leads to emissions of approx. 23 kg CO_2/t crude steel [31] resulting in an overall emissions factor of 0.03 t CO_2/t steel.

In the case of iron sponge production, further CO_2 is emitted due to the reduction process. The emission factor is stated as 666 kg CO_2/t crude steel [32]. Here, the emission factor for direct reduction is not used since the detailed amount of iron sponge production is not available. The total amount for the location Hamburg according to [31] accounts for 258 kt CO_2 and is added to the emissions from electrode consumption and foaming coal injection.

The production figures for the various electro steel plants are obtained from [15]. These values are multiplied with the emission factor of 0.03 t CO_2/t steel. The data for direct reduced iron is obtained from [31]. The total CO_2 emissions of each plant are used from the 2017 data of the register of installations. Again, it is assumed that the specific production figures from 2016 also apply to 2017.

4.1.3. Scenarios

Since the development of the oxygen steel route and the electric steel route cannot be considered independently, as the development of one route has a strong impact on the other, the scenarios for both production routes have been combined below.

According to [32], direct reduction using hydrogen can reduce CO_2 emissions by up to 95% compared to the blast furnace route. Since the directly reduced iron is subsequently fed in an electric arc, the process-related emissions cannot be completely avoided due to anode consumption. If natural gas is used as the reducing agent in the process and no iron scrap (i.e., only sponge iron is used) 40% of the CO_2 emissions can be avoided compared to the blast furnace process. Such a complete conversion of the German steel industry to the direct reduction process would need an extra 120 TWh/year of electricity. The technology readiness level (TRL) for a direct reduction in the shaft furnace using natural gas is stated as 9, for using pure hydrogen as 6 to 8 [32]. The earliest possible large scale application of direct reduced iron using hydrogen is assumed for the years between 2025 and 2030 [16].

Scenario RFS: scenario RFS assumes that the production of iron and steel is completely shifted to the electric steel route and direct reduction of iron ore with “renewable” methane. The resulting emissions were determined via the specific emission factor of iron sponge production (0.47 t CO_2/t iron sponge) obtained from data of the production unit in Hamburg [31] and the emission factor of electric arc furnaces (0.03 t CO_2/t steel). Furthermore, onsite rolling and casting facilities use mainly “renewable” methane as fuel. Industrial power plants onsite the steel manufacturing are shut down and the electricity is obtained from the national grid being fully GHG neutral by the year 2050.

Scenario ATRES: scenario ATRFS is based on scenario RFS, but the direct reduction is carried out with green hydrogen and the casting and rolling plants use only electricity for heat supply.

4.2. Casting and Rolling Mills

4.2.1. Methodology

Besides the casting and rolling of iron and steel at electric steel plants and integrated steel mills, several casting and rolling mills operate separately. The process does not emit process-related emissions. Therefore, it is not analyzed in a dedicated methodology and no detailed process description is given. There is a high demand for process heat and electricity, which is also partly used for heat supply. Separate iron casting mills obtain the required heat mainly by hard coal and rolling mills by natural gas [18]. Integrated rolling and casting mills also use conditioned blast furnace gases as a fuel. CO_2 emissions from rolling and casting at the integrated mills as well as electric steel plants are included in the emissions of the respective mills and plants.

4.2.2. Scenarios

For the prospective emissions of separate casting and rolling mills, it is assumed that the heat supply is provided by "renewable" methane for scenario RFS. Emissions from the use of "renewable" methane were calculated using the specific emission factor of natural gas and the respective amount of energy provided by the substituted fossil fuels. The proportional emission reduction was then applied to the emissions of each site to determine the remaining emissions for 2050. In scenario ATRES, it is assumed that renewable produced electricity is used for heat supply in, e.g., crucible induction furnaces in casting mills and inductive heated rolling mill furnaces.

4.3. Summary

Below the results are summarized and discussed.

4.3.1. Steel Mills

Results: there are currently 26 operational production sites in Germany, of which 6 are integrated steel mills, 17 are electric steel plants, 1 is a recycling facility, and 2 are oxygen steelworks. In addition, there are 3 coke plants. In contrast, production capacities are strongly dominated by integrated steel mills, which also applies to CO_2 emissions. The overall emissions amount to approx. 54,900 kt CO_2 in 2017, of which integrated steel mills emitted 88%. About 48,000 kt CO_2 are process-related in 2017 (Figure 6). The locations with the largest amounts of CO_2 emissions in Figure 7 represent the integrated steel mills. It can be seen that these plants emit very large quantities of CO_2 in comparison to the other locations, which are mainly electric steel plants. An agglomeration of production sites can be seen in the Ruhr area and in the Saarland, which results from the historical context of these areas and still has an impact on the present-day situation.

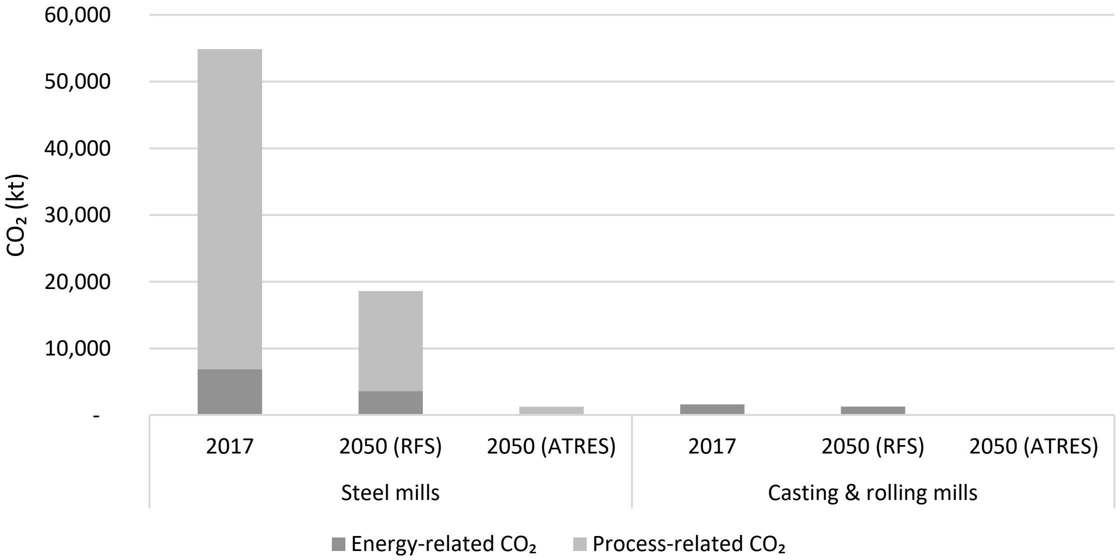

Figure 6. Energy- and process-related CO_2 of the iron and steel industry in 2017 and 2050 (RFS and ATRES).

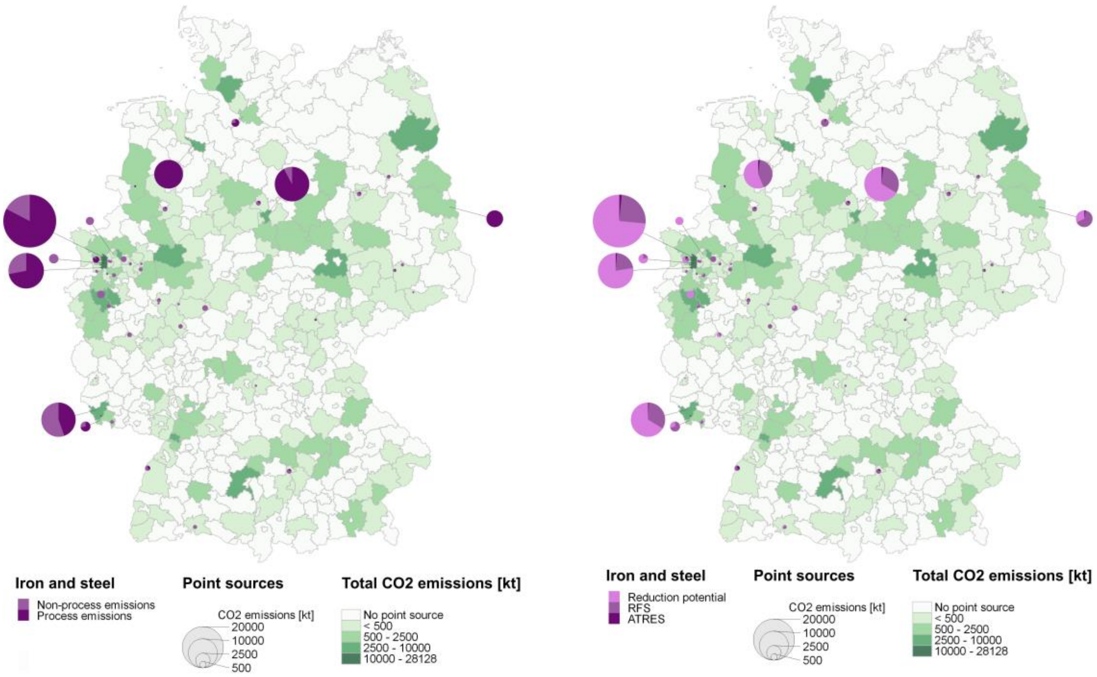

Figure 7. Distribution of CO_2 potential from the iron and steel industry in 2017 (**left**) and 2050 (**right**, scenario RFS and ATRES).

