

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**COMPILATION OF AN
INDUSTRIAL EMISSION INVENTORY FOR TURKEY**

M.Sc. THESIS

Ümmügülsüm ALYÜZ

Department of Environmental Engineering

Environmental Sciences and Engineering Programme

JUNE 2012

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FOREWORD

During the preparation period of this thesis I have groped toward a comprehensive view of all the constituents effectuate an Emission Inventory. The sectors in this thesis were chosen attentively with considering local parameters which represents conditions in which Turkey stands. The preparation period of the thesis took 3 semesters to organize all data, make calculations and summarize.

The emissions calculated in the thesis are not accurate emissions of the industries. The production and control technologies were derived from related industries web sites, annual reports, presentations, internship reports etc. If these were not sufficient for calculation, then concerned people were contacted via e-mail, fax or telephone. Nevertheless there was no adequate information for some industries to calculate emissions right, finally approximation method was used.

Emission factors listed in the study should not be used for other studies directly due to the inclusion of specific conditions in each emission factor.

In this thesis you will find not only my effort but also diligence of my thesis advisor, Prof. Dr. Kadir ALP, whom I should like to thank by spending lots of days with me by actively attending on calculations.

I also thank to my family for being behind me in every circumstances.

May 2012

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Environmental Engineer

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ABBREVIATIONS and ACRONYMS

°C	: Degrees Celsius
ACN	: Acrylonitrile
API	: American petroleum institute
BTX	: Aromatics (benzene, toluene, xylene)
CaCO₃	: Calcium carbonate
CBR	: Cis polibutadiene rubber
CH₄	: Methane
Cl₂	: Chlorine
CO	: Carbon monoxide
CO₂	: Carbon dioxide
Cr⁺⁶	: Hexavalent chromium
DAP	: Diammonium phosphate
DBM	: Dead Burned Magnesia (mgo), Sintered Magnesia
DCP	: Dicalcium phosphate
DEG	: Di ethylene glycol
EAF	: Electrical arc furnaces
EEA	: European environmental agency
EF	: Emission factor
EG	: Ethylene glycol
EO	: Ethylene oxide
EPA	: Environmental protection agency, USA
EUAS	: Electricity generation company, Turkey
FGD	: Flue Gas Desulphurisation
g/hr	: Grams per hour
H₂O	: Water
H₂S	: Hydrogen sulphide
H₃PO₄	: Phosphoric acid
HCl	: Hydrogen chloride
HCl	: Hydrochloric acid
HDPE	: High density poly ethylene
HNO₃	: Nitric acid
IEA	: International energy agency
IPCC	: Intergovernmental Panel on Climate Change
IPPC	: Integrated Pollution Prevent and Control
KCl	: Potassium chloride
kg/hr	: Kilograms per hour
kg/yr	: Kilograms per year
KOH	: Potassium hydroxide

LDPE	: Low density poly ethylene
LHV	: Low heating value
LLDPE	: Linear low density poly ethylene
MEF	: Ministry of Environment and Forestry
MEG	: Mono ethylene glycol
MENR	: Ministry of Energy and Natural Resources
MgCO₃	: Magnesit, magnesium carbonate
MgO	: Magnesia, magnesium oxide
µm	: Micrometer
N.D.	: No data
NE	: Not Estimated
N₂O	: Nitrous oxide
NaCl	: Sodium chloride
NaOH	: Sodium hydroxide
NH₃	: Ammonia
NMVOC	: Nonmethane volatile organic compounds
NO	: Nitric oxide
NO₂	: Nitrogen dioxide
NO_x	: Nitrogen oxides
NPK	: Compose fertilizer (nitrogen, phosphorus, potassium)
O₂	: Oxygen
PAH	: Polycyclic aromatic hydrocarbons
PAN	: Phtalic anhydride
PCB	: Polychlorinated biphenyls
PE	: Poly ethylene
PFCs	: Perflorocarbons
PM	: Particulate matter
PM₁₀	: PM emissions that are 10 µm in diameter or less
PM_{2.5}	: PM emissions that are 2.5 µm in diameter or less
POM	: Polycyclic organic matter
PP	: Poly propylene
PVC	: Poly vinyl chloride
SBR	: Styrene butadiene rubber
SCR	: Selective catalytic reduction
SNCR	: Selective non-catalytic reduction
SO₂	: Sulphur dioxide
SO_x	: Sulphur oxides
STPP	: Sodium tri poli phosphate
TCCU	: Thermal catalytic cracking unit
TEIAS	: Turkey electricity transmission corporation
TKI	: Turkey Coal/lignite Enterprise
TOC	: Total organic compound
tons/yr	: Tons per year
TSP	: Triple super phosphate
TUPRAS	: Turkey petroleum corporation

TurkStat : Turkish statistical institution
VOC : Volatile organic carbon
wt. : Weight

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COMPILATION OF AN INDUSTRIAL EMISSION INVENTORY FOR TURKEY

SUMMARY

The broad objective of this study is to examine air emissions of key industries of Turkey for 2010. The key industries are; energy production industries, petroleum refining, petrochemical industry (organic chemicals), inorganic chemicals industry (fertilizer, boron, soda ash, chromium oxides, acids), mineral products industry (cement, lime, magnesium oxide, carbide, glass), metallurgical industry (ferrous, non-ferrous metals), pulp and paper and sugar.

Main pollutant parameters considered in this study for the calculation of emissions are SO₂, NO_x, CO, NH₃, VOC, PM and CO₂ for uncontrolled and controlled conditions. The study employed an approach designed in three stages; activity data and emission factor search, emission factor analyzing and finally calculation of final emissions. Emission factor analyzing required aggregate and firmly analysis of sectors and subsectors and required deeper insights into the underlying specific production methods used in the industry to decide the most accurate emission factor.

Each of the industry was separated into two parts regarding to their emission emitting sources; process emissions and fuel consumption emissions and each of the sub-sector was calculated for both controlled and uncontrolled conditions. Unlike other studies or inventory reports, industries were evaluated as a whole with combining process and fuel originated emission sources in one pot. Thus, all emissions which were emitted by each sector was examined under a title. Production capacity and fuel consumption data were obtained from open sources.

In the development of industrial emissions, available source data was reviewed for flow chart of each local industry and related emission factors. There were no adequate information for some of the sectors, assumption method and most generalized emission factors were used with comparing final emissions with other countries' industries. Currently, some of the sectors had not default emission factors, in such cases emission factors were developed with using mass balances of the processes.

Regarding to results of the study, the most emission emitting sector was determined as energy production and cement industries. This result was compatible with fuel consumption of industries. Respectively, petrochemical, petroleum refining, metallurgical and pulp & paper industries had serious contributions to Turkey's air pollutants emission inventory.

Nowadays, determining national emission ceilings is a very important issue in the adaptation period of Turkey to the European Union. Therefore such studies should be maintained for determination of the ceilings with considering development up to 2030.

The study has several suggestions for further future research work; since the study focused on only the sectors determined as key categories; there is a need to broaden

the study to include other sectors like automotive and medical products.. In this study, time factor and resources constraint limited our scope. Second, it would also be interesting to conduct similar studies in other sectors.

TÜRKİYE İÇİN SEKTÖREL BİR EMİSYON ENVANTERİ OLUŞTURULMASI

ÖZET

Bu çalışmanın genel amacı, Türkiye’deki ana endüstriler için 2010 yılına ait bir hava kirletici emisyon envanteri hazırlamaktır. Hesaplar SO₂, NO_x, CO, NH₃, VOC, PM, CO₂ ana kirletici parametreleri için ve kontolsüz-kontrollü durumlar ile proses-enerji kaynakları için ayrı ayrı yapılmıştır. Bazı endüstriler için PM₁₀ ve PM_{2.5} parametreleri de hesaplanmıştır.

Bu çalışmada değerlendirilen ana endüstriler; enerji üretimi, petrol rafinasyonu, petrokimya endüstrisi (organik kimyasallar), inorganik kimya endüstrisi (gübre, bor, soda külü, krom kimyasalları, asitler), mineral endüstrisi (çimento, kireç, magnezyum oksit, karpit, cam), metalürji endüstrisi, kâğıt ve karton, şeker endüstrileri olarak belirlenmiştir.

KontROLSÜZ durum; hava kirletici emisyonların giderimi için herhangi bir kontrol teknolojisinin uygulanmadığı, emisyonların direk olarak atmosfere verildiği durumu temsil ederken, kontrollü durum bu emisyonlar için bir kontrol teknolojisinin uygulanması sonucunda azaltılmış emisyon durumunu temsil etmektedir.

Her bir endüstri, emisyon yayma kaynaklarına göre proses emisyonları ve yakıt tüketimi kaynaklı emisyonlar olmak üzere ikiye ayrılmıştır ve her bir alt sektöre ait kontrollü ve kontROLSÜZ durum emisyonları hesaplanmıştır. Proses emisyonları hesaplanırken olabildiğince yanma kaynaklı emisyonlardan ayırtedilmeye çalışılmış, çimento sektörü gibi net bir ayrımın mümkün olmadığı sektörlerde ise o sektör için özel bir yaklaşım benimsenmiş ve ilgili bölümde açıklanmıştır.

Diğer çalışmalar ve emisyon envanterlerinden farklı olarak, endüstriler proses ve yakıt kullanımı kaynaklı emisyonları da içerecek şekilde bir başlık altında değerlendirilmiştir. Böylece, bir sektör tarafından yayılan bütün emisyonlar bir başlık altında incelenebilmiştir. Üretim verisi ve yakıt kullanımı ile ilgili veriler, halka açık kaynaklardan derlenmiştir. Elektrik üretimi kaynaklı emisyonların hesabı için ilgili veriler EÜAŞ (Elektrik Üretimi Anonim Şirketi)’nden istenmiştir. Bazı veriler ise kurumlardan ve/veya kişilerden istenmiştir.

Alt sektörlerle ait yanma emisyonlarını hesaplamak için gereken yakıt tüketimi verisi mevcut olmadığı için, bu sektörlerle ait yanma emisyonları her bir bölümün sonunda toplu olarak hesaplanmıştır. Bazı alt sektörlerle ait yakıt miktarı verisine ulaşılabildiği için bu alt sektörlerin spesifik yakıt yanması kaynaklı emisyonları incelenmiş fakat bölüm sonundaki hesaplamalar içine dahil olduğu için, yalnız o sektöre ait bilgilendirme olması amacıyla verilmiştir.

Çalışmada üç aşamalı bir yaklaşım benimsenmiştir; emisyon faktörü araştırması, emisyon faktörü analizi ve nihai emisyonların hesaplanması. Emisyon faktörü analizi süreci, en doğru emisyon faktörüne karar verebilmek amacıyla, sektör ve alt sektörlerin üretim yöntemlerinin detaylı olarak incelenmesini ve spesifik üretim yöntemlerinin anlaşılmasını gerektirmiştir.

Endüstriyel emisyonların hesaplanması aşamasında sektörel veri kaynakları; o endüstriye ait akım şemaları ve spesifik emisyon faktörleri bakımından değerlendirilmiş ve emisyon faktörüne karar verilme aşamasında birçok kaynaktan faydalanılmıştır. Örneğin bir tesis için emisyon hesabı yapılmadan önce mevcut bütün kaynaklardan faktör taraması yapılmış, daha sonra mevcut tesisin prosesi ile en uyumlu olanı emisyon faktörü seçilmiştir. Bazı sektörler için yeterli bilgi yoktur, bu durumda ise yaklaşım metodu uygulanmıştır ve benzer ülkelerde o endüstriler için uygulanmış ve genelleştirilebilir emisyon değerleri ve üretim miktarlarından hareketle veya sıfırdan oluşturulmak suretiyle hesaplanan emisyon faktörleri kullanılmıştır. Emisyon faktörüne hiçbir şekilde ulaşamayan bazı sektörler için ise, o endüstriye ait kütle dengeleri kullanılarak emisyon faktörü geliştirme yoluna gidilmiştir.

Emisyon faktörü kaynağında kontrollü durum emisyon faktörü verilmemişse, ilgili prosesler için Türkiye koşullarına uygun olarak bir kontrol teknolojisi belirlenmiş ve bu teknolojinin arıtma verimine göre kontrollü durum emisyonu hesaplanmıştır.

Elektrik üretimi kaynaklı CO₂, SO₂ ve PM emisyon faktörleri literatürden alınmamış, tesislere ait veriler kullanılarak oluşturulmuştur. Ayrıca linyit kaynaklı tesisler için emisyonlar termik santral bazında hesaplanmıştır. Linyit yakıtlı elektrik üretim tesislerinin 2010 yılına ait yakıt özellikleri resmi yollardan istenilerek, CO₂ ve SO₂ emisyonlarının hesaplanması aşamasında, tesis bazında emisyon faktörleri oluşturulmuştur.

Bu çalışmanın sonucunda, en çok emisyon yayan sektörler sırasıyla enerji üretimi, çimento endüstrisi, demir çelik ve kimya endüstrisi olarak belirlenmiştir. Daha sonra sırasıyla petrol rafinasyonu, metalürji, kağıt ve karton endüstrilerinin Türkiye'nin emisyon envanterine ciddi oranda katkıda bulundukları görülmüştür.

Tezin 'Sonuçların Değerlendirilmesi' başlıklı bölümünde ise çalışmanın sonuçları daha önce yapılmış olan çalışmalarla ve başka ülkelerin 2010 yılı ulusal emisyon envanterleri ile kıyaslanmıştır. Böylelikle bu çalışmanın diğer çalışmalar arasındaki konumu ile Türkiye'nin diğer ülkeler arasındaki konumu hakkında kıyaslama yapma imkanı bulunmuştur.

Bu çalışmanın sonuçlarını kıyaslamak amacıyla kullanılan en önemli kaynaklar Tük (Türkiye İstatistik Kurumu) tarafından her yıl hazırlanan ve Türkiye'nin taraf olması dolayısıyla, Birleşmiş Milletler İklim Değişikliği Çerçeve Sözleşmesi kapsamında Birleşmiş Milletler'e sunulan sera gazları ile ilgili Ulusal Emisyon Envanteri ile Birleşmiş Milletler Avrupa Ekonomik Komisyonu (UNECE) bölgesini kapsayan Uzun Menzilli Sınırlar Ötesi Hava Kirliliği Sözleşmesi (LRTAP) kapsamında sunulan hava kirlleticileri ile ilgili emisyon envanteridir. tezin hazırlanması aşamasında bu ulusal emisyon envanterlerinden Tük'in hazırlamış olduğu envanter en son 2010 yılı için, LRTAP'a sunulan envanter ise 2009 yılı için mevcuttur. Kıyaslama sonuçları detaylı olarak 'Hesaplama Sonuçları' bölümünde verilmiştir.

Türkiye için hazırlanmış bu envanterlerin incelenmesi sonucunda, TÜİK tarafından hazırlanan envanterin proses kısmında mineral endüstrisinin detaylı olarak incelendiği, petrol rafinasyonunda yalnız 3 parametrenin incelendiği (CO₂, NO_x, CH₄), demir çelik ve şekerde ise yalnız birer parametrenin incelendiği görülmüştür. LRTAP için hazırlanan envanterde ise SO_x, NO_x, NMVOC, NH₃, N₂O parametrelerinin incelendiği, proseslere detaylı olarak bakıldığında ise her bir alt sektör için en fazla 6 parametrenin incelendiği görülmüştür. Bu çalışmada ise, PM dahil, ilgili bütün parametrelere, emisyon faktörleri bulunabildiği ve/veya

geliştirilebildiği ölçüde, hem kontrollü, hem de kontrolsüz koşullar için yer verilmiştir.