In scenario RFS, process-related CO_2 is decreased by about 70% and energy-related CO_2 by 47% compared to 2017 (Figure 6). Steel production by direct reduction using green hydrogen and subsequent electric arc furnaces (scenario ATRES) has a very high reduction potential. The extensive conversion to this process would result in 2% of the emissions in 2017 being available for use in 2050. This can also be seen in Figure 7 as locally emitted CO_2 emissions are significantly reduced.

Discussion. The data on specific production quantities of the iron and steel industry in 2016 is not always available individually for each plant. In some cases, only the overall sum for several plants operated by one company are accessible. Additionally, for some plants, no specific values could be identified. For this reason, the total production capacities of the respective company are distributed evenly among the various plant locations. This might have the consequence of a calculated over- or under-capacity for one respective site. The site-specific amount of pig iron and crude steel produced used to determine process-related emissions in 2017 is obtained from 2016, as no corresponding information was found for 2017. For the analysis, the total CO_2 emissions per site in 2017 were used. This might lead to an incorrect ratio when determining process-related and energy-related emissions per site. This true for the oxygen steel mills in Bremen and Eisenhüttenstadt, which show a greater amount of process-related CO_2 than overall CO_2 emissions in 2017 (Supplementary Material).

4.3.2. Casting and Rolling Mills

Results: there are 20 separate rolling and casting mills and integrated power stations or boilers mostly located close to the integrated steel mills and electro steel plants (Figure 7). The total amount of the energy-related CO_2 emissions in Germany in 2017 from these facilities sum up to 1638 kt (Table 8). The amount is comparatively small regarding the CO_2 emissions from pig iron production, especially compared to the emissions from integrated steel mills (Figure 6), as process-related emissions from, e.g., reduction agents are not emitted. The emissions result mainly from the heat supply by the combustion of fossil fuel energy. Scenario RFS results in emissions of about 1303 kt/year resulting from the substitution of solid and liquid fossil fuels with "renewable" methane. If these facilities are only provided by electrical power (scenario ATRES) for heat supply, the site-specific emissions would be negligible in 2050 and result in a reduction of available CO_2 point sources as shown in Figure 7. A comprehensive list of the different production sites is given in the Supplementary Material.

5. Non-Ferrous Metal Industry

Below, the production of primary aluminum, lead, zinc, copper, and silica are discussed in detail.

5.1. Primary Aluminum

In the following sections, the process description of primary aluminum and the methodology for the site-specific CO_2 emission determination in 2017 and 2050 is presented.

5.1.1. Process Description

The production of aluminum consists of three process steps. The raw material bauxite is extracted in open-pit mines located at various locations all over the world; major producers are Australia, China, and Guinea [33]. Then, aluminum oxide (Alumina) is extracted from this bauxite by applying the Bayer process using sodium hydroxide to solve aluminum hydroxide and separate iron-containing minerals. The provided aluminum hydroxide is then burned in kilns to obtain aluminum oxide. No process-related CO_2 emissions, as defined above, are caused during this process. However, the high energy demand for mining and the Bayer process result in energy-related and indirect emissions mainly related to the provision of the desired electricity.

The provided aluminum oxide is further refined within the Hall–Héroult process by dissolving the aluminum oxide in molten cryolite to decrease the required melting point of the electrolyte. The electrolyte is embedded in a steel tub lined with graphite that acts as a cathode. The anode in form of graphite blocks (prebaked electrode cells) is immersed from above in the electrolyte. A DC voltage and high ampere current are applied to the poles forcing the dissociated aluminum cations to migrate to the cathode at the bottom of the cell and the acid-containing ions to the anode on top.

The overall chemical reaction is shown in Equations (9) and (10). The process-related CO_2 emissions from primary aluminum production mainly result from the combustion of the carbon anodes during the electrolysis of the aluminum oxide.

$$\mathrm{Al_2O_3} + 3\,\mathrm{C} \rightarrow 2\,\mathrm{Al} + 3\,\mathrm{CO}. \tag{9}$$

$$\mathrm{Al_2O_3} + \frac{3}{2}\,\mathrm{C} \rightarrow 2\,\mathrm{Al} + \frac{3}{2}\,\mathrm{CO_2}. \tag{10}$$

The carbon–oxygen compounds formed at the anode are predominantly CO_2. During their formation, carbon from the anodes is continuously consumed requiring a replacement from time to time. The liquid elemental aluminum at the bottom of the cell is collected and discharged via a siphon since it is denser than molten cryolite [34].

Aluminum electrolyzing cells might be equipped with prebaked anodes (so-called prebaked cells). Thus pre-baked anode manufacturing is—besides its consumption during the process—another CO_2 emission source [35]. These prebaked anodes are manufactured in oil- or gas-fired furnaces. A mixture of petroleum coke, coal tar pitch and crushed spent anodes are pressed in pits and baked between 22 and 32 h at about 1200 to 1300 °C [36]. After the anodes are cooled down, steel stubs are inserted in stub holes on top of the block and fixed with poured cast iron. These are connected to an aluminum or copper rod to conduct the electrical flow into the anode [34].

5.1.2. Methodology

Carbon from the anodes reacts with oxygen separated from alumina to form CO_2. The average anode consumption per ton of aluminum is 430 kg [14]. Assuming an average carbon content of the anode of 857 kg/t and a stoichiometric conversion to CO_2, this results in a specific emission factor of 1367 kg CO_2/t aluminum [14]. Due to Equation (9), CO is also formed during the electrolysis. It is assumed that this CO is further oxidized to CO_2 by contact with ambient air and is thus included in the emission factor mentioned above [37].

CO_2 emissions from anode baking result basically from three combustion processes: the combustion of fuel for firing the furnace, the combustion of volatile matter, and the combustion of baking furnace packing material [37]. Half of the total emissions from anode manufacturing are emitted by burning fuel. The other 50% are process-related emissions from the combustion of pitch volatiles and packing coke. Total emissions from prebaked anode production vary between 320 and 575 kg CO_2/t product [38]. As an approximation the arithmetic mean of about 448 kg CO_2/t baked anode is applied, of which ca. 224 kg CO_2/t are process-related.

The anode baking capacities are given for the refineries in Hamburg and Voerde [39]. The third anode baking facility in Germany is located at the refinery in Neuss. The determination of process-related emissions from the anode baking facility is based on data obtained from the register of installations. The total CO_2 values of each aluminum refinery in 2017 are obtained from thru. Because of the lack of detailed primary aluminum production values of each refinery, these values have been approximated by reducing the installed capacity of each facility by the proportionate amount of the total primary aluminum production of 550 kt in 2017 [40]. This aluminum output in 2017 was about 75 kt below the installed capacity of 625 kt. Since the specific production output for each refinery is not available, this 75 kt (2017) gap is allocated to the four refineries. The quantity distributed to each refinery is based on the share of each production capacity related to the overall capacity of 625 kt.

Furthermore, there are four aluminum foundries/processing facilities emitting more than 40 kt CO_2 in 2017. These sites only emit energy-related CO_2 mainly caused by burning oil (13%) and gas (87%) [41].