Avrupa Birliği'ne katılım sürecinde olan Türkiye için ulusal emisyon tavanı belirleme çalışmaları günümüzde oldukça önemli bir konudur. Bu nedenle, 2020 yılına kadar olan emisyon tavanımızı belirlemek amacıyla bu tarz çalışmaların sürdürülmesi faydalı olacaktır.

Bu çalışma sadece sektörel bazda emisyonlara yoğunlaşmıştır ve bu çalışmanın sonuçlarını ileriye taşımak için kapsamı genişletilip otomotiv, ilaç gibi sektörler ilave edilebilir. Ayrıca bu çalışmada zaman faktörü ve veri kaynaklarının kısıtlı olması nedeniyle çalışmanın alanı belli sektörlerde sınırlı kalmıştır.

1. INTRODUCTION

The industrial revolution is a major turning point in growing history of countries and also environmental history. The most important benefits are not only having a good financial welfare, but also increasing culture and easily access power to basic human needs. Of course it would also have some side effects like increasing working hours, child labour and environmental pollution.

Environmental pollution can be in five forms; air, water, soil, air noise and light pollution. Air pollution is one of the most important pollution types which is contamination of air by some of chemical, physical or biological agent that modifies the natural characteristics of the atmosphere [1]. Burning of fossil fuels in electricity generation, transport, industry and households, industrial processes and solvent use, for example in chemical and mineral industries, agriculture, and waste treatment are the anthropogenic sources of air pollution. Also there are natural sources of air pollution such as windblown dust and emissions from plants.

The important effect of the air pollution is damage to the atmosphere and man. Evidence of increasing air pollution is seen in lung cancer, asthma, allergies, and various breathing problems along with severe and irreparable damage to flora and fauna. By reducing air pollution levels, we can help countries reduce the global burden of disease from respiratory infections, heart disease, and lung cancer [1].

Important air pollutants are carbon monoxide (CO), lead (Pb), nitrogen dioxide (NO₂), ozone (O₃), particulate matter (PM), and sulphur dioxide (SO₂). These 6 common found pollutants are named as “criteria pollutants” by EPA because EPA regulates them by developing human health-based and/or environmentally-based criteria (science-based guidelines) for setting permissible levels. The set of limits based on human health is called primary standards. Another set of limits intended to prevent environmental and property damage is called secondary standards [2].

The other important air pollutants are carbon dioxide (CO₂), Lead (Pb), Mercury (Hg), Hydro chlorofluorocarbons (HCFC), Volatile Organic Compounds (VOCs), Aerosols and Asbestos.

This study estimates the approximate amounts of air pollutants emitted by Turkish industries for controlled and uncontrolled conditions.

1.1. Importance of the Thesis

Air pollution as a one form of environmental pollution is an important issue since industrial revolution after understanding its effects to both human and environment and makes it a global problem which should be solved by all the countries. Therefore countries started to look for collaborations and take some decisions about this issue. The collaborations generally require abatement promises and require identifying current emissions and future emissions by applying some scenarios.

The first step is quantifying the present emissions by emission inventories by including all emission sources of the country or region. Then future scenarios are determined and future emissions are calculated to see the progress. Finally emission ceilings and emission reduction strategies are identified and necessary measures are taken. Emission inventories should be prepared in specific time intervals, commonly annual, to follow the process. Also these calculations should be supported by air quality measurements and parties should struggle to prepare more realistic, containing more details emission inventories.

Turkey as a candidate of European Union has to harmonize its legislation with EU legislation. Related with this subject, studies on National Emissions Ceilings Directive (NECD) are being conducted nowadays. Emission inventories and emission projections, Regulatory Impact Assessments, establishing long term air quality strategies, and generating procedures for corporate structure, technical capacity are being conducted.

Also there are some annual reporting requirements of national total emissions of greenhouse gases and air pollutants in response to obligations under international conventions and protocols; United Nations Framework Convention on Climate Change (UNFCCC) for greenhouse gases and to the UNECE Convention on Long-Range Transboundary Air Pollution (LRTAP) for air pollutants.

Turkey prepares an annual emission inventory to submit UNFCCC (a treaty leads to Kyoto Protocol that sets mandatory emission limits for the parties signed the protocol) for CO₂, CH₄, N₂O, HFCs, PFCs, NO_x, SO_x, NMVOC, CO emissions for both energy and industrial processes. 2010 emission inventory is submitted in 13 April 2012. CO₂, CH₄, N₂O, CO, NO_x, NMVOC emissions are calculated for all of the energy industries; however SO_x emissions are calculated for only public electricity production industry. The air pollutant parameters calculated for industrial processes are less than energy industries; CO₂ emission is calculated only for cement, lime and iron and steel industries, NO_x emission is calculated only for petroleum refining, asphalt, road and glass industries. CO is calculated only for petroleum refining, soda ash and asphalt industries; NMVOC is calculated only for mineral, sugar and petroleum refining industries. N₂O, NH₃, CH₄ and PM emissions are calculated for neither of the process industries. That is why there is a need for a detailed emission inventory for aforementioned pollutants.

Turkey is also a party to the Long Range Air Pollution Convention and has to submit annual emission inventories on SO₂, NO_x, NMVOC, CH₄, CO, NH₃, various heavy metals and POPs according to this convention, nowadays 2009 emission inventory exists and includes both energy and process emissions for the mentioned pollutants. This study is not including PM emissions, too.

There are some other studies about emission inventories generally about energy industries or industrial emissions for a region or for large emission emitting sources. Up to now, there is no actual study investigates air pollutions of sub-sectors for all of these parameters for both of controlled and uncontrolled conditions.

Finally this thesis includes following unique points;

The industries are separated into two parts as process and fuel combustion emissions. CO₂, CH₄, N₂O, NH₃, NO_x, SO_x, NMVOC, CO, TSP, PM₁₀, PM_{2.5} emissions are calculated for each of the industry, if such an emission is emitted from the industry. So this study includes all sub-sectors which don't have calculated emissions.

Unlike other studies, uncontrolled condition is investigated for each of the sub-sector and existing and/ or possible abatement technologies are used for the calculations of controlled emissions.

Turkey specific emission factors are used for electricity production related CO₂ and SO₂ emissions. Emission factors are estimated for each of the plants and emissions are calculated for each of the plant.

Final emissions are compared with other studies and countries to see the place of the study and Turkey.

1.2. Objective

The objective of this study is to calculate air pollutant emissions, especially CO₂, PM, PM₁₀, PM_{2.5}, SO₂, CO, NO_x, NMVOC, VOC, CH₄, and N₂O, of industries in Turkey for year 2010 by separating source of emissions into two sub-categories as processes and fuel combustion activities and for controlled and uncontrolled conditions.

In addition to former investigations about industrial emissions of Turkey, this thesis aims to calculate air emissions of each specific sector to look to industrial pollution from a detailed window. Up to now, there is no actual study investigates air pollutions of sub-sectors for all of these parameters for both of controlled and uncontrolled conditions.

Abatement technologies are decided by considering the industrial structure of the Turkish industry. If there is adequate information about the emission control technology used in the industry, then emission factor is selected / generated for this technology, otherwise a control technology is assumed and explained in the process emissions section of each sub-sector.

1.3. Scope

The emission inventory is prepared for the industries located in Turkey.

The industries investigated in the thesis are divided into two sections. First one is energy industries and second one is industrial processes. Then each of the sub-sectors is investigated for both controlled and uncontrolled conditions.

Energy industries are divided into two sections; public electricity and heat production, and energy use in the industry.