5.1.3. Scenarios

Scenario RFS: there are research activities in which bio-oil has been produced by fast pyrolysis, having similar properties to fossil petroleum coke, and could be used for the production of anodes [42]. Based on these research activities in scenario RFS, the use of biomass-based anodes and “renewable” methane as a fuel for the anode baking process is assumed. Therefore, the CO_2 emissions remain constant compared to 2017 but change from fossil to biogenic carbon. For the prospective emissions of aluminum foundries and processing sites, it is assumed that the heat supply is provided by “renewable” methane for scenario RFS. The proportional emission reduction was then applied to the emissions of each site to determine the remaining emissions for 2050.

Scenario ATRES: there is no scenario ATRES defined for the primary aluminum production (electrolysis) since there are no promising alternative technologies to enter the market until 2050. An alternative for reducing process-related emissions at all is the use of inert anodes. This technology has been investigated for more than 50 years already without making promising progress for industrial-scale implementation [17]. For the prospective emissions of aluminum foundries and processing sites, it is assumed that “renewable” electricity is used for heat provision.

5.2. Zinc, Lead, Copper, and Silica

Zinc: in Germany, primary zinc is produced by the hydrometallurgical process. In this process, ore concentrates (mainly so-called zinc blende) are desulfurized in a roasting process. By adding carbon carriers, zinc oxide and sulfuric acid are formed at approx. 900 °C; the latter is removed as a by-product. The zinc oxide is then fed to the electrolysis, where pure zinc is accumulated on the anode. In secondary zinc production, secondary materials containing zinc are oxidized to zinc oxide in rotary kilns by adding petroleum coke, which is fed into the production process of leaching and electrolysis [43]. Process heat is obtained from using oil (22%) and natural gas (78%) [41].

Concerning alternative technologies for CO_2 reduction, it can be assumed that biomass might also be applicable as an alternative to coke. In principle, direct reduction using hydrogen also seems possible in this sector, but further verification is required. If oil and natural gas fossil fuels are substituted by "renewable" methane and biomass is used as a reduction agent until 2050, the total emissions would decrease by the proportion of the substituted fossil fuels (scenario RFS). If hydrogen is applied as a reduction agent and process heat is provided by "renewable" electricity, the overall CO_2 emissions in 2050 are negligible (scenario ATRES).

Lead: the production of primary and secondary lead emits process-related CO_2 by the usage of fossil reduction agents coal and coke in the direct smelting process in bath smelting furnaces (Isasmelt-Ausmelt) or QSL-Reactors (primary). Short rotary furnaces or shaft furnaces processes are used for secondary lead production.

The substitution of fossil fuels with "renewable" methane and coke with biomass would result in a small reduction of the overall emissions (scenario RFS). The use of "renewable" electricity for the provision of process heat and the application of hydrogen as a reduction agent would lead to insignificant CO_2 emissions in 2050 (scenario ATRES).

Copper and silica: primary copper is obtained from copper concentrates, which are produced from copper ore at the mining site. The concentrate is processed in further enrichment stages up to a copper content of 98%. This so-called blister copper is refined in a subsequent electrolytic refining process to pure copper (>99.99%). The CO_2 emissions from the production of copper are mainly energy-related due to the needed thermal energy during the enrichment stages. Process-related CO_2 emissions are relatively low [14].

In the large-scale production of silica, quartz sand and gravel (SiO_2) together with carbon (coke, coal, wood) are fed into an electric arc furnace where SiO_2 is reduced to metallic Si. Process-related CO_2 is emitted by the reaction of the reducing agent with the oxygen obtained from quartz sand. The determination of process-related CO_2 from silica production was not possible.

If process heat is provided by "renewable" methane instead of fossil fuels, these emissions would decrease according to the proportion of substituted fossil fuels (Scenario RFS). If hydrogen is applied as a reduction agent and process heat is provided by "renewable" electricity, the overall CO_2 emissions in 2050 are negligible (scenario ATRES).

5.3. *Summary*

Below the calculated results are summarized and discussed.

5.3.1. Aluminum

Results: there are four primary aluminum refineries in Germany, of which three have their own anode backing facilities. The overall CO_2 emissions in 2017 amount to roughly 1.4 Mt, of which around half are process-related. The distribution is caused by the anode consumption during electrolysis (process-related CO_2) and the limited use of fuels, which are mainly used in anode baking. The majority of the energy required for primary aluminum production is provided by electricity which does not cause direct emissions at the respective production site. A list of the different facilities and their emitted amount of CO_2 is given in the Supplementary Material. The regional distribution of the point sources is presented in Figure 8. The facilities are located in Hamburg as well as in the south of North Rhine-Westphalia.

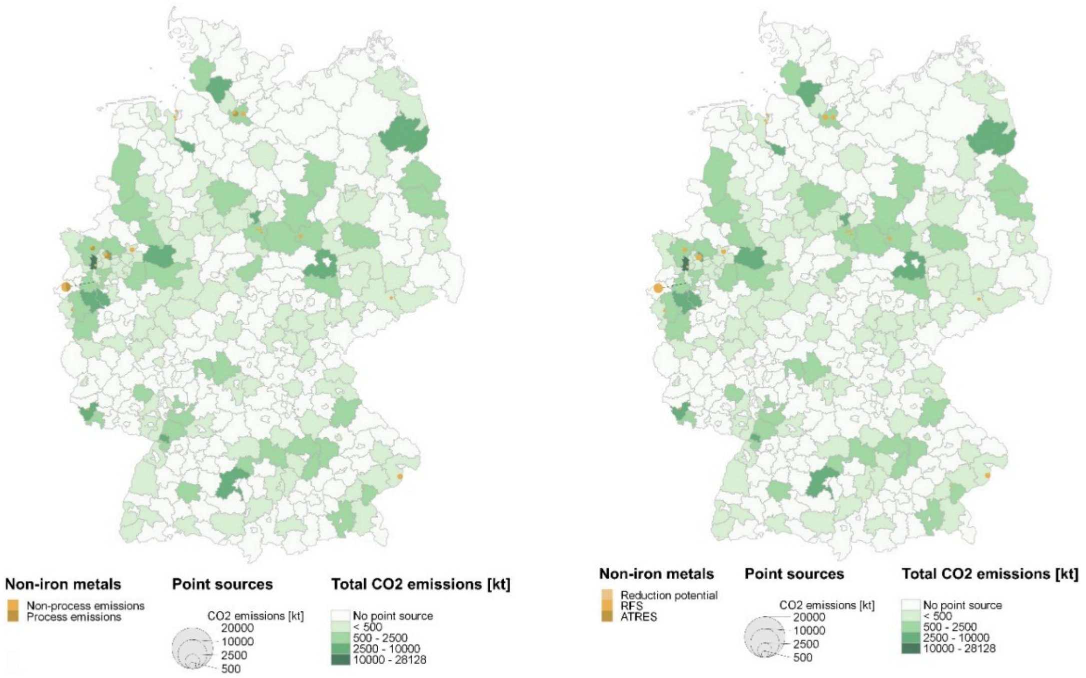

Figure 8. Distribution of CO_2 potential from the non-ferrous industry in 2017 (**left**) and 2050 (**right**, scenario RFS and ATRES).

The emissions in the scenario RFS show similar quantities as for 2017 (Figure 9) which is due to the high share of natural gas as fuel for the anode backing and the assumption that the anodes are made of biogenic carbon which would result in similar emissions as for use of fossil carbon. The emissions in scenario ATRES are not determined because the analysis showed no promising alternative technologies to enter the market until 2050.

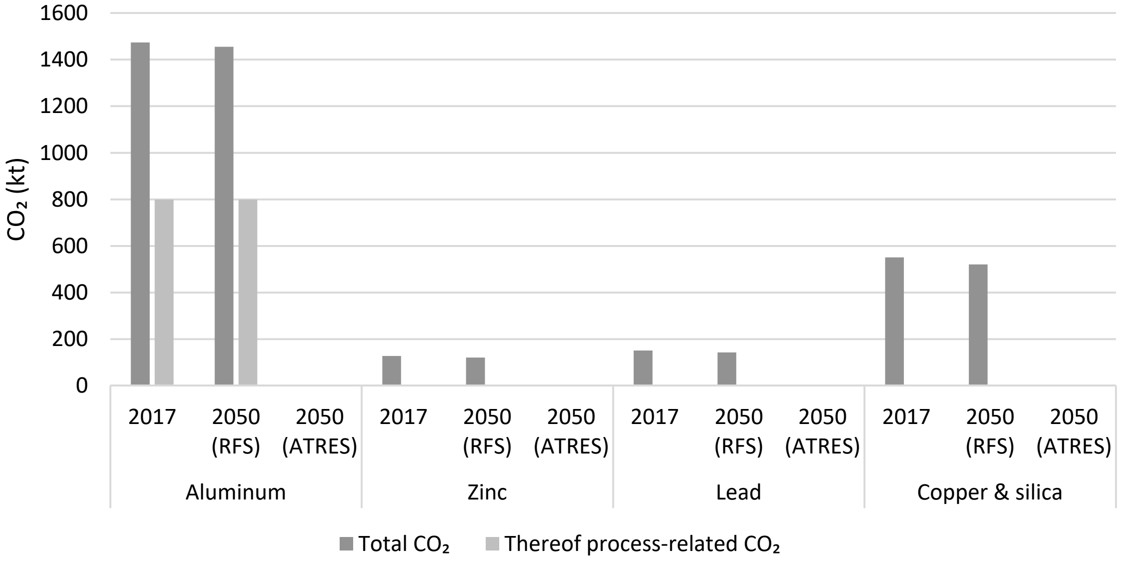

Figure 9. Total and process-related CO_2 of the non-ferrous metal industry in 2017 and 2050 (RFS and ATRES).

The total emissions of the aluminum foundries and processing sites amount to 472 kt in 2017. Process-related CO_2 is not emitted. The emissions stem from heat provision, using mainly natural gas as fuel. When "renewable" methane is used for heat provision in 2050 (scenario RFS) the emissions decrease to about 452 kt CO_2. The provision of heat by "renewable" electricity in scenario ATRES leads to negligible emissions in 2050.

Discussion: the calculated production quantities for 2017 of the primary aluminum sector may differ from the real production figures, as these are calculated based on the total production of all plants and their corresponding share of the total production alone. Thus, the CO_2 emissions of the respective plant can also vary from the actual quantities emitted. Emissions from cathode production are not included in the calculation. It is assumed that the cathodes are much more durable than the anodes since literature only reports the consumption of the anode as a relevant CO_2 source. However, the emissions from cathode production should still be included for an all-embracing analysis. However, these emissions are likely to be marginal compared to those from anode production and consumption.

5.3.2. Zinc, Lead, Copper, and Silica

Results: CO_2 emissions from these sectors are relatively small compared to the primary aluminum production and casting and rolling of aluminum (Figure 9). In 2017, the overall CO_2 emissions amount to 830 kt, of which the two copper production sites shows the greatest proportion (342 kt CO_2). Two zinc-producing facilities released 128 kt CO_2 and three lead-producing plants emitted a total of 151 kt CO_2. The silica production at one site emitted 209 kt CO_2. A specific determination of energy-related and process-related emissions within the total amount is not possible due to a lack of data. The spatial distribution is inhomogeneous at different locations (Figure 8). The emissions in the scenario RFS amount to 785 kt CO_2 and show similar quantities as for 2017 due to the high share of natural gas as fuel for these sectors in 2017. The emissions of the sites are reduced by an average of 5%. The results of scenario ATRES show negligible emissions. Figure 8 shows the distribution of the remaining CO_2 for the scenario RFS and ATRES.

Discussion: the total process-related emissions (zinc 300 kt, lead 77 kt) obtained from literature [14] may exceed the total amount given in Table 8 since these process-related emissions represent the agglomerated amount of all processing facilities in Germany. The analyzed data do not indicate where the other zinc factories are located. It is not possible to specify the proportions of process-related and energy-related CO_2 per site (zinc and lead) because the required data is not available. These circumstances cause an incomplete determination of the CO_2 resource potential of the zinc and lead production. Therefore, the results of the determination of 2050 emissions in the two scenarios may also be approximate.

6. Chemical Industry

Below the production of soda, carbon black and ammonia are discussed in detail as well as the petrochemical sector and refineries.

6.1. Soda

The use of soda in other applications then the glass industry led to process-related emissions of about 185 kt CO_2 in 2017 [14]. Other major applications of soda are the production of detergents and cleaners as well as the chemical industry. Since detailed information about the amount of used soda in each sector is missing, the resulting emissions from soda could not be allocated to a specific industrial sector.

The synthetic production of soda also emits process-related CO_2 during the Solvay-process (production of sodium carbonate). The CO_2 occurring from the input material calcium carbonate is partly embedded into the product Na_2CO_2; however, the process runs under CO_2 excess, resulting in process-related emissions of about 460 kt CO_2 in 2017 [14].

Process heat is mainly obtained from natural gas. Thus a substitution with "renewable" methane would lead to similar emission values in 2050 (scenario RFS). The emissions in scenario ATRES are not determined because the analysis showed no promising alternative technologies to enter the market until 2050.

6.2. Carbon Black

Carbon black is produced in lamp black or gas black facilities and furnace black process. The CO_2 emissions from this process result from the combustion of hydrocarbons for heat supply in the reactor and incomplete combustion of e.g., cracker or distillation residues as product feedstock; the latter is classified as process-related. The overall process-related CO_2 obtained from [14] amount to 664 kt in 2017.

Carbon black can be obtained by processing biomass instead of fossil hydrocarbons [44]. This would shift fossil to biogenic emissions. Total avoidance of process-related emissions does not seem possible due to the required product specification of the carbon black. Again, process heat is mainly obtained from natural gas. That means that a substitution with "renewable" methane would lead to similar emission values for scenario RFS. The emissions in scenario ATRES are not determined because the analysis showed no promising alternative technologies.

6.3. Petrochemistry, Refineries, and Bulk Chemical Production

The CO_2 emissions from the petrochemistry and bulk chemical industry are mainly determined by the production of methanol, ethylene, ethylene dichloride, vinyl chloride, ethylene oxide and acrylonitrile. The process-related share in the overall emissions is relatively small and results from flares and decoking [14]. The data obtained from [14] comprehends only emissions from flares, which amount to about 255 kt CO_2 in 2017. The majority of CO_2 emissions are caused by heat provision for cracking furnaces (e.g., steam crackers). Steam cracking is used to produce a variety of short-chain olefins. In smaller quantities, these are also separated from refinery gases. Aromatics (predominantly benzene) are also produced via this process route. The raw materials used are gaseous hydrocarbons, naphtha, or gas oil, whereby naphtha is the predominant raw material used in Germany. The process includes the pyrolysis furnace, the compression section, and the separation step. The cracking reaction runs at temperatures above 800 °C and is endothermic.

Theoretically, all CO_2 emissions might be avoidable in 2050 due to various alternative technologies (scenario ATRES). These are, e.g., electrically heated steam cracker (TRL: 1 to 3, earliest possible large-scale application 2035 to 2045), chemical recycling of carbon feedstock, such as plastic waste (TRL: 6 to 7, earliest possible large scale application 2025 to 2030), or alternative processes like the methanol-to-olefin route (TRL: 6 to 9, earliest possible large scale application 2025 to 2030). Hydrogen provision by water electrolysis is an alternative almost CO_2 neutral process to steam reforming if the required electricity is obtained from renewable sources of energy (TRL: 6 to 9, earliest possible large scale application 2025 to 2030) [16].

The hydrogen provision in refineries also emits large quantities of process-related CO_2 from steam reforming of natural gas or gasification and a subsequent water-gas-shift-reaction of petrol coke. The hydrogen net demand (hydrogen as a by-product in refinery processes excluded) of the German refineries is estimated at 177 kt/year resulting in about 1.7 Mt CO_2/year [45]. These emissions are energy-related and might be avoidable in 2050 due to alternative technologies as described above (scenario ATRES).

A reduction potential for scenario RFS cannot be determined in site-specific and absolute terms because these sectors have a large variety of processes and fuels and insufficient data is available to give sound information about remaining emissions for scenario RFS.