Industrial processes are divided into seven sections;

Organic Chemicals Industry: Carbon black, Synthetic rubber, SBR and CBR, Styrene-Butadiene copolymer production, Ethylene – Propylene, Aromatics – BTX, Vinyl chloride monomer (EDC/VCM), Ethylene oxide – Ethylene glycol (EO/EG), Acrylonitrile (Vinyl Cyanide), Phthalic Anhydride, Poly Ethylene (LDPE – HDPE – LLDPE), Polypropylene, Polystyrene, Polyvinyl Chloride, Synthetic Fibre and Yarn, Formaldehyde, Isopropyl Alcohol, Methanol, Ethanol, Soap, Detergents, Paint, Varnish and Ink.

Inorganic Chemicals Industry: Boron Compounds, Soda Ash, Chromium Oxides, Primary Magnesium Production, Fertilizer (Ammonium sulphate, Ammonium nitrate, Urea, Triple super phosphate, Diammonium phosphate, Compound fertilizer), Inorganic Phosphates (Sodium tri poly phosphate, Dicalcium Phosphate), Sulphuric Acid, Phosphoric Acid, Hydrofluoric Acid, Chlor Alkali, Hydrochloric acid, Ammonia, Nitric Acid.

Mineral Products Industry: Cement, Clay, Lime, Glass, Magnesium Oxide (Magnesia), Refractor, Calcium Carbide

Metallurgical Industry: Iron and Steel Industry -Integrated Steelworks, Metallurgical coke production, Electrical arc furnaces, Foundries - Non-Ferrous Metal Industry, Ferroalloys, Aluminium (Primary aluminium production, Secondary aluminium production, Aluminium foundries)

Wood Products Industry: Pulp and paper

Petroleum Refining Industry

Food and Beverages Industry: Sugar

2. LITERATURE REVIEW

Current knowledge about emissions of sectors in Turkey is investigated in this section to see methodological, theoretical approach of former studies. For this purpose, master theses, scientific articles, unofficial reports, national inventory reports are examined.

In 2004, the United Nations Framework Convention on Climate Change (UNFCCC) and in 2009, The Kyoto Protocol were ratified by Turkey. As an Annex I party to Convention, Turkey is required to develop annual inventories on emissions and removals of greenhouse gases (GHG), not controlled by the Montreal Protocol, using the Intergovernmental Panel on Climate Change (IPCC) methodology and sent to the UNFCCC Secretariat. In this context, the most important study is National Inventory Report (NIR) and common reporting format (CRF) tables which are prepared by Turkey Statistical Institute (TurkStat) – includes same emission values - and sent to the UNFCCC Secretariat by TurkStat as the focal point of Turkish National Emission Inventory. Turkey prepared its NIR and CRF tables for the period 1990 – 2004 and submitted to UNFCCC secretariat in 2006. This year, the 2010 report is submitted in 14.04.2012 [26]. Emissions of the six direct greenhouse gases were covered in this report, which are: CO₂, CH₄, N₂O, HFC, SF₆, and PFC. Also following four indirect greenhouse gases are reported: NO_x, CO, NMVOC, and SO₂. In this study, results are compared mainly with National Inventory Report of Turkey.

Turkey is also a party to the Long Range Air Pollution Convention, therefore annual emission inventories on SO₂, NO_x, NMVOC, CH₄, CO, NH₃, various heavy metals and POPs according to this convention has to be submitted. Nowadays 2009 emission inventory exists and includes both energy and process emissions for the mentioned pollutants. This source is used for comparisons in this study.

Also there are some scientific articles related with the subject of this study. Scientific articles were listed using Science Direct databases with using “emission” and “Turkey” keywords in the title section. Additionally Web of Science database listing system was used for the “emission” and “inventory” keywords in the topic and

filtered “Turkey” as the country. Articles published before 1988 are not considered, because they are not up to date.

Master theses were listed with using National Council of Higher Education Online Thesis Centre [23] and listed theses were chosen with considering their conformity with this thesis’ topic. There were lots of theses for transportation, domestic heating sectors but these sectors are not calculated within this study, therefore related literature was not listed in this study.

Regarding to results of this literature review, there is no thesis directly related with the subject of industrial emission inventory development. Industrial emissions are calculated in some of the theses but not cover all industrial sectors. However there are 2 theses on the subject of ‘emission inventory development for Turkey’. One of them is prepared in 1991 by Palaogulları G., (1991) and not compatible with current data, therefore is not considered within this study. The second one is prepared by Agacayak T., (2010) [24] which is an inclusive thesis and include general emission emitting sources, also industrial sources. However, industrial emissions are calculated only for crude oil refineries, iron and steel industry, cement, pulp and paper industry. Other industries are not included in the thesis. The results of these theses are evaluated for comparisons in specific industrial chapters of this study.

Elbir et al. (2000) [52] prepared an article with the name of ‘*Evaluation of some air pollution indicators in Turkey*’. In this study, a national emission inventory was prepared by using the European emission factors for four main source categories (domestic heating, industry, power generation, and traffic) with respect to five major pollutants consisting of particulate matter (PM), SO_x, NO_x, NMVOCs and CO with 5-year intervals between 1985 and 2005. Also results are compared with Europe by using indicators such as emissions per unit area and emissions per capita.

Muezzinoglu A. et al. (1998) published an article with the name ‘*Inventory of emissions from major air pollutant categories in Turkey*’ in Environ. Eng. and Policy 1, 109–116 Q Springer-Verlag. In this study, an inventory of air pollutant emission estimates from major air polluting sources in Turkey for period between 1985 and 2005 with 5-year intervals were estimated. Inventory covers anthropogenic sources of five major air pollutants of PM, SO_x, NO_x, NMVOCs, CO. Their breakdown with

respect to main activity sectors was shown and their distribution by the largest industrial source categories was worked out as annual estimates.

Akbostanci et al. (2011) has an article with the name of *CO₂ emissions of Turkish manufacturing industry: A decomposition analysis*. Applied Energy 88 (2011) 2273–2278, Elsevier. In this study, CO₂ emissions of Turkish manufacturing industry are calculated by using the fuel consumption data at ISIC revision 2, four digit level. The study covers 57 industries, for the 1995–2001 period. Only fuel combustion related CO₂ emissions are covered in this study.

Rest of the theses is designed for specific industries of Turkey or only for a region. They are mainly used in this study for reference or comparison. Most of them are prepared for emissions from energy utilization. There are some other theses prepared for electricity production; the most related ones are listed below with considering their conformity with this study and methodology.

Ari (2010) [25] has a master thesis with the subject of “*Investigating the CO₂ emission of Turkish electricity sector and its mitigation potential*” in which generated electricity associated CO₂ emissions and the specific CO₂ emission factors are calculated based on IPCC methodology for each fuel type and each thermal power plant for Turkey between 2001 and 2008 and some scenarios are applied for 2011-2019 to evaluate the best scenario in terms of mitigation of CO₂ emissions.

“*Determining regional current carbon dioxide emissions based on electricity production and its long term forecast for Turkey*” is prepared by Saime Yeşer Aslanoglu as an MSc thesis in 2011 in Hacettepe University in consultation with Ass. Prof. Merih Aydınalp Köksal. In this thesis study current and planned electricity generation and associated CO₂ emissions, and scenarios on CO₂ emission reduction due to use of coal gasification have determined regionally. However, generated emission factors are given in region basis and not given for specific plants, and calculated emissions are valid for a region or overall and valid for a wide time range 2001-2020. The results of the study are used only for the comparison of the results found in this study.

Scientific articles related with electricity production in Turkey are investigated and evaluated below. Generally IPCC Tier 1/2 methods are used in these studies generally for only CO₂ or SO₂ emissions. Only 2 of the studies covers all air

pollutants emitted during electricity generation activities but one of them is prepared for the reference year 1987 by Tasdemiroglu (1992) and the second one covers only emissions of lignite-fired power plants of Turkey and published by Vardar et. al., (2010). Articles are listed below with the specific notes about their contents.