6.4. Ammonia

The production of ammonia led to process-related CO_2 emissions of approx. 4230 kt in 2017 [14]. The CO_2 is formed during the steam reforming process of mainly methane. Steam reforming is an endothermic process in which desulfurized hydrocarbons are mixed with steam and heated up to a temperature level of 700 to 900 °C, forming CO and H_2. The CO is then mixed with steam again at 250 to 300 °C in the shift-reaction, which produces CO_2 and increases the yield of H_2 in parallel. The hydrogen obtained from this reforming process is synthesized together with nitrogen (obtained from air separation) in the Haber–Bosch process to ammonia. A total of 1.8 t CO_2/t ammonia is emitted. Approx. 1.3 t is process-related due to the reforming of natural gas and 0.5 t results from the generation of steam (heat provision) [16].

For scenario RFS, it is assumed that process heat is provided by "renewable" electricity and that "renewable" methane is used as feedstock for the reformation. If hydrogen is produced via water electrolysis with "green" electricity these emissions would be negligible in 2050 (scenario ATRES).

6.5. Summary

6.5.1. Soda and Carbon Black

Results: there are four soda production facilities in Germany that emitted about 600 kt CO_2 as well as four carbon black production sites, which emitted another approx. 600 kt CO_2 in 2017 (Table 8). Compared to the CO_2 emissions of the other sectors of the chemical industry, the CO_2 amount is small (Figure 10). Two of the soda production sites are located at sites where the bulk chemical sector is also presented (Figure 11). Three of the four carbon black production units belong to one integrated plant in Cologne. Process-related CO_2 emissions could not be disclosed in a site-specific determination due to insufficient data for both sectors. If "renewable" methane is used in 2050 (scenario RFS), the CO_2 emissions would remain more or less constant, since the main energy source is currently already natural gas. Therefore, it is assumed that these sites will be available as potential point sources in the future (Figure 11).

Discussion: the process-related CO_2 emissions shown above (Sections 6.1 and 6.2) for the sectors soda and carbon black are obtained from literature [14] and represent the overall process-related emissions of the respective sectors. The process-related CO_2 emissions reported from carbon black production exceed the absolute emissions in Table 8 by about 60 kt CO_2. It is possible that further plants are included in the data from literature or the data used for the determination differ from the one used here. This is not evident from the presentation of the data.

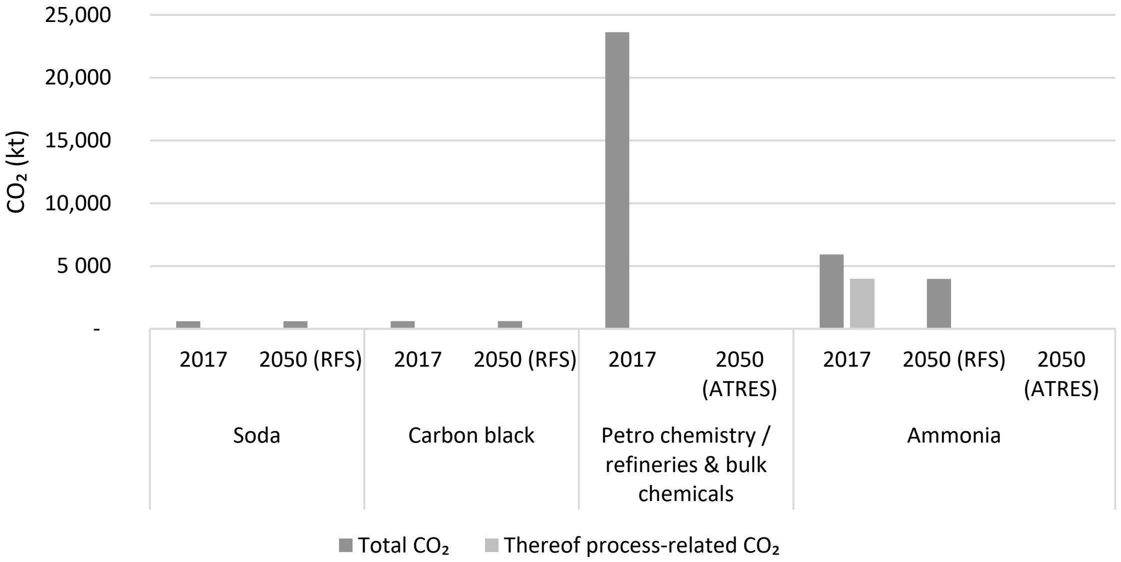

Figure 10. Total and process-related CO_2 of the chemical industry in 2017 and 2050 (RFS and ATRES).

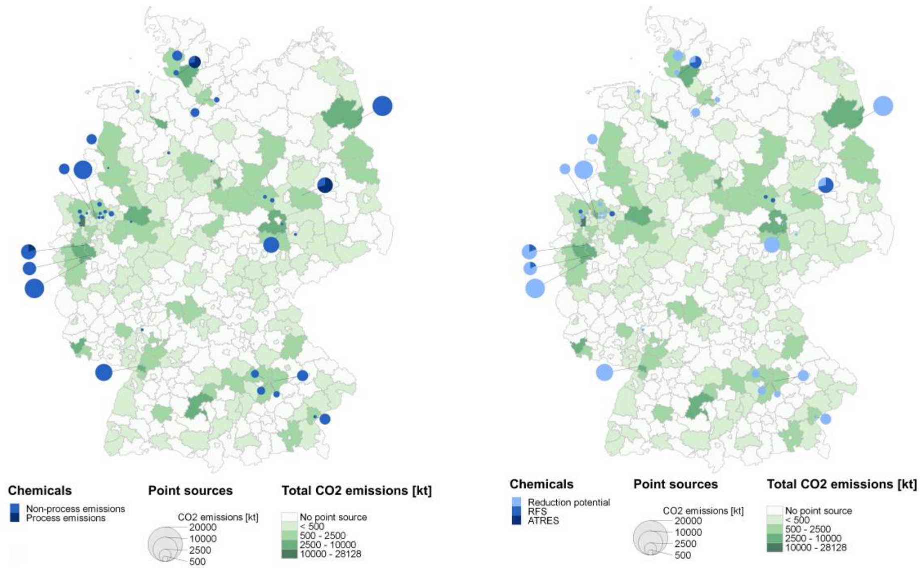

Figure 11. Distribution of CO_2 potential from the chemical industry in 2017 (**left**) and 2050 (**right**, scenario RFS and ATRES).

6.5.2. Petrochemistry, Refineries and Bulk Chemical Production

Results: these sectors dominate the total CO_2 emissions in 2017 within the chemical industry with an amount of approx. 32.6 Mt (Figure 10). The site-specific distribution of the chemical industry in 2017 is presented in Figure 11. The majority of point sources is related to the petrochemical sector and refineries. A presentation of the various facilities of the different sectors and the respective CO_2 emissions are given in the Supplementary Material. Apart from indeterminable process-related CO_2 from flares and decoking, these sectors emit energy-related CO_2 only. Therefore, these emissions might decrease to a negligible amount in 2050 (scenario ATRES) if the presented alternative technologies are implemented extensively (Figure 11). The figure shows the emissions for scenario RFS for ammonia, soda, and carbon black production since scenario RFS is not determined for the bulk chemical and petrochemical sector. A reduction potential cannot be shown in site-specific terms because these sectors have a large variety of processes and fuels and insufficient data is available to give a sound determination of remaining emissions in scenario RFS. If "renewable" methane is applied it can be assumed that the remaining absolute emissions will be below the value for 2017 (23,600 kt CO_2).

Discussion: the CO_2 potentials can be overestimated due to GHG emissions, e.g., CH_4 or N_2O, that cannot be sufficiently allocated, since several processes for the production of different substances are usually found at sites of the bulk chemical sector. The emissions from flares and decoking as described in Section 6.3 reflect the process-related emissions of these sectors. A precise site-resolved determination and presentation of these emissions is not possible due to missing data. Therefore, it must be assumed that an unspecified part of the amount reported as energy-related CO_2 is process-related.

6.5.3. Ammonia

Results: the overall emissions amount to about 6 Mt CO_2 in 2017 (Table 8). This sector has the second greatest contribution to the overall emissions from the chemical industry (Figure 10). Approximately 67% of these emissions are process-related and result from the steam reforming of mainly natural gas. Ammonia is produced at four different locations in Germany (Figure 11). The largest single emitter is found in Eastern Germany. The CO_2 emissions in the scenario RFS are comparable with the process-related emissions in 2017 (Figure 10). This is based on the assumption that process energy is provided by electricity and that "renewable" methane is used as feedstock for the reformation. The large-scale use of water electrolysis for the production of hydrogen would lead to negligible CO_2 emissions in 2050 (scenario ATRES).

Discussion: applying flat-rate proportions of process-related and energy-related CO_2 emissions to the absolute emissions from ammonia production might result in discrepancies within the stated proportions. This is the case if CO_2 emissions from, e.g., the periphery of the actual ammonia plant distort the distribution of process- and energy-related CO_2 emissions, as these do not result from the ammonia production process.

7. Pulp and Paper Industry

Below, the production of pulp and paper is discussed.

7.1. Process Description

For paper production, first, primary fibers (pulp and mechanical pulp) or secondary fibers (recycled pulp) are produced. Then pulp is provided by a chemical pulping and cooking process. Here, the fibers are separated from the wood by boiling in sulfurous acid or lye. The residues from this process, a mixture of lignin, cooking suds, and other dissolved wood substances, are thickened and burned (so-called black liquor). The provided energy is used for steam provision needed within the overall production process. The respective emissions reflect the biogenic CO_2 emissions of the paper industry. The chemicals are treated in a recovery boiler and returned to the elimination process. In mechanical pulping, the fibers are separated from the wood by grinding and are used to produce wood-like papers. Recycled pulp is produced by dissolving waste paper and subsequent deinking. The pulp is then processed in paper machines to produce different types of paper and, if necessary, refined.

In addition to biogenic fuels, fossil fuels such as coal or natural gas are also used for process steam generation. The CO_2 emissions resulting from paper production are energy-related.

7.2. Summary

Results: there are 44 facilities in Germany dedicated to pulp and paper production as well as veneer and chipboard production in 2017 (Figure 12). The majority produces paper, carton, and paperboard. Four facilities produce veneer, plywood, wood fiber, and chipboard, and two sites are dedicated to wood pulp and cellulose production. The locations of the different sites are homogeneously distributed. The total emissions of these sites sum up to roughly 9.5 Mt CO_2 in 2017 (Table 8). These emissions also contain biogenic CO_2 resulting from organic waste material occurring during different production steps of the pulp and paper provision.

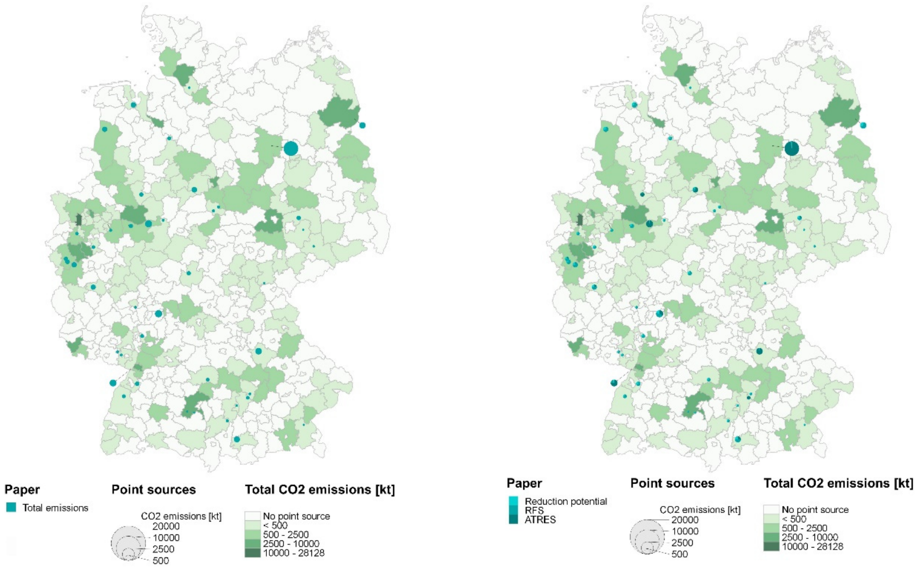

Figure 12. Distribution of CO_2 potential from pulp and paper industry in 2017 (**left**) and 2050 (**right**, scenario RFS and ATRES).

The total amount of CO_2 is caused by heat provision and no process-related emissions occur during the process. In case that "renewable" methane is used to substitute fossil fuels and the share of organic waste material remains constant overall emissions would sum up to 7778 kt of CO_2 in 2050 (scenario RFS). If the share of biogenic waste is constant and additional heat is provided by electric steam boilers the overall emissions in 2050 could be reduced to 4100 kt CO_2 (scenario ATRES). The distribution of the remaining CO_2 amount is shown in Figure 12. It can be seen that the number of point sources is strongly decreased compared to the situation presented in Figure 12, which is due to the large-scale application of electric heat supply.

Discussion: the biogenic proportion was not indicated for all the plants included in thru. By manual search, this data was supplemented where possible. The plants without explicit indication of biogenic emissions were assumed to be 100% fossil fuel-fired. The same applies to the sites from the register of installations. Therefore, it is possible that the biogenic share of the reported emissions is higher than shown in the results. As a result, there may be more emitters in 2050 (scenario ATRES and RFS) than those shown in Figure 12.

8. Conclusions

The aim of this paper is to determine the CO_2 emissions from the German industry as a resource for PtX applications in 2017 and potentially in 2050 for two different scenarios.

8.1. Overall Results

2017: the overall CO_2 emissions of the analyzed industrial sectors amount to approx. 143 Mt CO_2 in 2017. The largest proportion of 56.5 Mt CO_2 results from the iron and steel industry, followed by the chemical industry with about 40 Mt CO_2. The largest share of process-related emissions in 2017 results from the iron and steel industry, followed by the mineral industry (Figure 13). The largest number of emitters can be found in the glass and ceramics industry and in the chemical industry; thus, the various production sites and therefore the different emitter of the glass and ceramic are relatively small. The pulp and paper industry only emit energy-related CO_2 emissions.

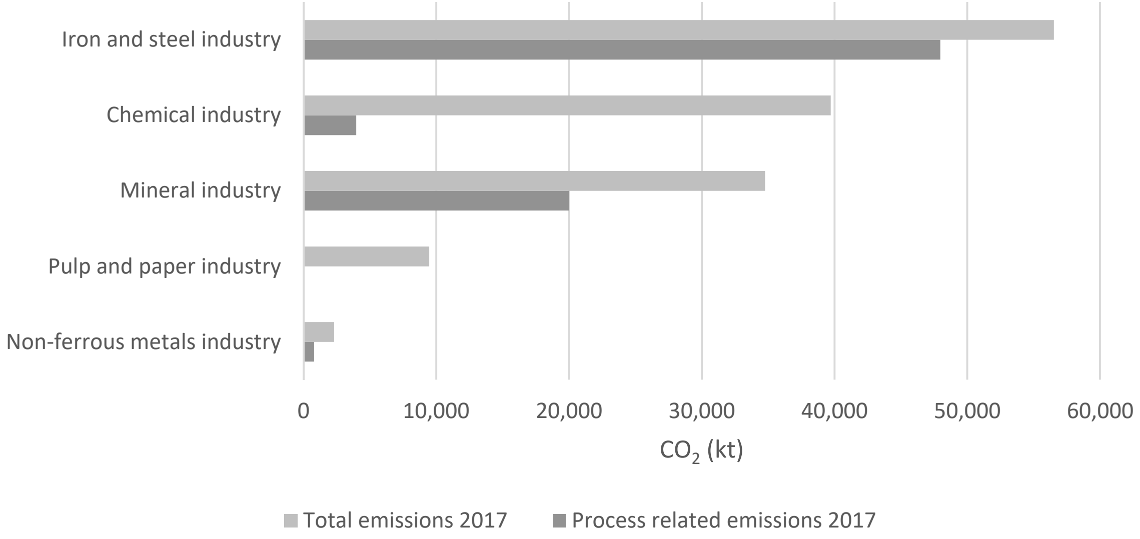

Figure 13. Total CO_2 and the respective share of process-related CO_2 of the analyzed industrial sectors.