Ari and Koksall (2011) have an article with the name of *Carbon dioxide emission from the Turkish electricity sector and its mitigation options*. Energy Policy 39 (2011) 6120–6135, Elsevier. This is a ‘derived from thesis article’ and evaluated in Section 5.1.

Tunc et al. (2009) have an article as *a decomposition analysis of CO₂ emissions from energy use: Turkish case* and published in Energy Policy 37(2009)4689–4699. CO₂ emissions of each sector are calculated with using decomposition method. Unfortunately, industrial emission details are not clear in this study.

Tasdemiroglu (1992) has an article as *Air pollutant emissions due to energy utilization in Turkey*, Energy Vol. 17, No. 1, pp. 95-97, 1992, Britain. Pollutant emissions due to fossil fuel and biomass energy utilization in Turkey have been estimated. Standard emission factors were used for estimating the levels of PM, SO_x, NO_x, CO, VOCs and aldehydes. The results are presented for different fuels and energy consuming sectors for the reference year 1987. This study is not current and does not reflect today industry.

Vardar et al. (2010) have an article as *Emissions estimation for lignite-fired power plants in Turkey*, Energy Policy 38 (2010) 243–252, Elsevier. The major gaseous emissions (e.g. SO_x, NO_x, CO₂, CO), some various organic emissions (e.g. benzene, toluene and xylenes) and some trace metals (e.g. arsenic, cobalt, chromium, manganese and nickel) generated from lignite-fired power plants in Turkey are estimated. The estimations are made separately for each one of the thirteen plants that produced electricity in 2007, because the lignite-fired thermal plants in Turkey are installed near the regions where the lignite is mined, and characteristics and composition of lignite used in each power plant are quite different from a region to another. Emission factors methodology is used for the estimations. The emission factors obtained from well-known literature is then modified depending on local moisture content of lignite.

Energy consumption and CO₂ emissions in Turkey: Empirical analysis and future projection based on an economic growth (Energy Policy 34 (2006) 3870–3876) is the article of Say (2005). The CO₂ emissions are calculated in two methods, one includes economical approach and not related with the subject of this thesis and the second one is the calculation of CO₂ emissions by IPCC Tier 2 method.

The other article of Say (2006) is *lignite-fired thermal power plants and SO₂ pollution in Turkey* (Energy Policy 34 (2006) 2690–2701, Elsevier). The related part of the study is calculation of SO₂ emissions regarding to IPCC method. Results of the study are evaluated for comparison in Section 5.1.1.2.

Articles presented in conferences, national symposiums and not published in peer-reviewed journal as a scientific article are listed in this section. It should be noted that, these listed articles does not cover all despite of limited constraints to achieve symposium or other related books online.

Can, and Atimtay (2004) has a study as Carbon Dioxide Emission Inventory for Turkey. "13th World Clean Air and Environmental Protection Congress", 1, p.Paper # 148. In this study, CO₂ emission data for the year of 1995 to 2000 from the households, manufacturing industry, thermal power plants and road vehicles were calculated for all 910 districts of Turkey and this has been investigated by using Geographic Information System (GIS) techniques. The emission of CO₂ was calculated by using the IPCC Tier 1 method.

Tunc et al. (2006) has the publication as *CO₂ Emissions vs. CO₂ Responsibility: an Input-Output Approach for the Turkish Economy*. ERC Working Papers in Economics 06/04. In calculation of CO₂ emissions of different types of fuels Intergovernmental Panel on Climate Change (IPCC) manual is used for each sector.

Generally iron and steel, cement, leather and petroleum refining industries' air pollution capacity is investigated by emission inventory studies.

Chaudhary and Atimtay (2004) have a study as Management of Air Quality in Iron-Steel Industry Region in South-Eastern Turkey and Emission Inventory of Several Pollutants. "13th World Clean Air and Environmental Protection Congress", 1, p.Paper # 114. In this study, an emission inventory has been done in Iskenderun region for the first time. The types of sources included in this study were industrial, domestic heating and traffic on intercity as well as urban roads. Pollutants included

were PM, SO₂, NO_x, and CO. The emissions from industrial sources were determined by stack gas measurements and from domestic and traffic sources emissions were calculated by using emission factors.

Elbir et.al. (2008) has a study as *VOC emissions from petroleum storage tanks*. Air pollution and control national symposium, 2008. Fugitive volatile organic compound (VOC) emissions from storage tanks and from land/sea based petroleum product transfer (filling/emptying) operations associated with tankers were estimated at TUPRAS refinery located near Aliaga, Izmir, Turkey. Fugitive VOC emissions from 155 storage tanks in refinery were estimated using the TANKS model by EPA. VOC emissions associated with product transfer operations were also estimated using an EPA method.

Additionally in some studies specific industrial emission factors are derived; Canpolat, B.R., Atımtay, A.T., Munlafalıoğlu, İ., Kalafatoğlu, E. and Ekinci, E., Renewed Emission Factors of Cement Industry in Turkey. "Second International Symposium on Air Quality Management at Urban, Regional and Global Scales", 1, (2001), p.587-594.

Finally, as a result of this literature review, there is not a study investigates air pollutant emissions on a detailed industrial sub-sector based for controlled and uncontrolled conditions.

3. MATERIALS AND METHOD

Method of the study is summarized in four steps and used materials are summarized within each step. Also some important points are explained at the end of the section.

In the initial step, key categories were determined by investigating former studies, other countries' emission inventories and national emission inventory (NIR) of Turkey [26] which is prepared by TurkStat every year. A key category as a source or sink category that is prioritized within the national inventory system because its estimate has a significant influence on a country's total inventory in terms of the absolute level of emissions, the trend in emissions, or both". By definition, key categories include sources that have the greatest contribution to the absolute level of national emissions [9].

Some of the sectors are not included in NIR Turkey 2010 [26], therefore industries were generally investigated from the 9th Development Reports of Prime Ministry, State Planning Organisation General Directorate for Economic Sectors and Coordination Industry Department, thus other important industries were added to the key categories list with considering each industry's production amounts and possible pollution potentials.

Finally selected key categories: Public electricity production, Sectoral energy production, Oil refineries, Organic Chemical Industry (Carbon black, Synthetic rubber, SBR and CBR, Styrene-Butadiene copolymer production, Ethylene – Propylene, Aromatics – BTX, Vinyl chloride monomer (EDC/VCM), Ethylene oxide – Ethylene glycol (EO/EG), Acrylonitrile (Vinyl Cyanide), Phthalic Anhydride, Poly Ethylene (LDPE – HDPE – LLDPE), Polypropylene, Polystyrene, Polyvinyl Chloride, Synthetic Fibre and Yarn, Formaldehyde, Isopropyl Alcohol, Methanol, Ethanol, Soap, Detergents, Paint, Varnish and Ink), Inorganic Chemicals Industry (Boron Compounds, Soda Ash, Chromium Oxides, Primary Magnesium Production, Fertilizer (Ammonium sulphate, Ammonium nitrate, Urea, Triple super phosphate, Diammonium phosphate, Compose fertilizer), Inorganic Phosphates (Sodium tri poli phosphate, Dicalcium Phosphate), Sulphuric Acid, Phosphoric Acid,

Hydrofluoric Acid, Chlor Alkali, Hydrochloric acid, Ammonia, Nitric Acid), Mineral Products Industry (Cement, Clay, Lime, Glass, Magnesium Oxide (Magnesia), Refracter, Calcium Carbide), Metallurgical Industry (Iron and Steel Industry - Integrated Steelworks, Metallurgical coke production, Electrical arc furnaces, Foundries - Non-Ferrous Metal Industry, Ferroalloys, Aluminium (Primary aluminium production, Secondary aluminium production, Aluminium foundries), Sugar Cane, Pulp and Paper.

In the second step activity data and other important specific data were collected. Activity data are defined as data on the magnitude of human activity resulting in emissions or removals taking place during a given period of time [9].