The distribution of point sources in 2017 and the potential plotted on NUTS3 level is presented in Figure 14. An agglomeration of point sources can be seen in the Ruhr valley area. This is due to the relatively large proportion of industry (e.g., integrated steel mills and chemical parks) in this region.

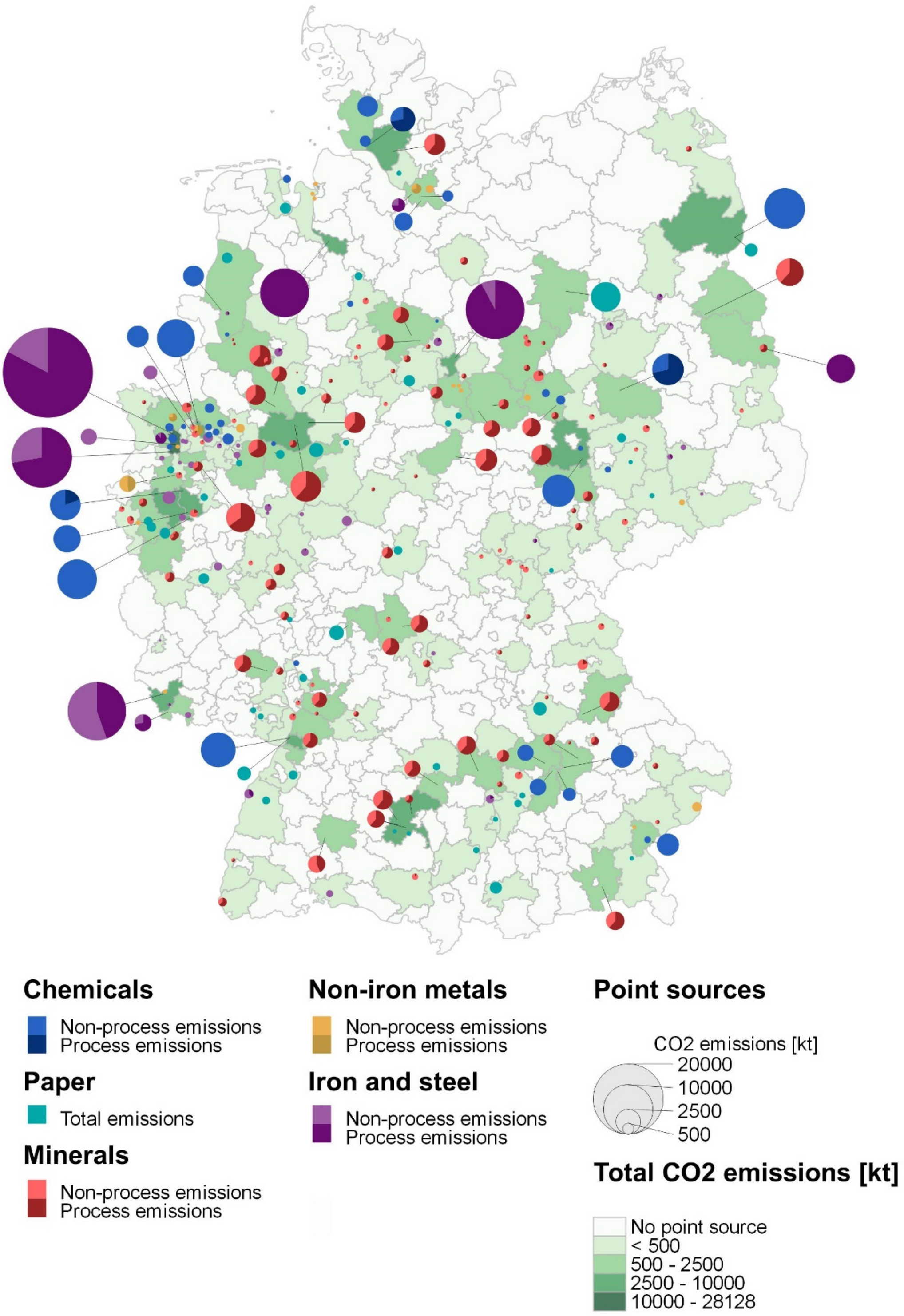

Figure 14. Distribution of CO_2 emissions from different industries in Germany in 2017.

2050: the development of CO_2 emissions in the respective scenarios is given in Figures 15 and 16. The overall emissions in 2050 can be decreased by approx. 77 Mt to 117 Mt CO_2 against the assumptions and framework made in this study. Scenario RFS shows a great proportion of biogenic CO_2 in 2050 due to the assumed extensive use of "renewable" methane for heat supply (Figure 16). The decrease in CO_2 emissions is particularly evident in scenario ATRES. In the mineral as well as pulp and paper industries, emissions will be reduced by about half compared to 2017, while in the iron and steel and non-ferrous industries, they will be almost completely reduced. Figure 15 shows the remaining CO_2 sources in 2050 if scenario ATRES is applied. The map shows a significant decrease in emissions if in 2050 the corresponding alternative technologies with a high CO_2 saving potential are fully implemented. The most significant reduction in potential point sources is in the chemical industry. The number of plants that will still be emitting CO_2 in 2050, if the corresponding technologies are applied on a large-scale, is small compared to the initial situation in 2017 (Figure 15)

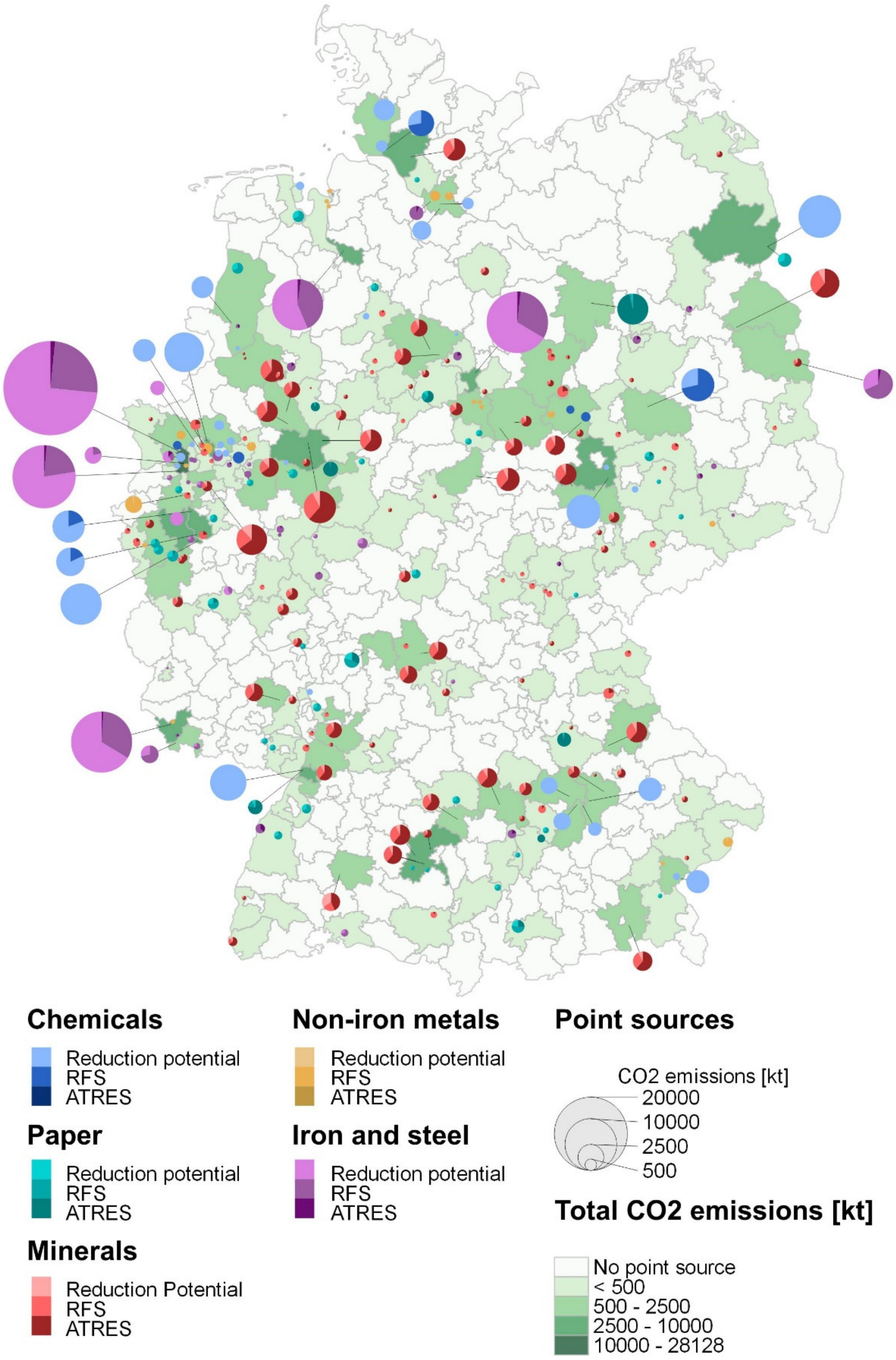

Figure 15. Distribution of CO_2 potential from different industries in Germany in 2050 (scenario RFS and ATRES).

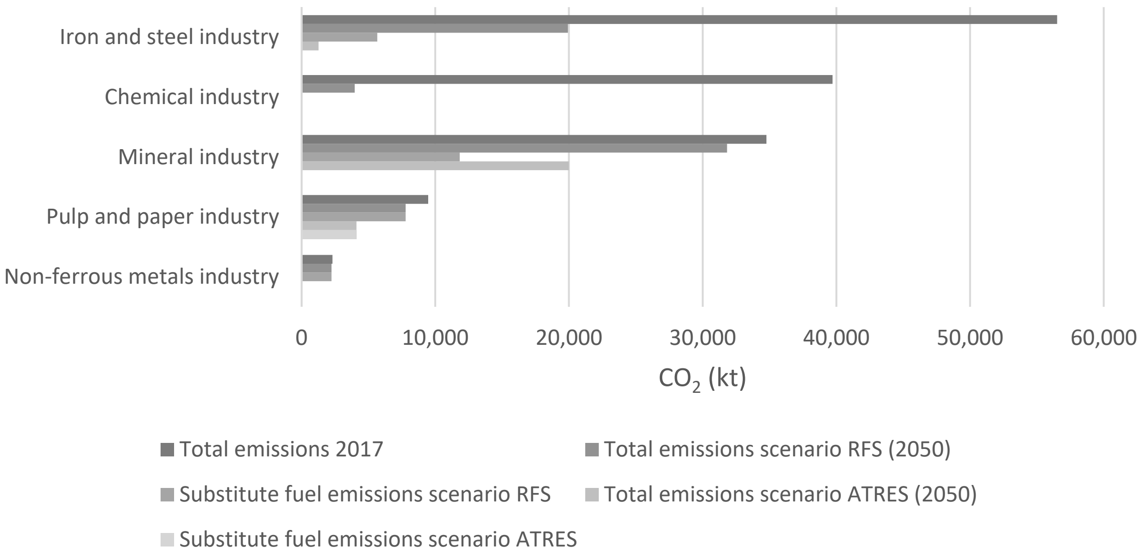

Figure 16. Development of total CO_2 emissions and biogenic CO_2 in 2050.

The potential to reduce or completely avoid these process-related emissions in the (near) future varies greatly by sector. Emissions from the mineral processing industry are currently difficult to reduce because there are no appropriate alternatives. In other industries, such as iron and steel production, technologies are already available, but not yet implemented on a large scale. In aluminum manufacturing, there are alternative production technologies that, however, do not yet go beyond the research and development status. Some of these technologies have been a subject of research for a very long time, without getting closer to any market launch.

In general, process-related emissions from all considered sectors might be reducible in the long-term perspective besides the mineral processing industry, especially the various applications of limestone, glass and ceramics.

Based on the results of the TRL and market penetration level of the respective alternative technologies it can be assumed that process-related CO_2 from the mineral sector will be available as feedstock in the long term. If biomass is implemented in the production of crude iron and steel (reduction agent, electrode material) as well as for the anode manufacturing in the aluminum industry these CO_2 emissions will also be available in the long term. If only hydrogen is used as a reduction agent, CO_2 from blast furnaces and iron sponge production will not be available in the future.

8.2. Comparison and Analysis of Results

In order to give a classification of the achieved results in comparison to other CO_2 emitters in Germany, Figure 17 shows the ratios of the amount of CO_2 emitted by the industries analyzed in 2017 compared to the amount of CO_2 emitted by the 10 largest German power plants in 2017 [7]. The total amount of CO_2 from power generation in these power plants is in the same order of magnitude as the emissions of the entire industrial sectors analyzed. It becomes apparent that CO_2 from the energy provision dominates the total German emissions. However, it also becomes obvious that CO_2 from the iron and steel industry has the greatest proportion compared to the other analyzed industries. The contribution of the non-ferrous metals industry is relatively small.

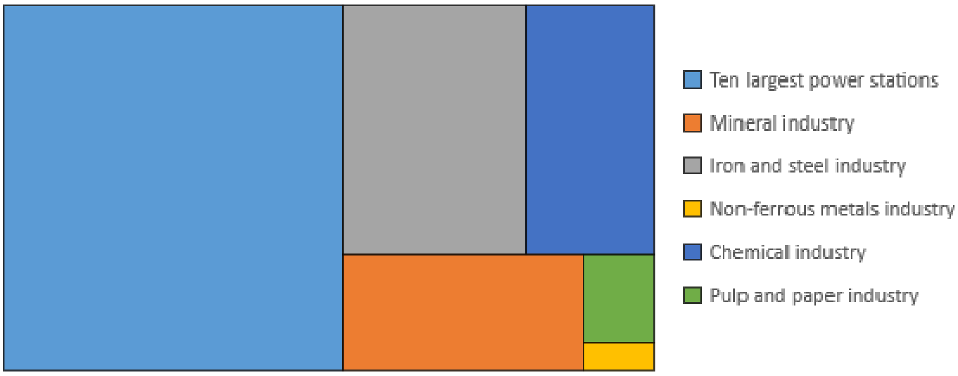

Figure 17. Ratio of CO_2 emissions from the industry analyzed to the CO_2 amount of the ten largest power plants in Germany.

The analysis and development of industrial CO_2 emissions was also addressed in other studies. The study CO_2 sources for PtX production in Germany [3] also gives an outlook on the expected CO_2 emissions in 2050, assuming a 95% reduction compared to 1990. The results show remaining CO_2 emissions of 10 Mt for the cement production and 4.5 Mt CO_2 emitted by the limestone and quicklime sector. The overall process-related emissions will decrease from 52 Mt in 2020 to 5 Mt in 2050 assuming an extensive application of carbon capture and storage (CCS). Metal production and processing is not considered a prioritized source of CO_2 in 2050. The chemical industry shows CO_2 emissions of 20 Mt in 2050 by the use of biomass for heat provision. In comparison, the results of this work show remaining emissions in cement production of 13.4 Mt to 20.2 Mt CO_2, depending on the applied scenario. Emissions from the limestone industry range from 8 Mt to approx. 6 Mt CO_2 in 2050. One possible explanation for the large deviation is the use of CCS in the study.

The economic aspects of CO_2 capture and utilization were not part of the scope here. Nevertheless, they have a great influence on the future situation, especially against the background of the progressive results of the scenario ATRES. It is highly uncertain whether and to what extent the alternative technologies discussed will be used by 2050. This is particularly critical against the background of the massive need for investment in the individual sectors. However, the study Climate neutral industry [16] shows that the investment requirements in the iron and steel (53% of blast furnace capacity), chemical (59% of steam cracker capacity) and cement industries (30% of the cement kiln capacity) in the years up to 2030 are high due to plant renewal, and therefore offer a certain chance of implementing these technologies. Therefore, a more detailed study of the economic aspects would be helpful in the future.

Assorting the location of the various CO_2 sources provides the basis for determining the potential of the raw material CO_2. Thus, the results for the site selection of Power-to-X plants, which require CO_2 as a raw material, can be used as a basis for the determination of the potential for the raw material CO_2.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-9276/9/12/149/s1, Table S1: Mineral industry, Table S2: Iron and steel industry, Table S3: NE-metal industry, Table S4: Chemical industry, Table S5: Pulp and paper industry.

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