There are two approaches for collecting activity data: "top down" and "bottom up." Top-down inventories rely on data collected and aggregated by state, national, and international agencies. Inventories that use a bottom-up approach generally collect and aggregate data from local end users, such as utilities [10]. In this study, activity data collecting approach is decided specifically for each of the sector and sub-sector. For instance, the fuel amount of fertilizer industry is gathered from the state for the calculation of fuel combustion emissions by using top down approach, however the production amount and process information of the petroleum refining industry is derived from utilities for the calculation of process emissions by using bottom up approach.

Generally, activity data is collected from public sources. Sectoral energy consumption amounts are gathered from 2010 Energy Balance Table [8] which is prepared annually by the Ministry of Energy and Natural Resources. The table is almost compatible with the IEA system of international energy statistics though there were some small differences in reporting conventions [11]. Sectoral process and other information were obtained from the special ad-hoc committee reports which are organized by Ministry of Development for most of the sectors in Turkey which covers general industrial structure. These reports are derived from Ministry web page and referred in each of the chapter. The other important data sources are the industrial databases prepared by TurkStat and The Union of Chambers and Commodity Exchanges of Turkey. TurkStat database is obtained via e-mail from TurkStat which is helpful to see which products are manufactured in Turkey but is inadequate for the amount of production because of confidentiality agreements

between the parties. Therefore only given data is used in calculations. The Union of Chambers and Commodity Exchanges of Turkey has an annually updated database [12] about number of industries for each of the product and used to have a general idea about the sectors by product base.

If abovementioned data was not adequate to calculate emissions then industries were directly communicated in order to obtain data by exercising the right given by the Information Law which is in force in Turkey since 2003. Unfortunately production and process specific data given by the industries were not sufficient in some industries then approximation method is used by comparing the industry with other countries.

The third stage is emission factor analyzing. An emission factor relates the quantity (weight) of pollutants emitted to a unit of activity of the source. Emission factors are derived from numerous sources. First of all emission factor is explored in main EF sources which are explained below. If emission factor does not exist in main EF sources, than an emission factor is generated using mass balances by using the manufacturing process details industry [13]. Though an emission factor would not be obtained yet, then it is generated from other countries' emission inventories by using approximation method.

Main EF sources are United States EPA and European Union IPCC guideline, EMEP guidebook and IPPC Bref Documents.

The document "Compilation of Air Pollutant Emission Factors" (AP-42) has been published by the U.S. Environmental Protection Agency (the EPA) since 1972. Supplements to AP-42 have been routinely published to add new emission source categories and to update existing emission factors. AP-42 is routinely updated by the EPA to respond to new emission factor needs of the EPA, state and local air pollution control programs and industry [13].

The 2006 IPCC Guidelines for National Greenhouse Gas Inventories (2006 Guidelines) were produced at the invitation of the United Nations Framework Convention on Climate Change (UNFCCC) to update the Revised 1996 Guidelines and associated good practice guidance which provide internationally agreed methodologies intended for use by countries to estimate greenhouse gas inventories to report to the UNFCCC [9].

[15] The EMEP/EEA (European Monitoring and Evaluation Programme / European Environment Agency) air pollutant emission inventory guidebook (formerly referred to as the EMEP CORINAIR emission inventory guidebook) is published by European Environment Agency and provides emission factors for emission inventories. The guidance gives opportunity to estimate emissions from both anthropogenic and natural emission sources. It is designed to facilitate reporting of emission inventories by countries to the UNECE Convention on Long-range Transboundary Air Pollution and the EU National Emission Ceilings Directive. The EEA publishes the Guidebook, with the UNECE's Task Force on Emission Inventories and Projections having responsibility for the technical content of the chapters.

The European IPPC (Integrated Pollution Prevent and Control) Bureau has been founded to organize the necessary exchange of information and produces Best Available Techniques reference (short: 'BREF') documents which Member States are required to take into account when determining best available techniques generally or in specific cases. These documents are referred in each of the chapter.

Emission factors are selected for both of controlled and uncontrolled conditions. Controlled emission factors are given for different control technologies in the main EF sources. However, controlled emission factors were not given for some sectors. It was hard to obtain control technologies of each process but some industries give this information in their environment reports, therefore control technologies were obtained right for these industries. Otherwise it is decided by personal communication with Prof. Kadir ALP by approximation method with considering industrial conditions in Turkey. Details about the selected control technologies are given for each sector in the related sections of this study.

The fourth stage is the calculation of both controlled and uncontrolled emissions by using activity data and emission factor which was selected by using the methodology mentioned above. Formula 1.1 is used generally in the calculations.

$$\text{Emission (ton/yr)} \quad (1.1)$$

$$= \text{Production(ton/yr 2010)} \times \text{Emission Factor(kg/ton)} / 1000(\text{ton/kg})$$

There are some important points to be highlighted for the method of this study. Process emissions are calculated for controlled and uncontrolled conditions as it is stated in Figure 3.1. Unfortunately there was no information about controlled and/or uncontrolled emission factors for some industries. In this situation, if uncontrolled emission factor exists, then controlled emission factor is calculated by assuming a control technology for the sector by considering compatibility of the assumed control technology with Turkey's conditions. In the opposite case, the problem is solved by going reverse from the described way.

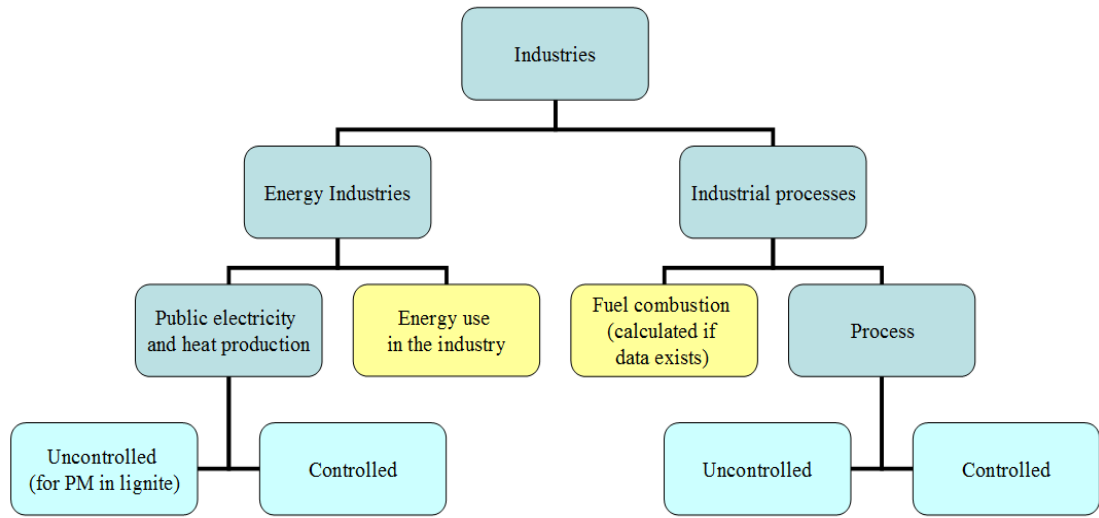


Figure 3.1 : General division of the emissions considered in the study.

Energy emissions are not calculated for uncontrolled conditions, except SO₂, TSP, PM₁₀ and PM_{2.5} emissions of the electricity production industry.

Energy emissions are calculated by using the general energy balance table of MENR [8]. Also other studies including NIR 2010 Turkey [26] use this table for the calculations.

Energy consumption regarding to the sectors is categorized in very general form in energy balance table of the MENR [8] when it is considered for this study, because this study aims to calculate energy and process emissions of sectors by using sub-categories as much as possible. Unfortunately it was not possible; therefore fuel combustion emissions are calculated under each section for all of the sub-sectors. For example inorganic and organic chemicals industry energy emissions are given after calculating process emissions of each subsectors (organic chemicals chapter 5.3. , inorganic chemicals chapter 5.4.) and fuel combustion emissions (fuel combustion

emissions of both organic and inorganic chemicals industry chapter 5.4.13) are given after process emissions.

However, overall process and fuel combustion emissions are given as an attachment at the end of the thesis.

Additionally fuel combustion amounts are calculated for some of the industries (as stated in Figure 3.1) which are Ethylene-Propylene, Vinyl Chloride Monomer, Aromatics, Boron, Magnesium Oxide, Lime, Pulp and Paper industries to show more details in the thesis for some of the sectors, but the amount of the fuel used in above industries are included in MENR table [8]. For instance, Ethylene-Propylene production sector fuel combustion emissions are calculated in this study, but included in chemical industry fuel combustion emissions chapter 5.4.13. There was no information for other industry specific fuel consumption values, therefore only abovementioned industries are considered.

4. BACKGROUND INFORMATION

In this section, parameters evaluated in the study are explained briefly with showing potential emitting sources and possible results. Also literature review is submitted to show studies which are directly related with this study.

4.1. Overview of Turkey

The area of Turkey is 783,562 km² land: 770,760 km², water: 9,820 km² [3] of which approximately 97% is in Asia and 3% is in Europe. Turkey's coast lines total more than 8,333 km. Turkey's geographical location makes it a natural land bridge connecting Europe to Asia. Therefore, it has an increasingly important role to play as an "energy corridor" between the major oil and natural gas producing countries in the Middle East and Caspian Sea and the Western energy markets [4]. Population is 74,724,269 as of January 2012 [5].

Turkish industry mainly depends on the private sector activities. The share of public sector in the manufacturing industry has been decreased through privatisation activities in recent years. Currently, more than 80 % of production and about 95 % of gross fixed investment in the manufacturing industry is realized by the private sector [6].

The impact of global crisis on the manufacturing industry was started to be felt as from the third quarter of 2008. In 2009, this impact became more noticeable in the form of high rates of decline in manufacturing industry production and employment. In 2010, it is observed that recovery from the crisis has started, that the exports and imports of manufacturing industry have started to rise again, and that significant rises have occurred in production and employment [7].



Figure 4.1 : Turkey map.

In the first eight months of 2010, manufacturing industry output grew by 15.3 percent on average, relative to the same period of the previous year. During the subject period, the sectors with highest output growth have been textile, leather, chemicals, rubber and plastic, fabricated metal products, computer-electronic and optical products, electrical equipment, machinery and automotive. Tobacco products and pharmaceutical industry have been the sectors with output decline [7].

4.2. Brief Information about Air Pollutants

Air pollutants included in this study and their effects on human health and the environment is given in this section as a brief summary.

4.2.1. Carbon dioxide (CO₂)

Carbon dioxide is emitted as a result of the combustion of fuels such as coal, oil, natural gas and biomass for industrial, domestic and transport purposes. CO₂ is the most significant greenhouse gas influencing climate change [16].

The largest source of CO₂ emissions globally is the combustion of fossil fuels such as coal, oil and gas in power plants, automobiles, industrial facilities and other sources. A number of specialized industrial production processes and product uses such as mineral production, metal production and the use of petroleum-based products can also lead to CO₂ emissions [17].

Carbon dioxide emissions are produced as a by-product of various non-energy related industrial activities and product uses. For example, during the production of cement, raw materials such as naturally occurring calcium carbonate are chemically transformed, producing CO₂ as a by-product. There are also a large number of ways petroleum based products are used for purposes other than energy production that can lead to CO₂ emissions. Petroleum products are used in plastics, solvents, and lubricants that may evaporate, dissolve, or wear out over time. There are four main types of industrial process CO₂ emissions, production and consumption of mineral products such as cement, lime and soda ash, production of metals such as iron and steel, aluminium, zinc and lead, chemical production (e.g., ammonia, petrochemicals and titanium dioxide), consumption of petroleum products in feedstock and other end-uses [17].

4.2.2. Nitrogen oxides (NO_x)

Nitrogen oxides are emitted from fuel combustion, such as from power plants and other industrial facilities.

Oxides of nitrogen (NO_x) formed in combustion processes are due either to thermal fixation of atmospheric nitrogen in the combustion air ("thermal NO_x"), or to the conversion of chemically bound nitrogen in the fuel ("fuel NO_x"). The term NO_x refers to the composite of nitric oxide (NO) and nitrogen dioxide (NO₂). Test data have shown that for most external fossil fuel combustion systems, over 95 percent of the emitted NO_x is in the form of nitric oxide (NO) [50].

NO_x contributes to acidification and eutrophication of waters and soils, and can lead to the formation of particulate matter and ground-level ozone. Of the chemical species that comprise NO_x, it is NO₂ that causes adverse effects on health; high concentrations can cause airway inflammation and reduced lung function [16].

4.2.3. Nitrous oxide (N₂O)

Nitrous oxide (N₂O) is not included in NO_x but has recently received increased interest because of atmospheric effects [50]. Nitrous oxide (N₂O) is a greenhouse gas with an atmospheric lifetime of approximately 120 years. Nitrous oxide is about 310 times more effective in trapping heat in the atmosphere than CO₂ over a 100-year period. The primary sources of human-influenced emissions of nitrous oxide are

agricultural soil management, animal manure management, sewage treatment, mobile and stationary fuel combustion, adipic acid production, and nitric acid production. Nitrous oxide is also emitted naturally from a wide variety of biological sources [18].

4.2.4. Sulphur dioxide (SO₂)

Sulphur dioxide (SO₂) is one of a group of highly reactive gasses known as “oxides of sulphur.” The largest sources of SO₂ emissions are from fossil fuel combustion at power plants (73%) and other industrial facilities (20%). Smaller sources of SO₂ emissions include industrial processes such as extracting metal from ore, and the burning of high sulphur containing fuels by locomotives, large ships, and non-road equipment [19].

As with NO_x, SO₂ contributes to acidification, with potentially significant impacts including adverse effects on aquatic ecosystems in rivers and lakes, and damage to forests. High concentrations of SO₂ can affect airway function and inflame the respiratory tract. SO₂ also contributes to the formation of particulate matter in the atmosphere [16].

4.2.5. Ammonia (NH₃)

Various industries were identified as emitters of ammonia. These include the fertilizer manufacture industry, coke manufacture, fossil fuel combustion, livestock management, and refrigeration methods. Most of the ammonia emitted is generated from livestock waste management and fertilizer production, comprising about 90% of total ammonia emissions [20].

Ammonia, like NO_x, contributes to both eutrophication and acidification. The vast majority of NH₃ emissions— around 94 % in Europe — come from the agricultural sector. A relatively small amount is also released from various industrial processes [16].

Fossil fuel combustion is different from the other industries identified in that ammonia is not emitted from the process itself, but from the control technology applied to the source in order to control nitrogen oxide (NO_x) emissions. Selective catalytic reduction and selective non-catalytic reduction are two technologies used to control nitrogen oxides in the post-combustion gases exhausting from combustion sources. These methods reduce nitrogen oxides by injecting urea or ammonia into the

exhaust gas to react with the nitrogen oxides, with or without a catalyst present, depending on the method selected. If the reaction is not complete, a portion of the ammonia may exit the system in the effluent. This condition is known as ammonia slip [20, 18].

4.2.6. Volatile organic compounds (VOCs)

VOCs are chemical compounds containing carbon that vaporize easily and enter the atmosphere. They can be released directly into the air, or by incomplete combustion in the burning of fossil fuels in automobile engines and power plants [16].

4.2.7. Methane (CH₄)

Methane (CH₄) is a greenhouse gas that remains in the atmosphere for approximately 9-15 years. Human-influenced sources include landfills, natural gas and petroleum systems, agricultural activities, coal mining, stationary and mobile combustion, wastewater treatment, and certain industrial process. Methane is also a primary constituent of natural gas and an important energy source [22].

4.2.8. Non-methane volatile organic compounds (NMVOCs)

Non methane fractions of VOC, NMVOCs, important ground-level ozone precursors, are emitted from a large number of sources including industry, paint application, road transport, dry-cleaning and other solvent uses. Certain NMVOC species, such as benzene (C₆H₆) and 1,3-butadiene, are directly hazardous to human health [16].

In this study, NMVOC, VOC and CH₄ emissions are calculated and VOC emissions can be identified as the sum of NMVOC and CH₄ emissions.

4.2.9. Particulate matter (PM)

In terms of potential to harm human health, PM is one of the most important pollutants as it penetrates into sensitive regions of the respiratory system, and can cause or aggravate cardiovascular and lung diseases [16].

PM is emitted from many sources and does a complex mixture comprise both primary and secondary PM; primary PM is the fraction of PM that is emitted directly into the atmosphere, whereas secondary PM forms in the atmosphere following the release of precursor gases (mainly SO₂, NO_x, NH₃ and some volatile organic compounds (VOCs)) [16].

4.2.10. Heavy metals

The heavy metals arsenic (As), cadmium (Cd), chromium (Cr) lead (Pb), mercury (Hg) and nickel (Ni) are emitted mainly as a result of various combustion processes and from industrial activities. As well as polluting the air, heavy metals can be deposited on terrestrial or water surfaces and subsequently build-up in soils and sediments, and can bio-accumulate in food chains. They are typically toxic to both terrestrial and aquatic ecosystems [16].

In this study, heavy metals are not considered.

4.2.11. Organic micro-pollutants

Benzene, polycyclic aromatic hydrocarbons (PAHs), and dioxins and furans are categorised as organic pollutants. They cause different harmful effects to human health and to ecosystems, and each of these pollutants is a known or suspected human carcinogen; dioxins and furans and PAHs also bioaccumulate in the environment. Emissions of these substances commonly occur from the combustion of fuels and wastes and from various industrial processes [16].

5. INDUSTRIAL EMISSIONS

Industrial emissions were calculated in this study for the following sectors;

Electricity and heat production

Inorganic chemicals industry

Organic chemicals industry

Mineral industry

Metallurgical industry

Wood products industry (pulp and paper)

Food and beverages (sugar) industry

Combustions emissions of all industries

Process emissions were calculated for controlled and uncontrolled conditions. There was no information about controlled and/or uncontrolled emission factors for some industries. In this situation, if uncontrolled emission factor exists, then controlled emission factor was calculated by assuming a control technology for the sector and considering compatibility of the assumed control technology with Turkey's conditions. In the opposite case, the problem was solved by going reverse from the described way.

Fuel combustion emissions were calculated under each section. For example inorganic and organic chemicals industry fuel combustion emissions were given after calculating process emissions of subsectors (organic chemicals chapter 5.3. inorganic chemicals chapter 5.4.) and fuel combustion emissions (fuel combustion emissions of both organic and inorganic chemicals industry chapter 5.4.13).

Additionally fuel combustion amounts were calculated for Ethylene-Propylene, Vinyl Chloride Monomer, Aromatics, Boron, Magnesium Oxide, Lime, Pulp and Paper industries to show more details in the thesis for some of the sectors, but the

amount of the fuel used by these industries were included in MENR table [8], therefore they were given only for individual sub-sector comparison.

Also public electricity and heat production sector was investigated in terms of the emissions emitted from this industry.

5.1. Public Electricity and Heat Production

Turkey's installed capacity for electricity production is 49,524 MW in 2010. 32,278 MW of this electricity was supplied from thermal power plants and rest of it, 17,245 MW, is supplied from Hydraulic, Geothermal and Wind electricity production plants [28]. Figure 5.1 shows the percentages for electricity production in Turkey in 2010.

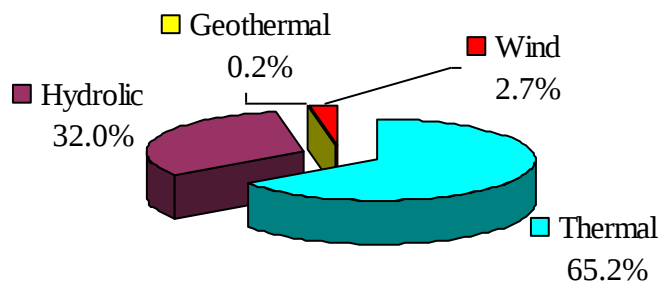


Figure 5.1 : Turkey's installed capacity in 2010 regarding to sources.

In terms of emitted air pollutants; hydraulic, geothermal and wind sources which reflects 35% of Turkey's installed capacity are respectively clean power production technologies in terms of air pollution when compared to 65% of installed capacity of thermal power plants. Therefore they were not accepted as key category for this study and were not evaluated.

Thermal power plants convert forms of heat energy into electricity by combustion of fuels such as coal, natural gas, fuel oil and diesel oil.

The fuels used in Turkey's thermal power plants are, according to frequency of use, natural gas, lignite (brown coal), hard coal, asphaltite + fuel oil, wood + plant and animal residue. Figure 5.2 shows the usage percentages of each fuel [8] in Turkish electricity generation industry by thermal power plants.

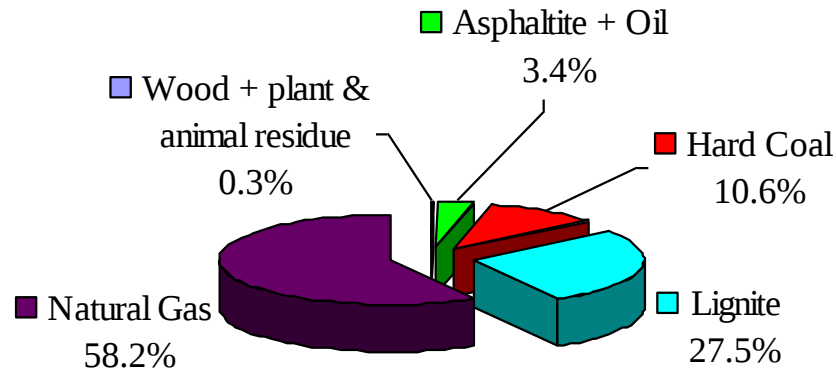


Figure 5.2 : Fuel usage share by thermal power plants.

Turkey's thermal power plants can be classified into two main groups. The first group is "*state-owned power plants*" that are named as public power plants owned by Electricity Generation Incorporated Company (EGIC). The second group is "*private power plants*" that produce electricity, connect to the network directly and sell generated electricity to the national electricity network and grid [25]. As of 2008 there are 16 public, 5 liberalized and 308 private thermal power plants.

Private power plants produce electricity in amounts decided annually with public electricity transmission company [29], therefore it was hard to obtain the real amount of produced electricity from public sources. Finally, approximation method was used for the electricity production amount.

5.1.1. Lignite-fired thermal power plants

Lignite-fired power plants are classified into 3 groups in Turkey; EGIC (public electricity production company) owned power plants, EGIC Subsidiaries which are affiliated partnerships of EGIC owned power plants and privatized from EGIC or private power plants.

The data used in this chapter were derived from Turkey Electricity Transmission Company (TETC) Statistics [27], EGIC Annual Report [30], and Turkey Coal/Lignite Enterprises (TCE) 2010 Annual Report [31].

Calculations were explained within three titles to ease the understanding. IPCC [32] methodology was used in calculations.

First of all, power plants were categorized with considering available data and capacity. Some of the plants have two sub-plants (like Soma A and B) in the same area, these are Afsin, Soma, Sivas and Tuncbilek. The highest-capacity Afsin-Elbistan power plants are divided into two sections to show separated lignite consumption in 2010. However Tuncbilek, Sivas, Soma power plants which have respectively lower production amounts in 2010 when compared to Afsin-Elbistan were not divided into two sections.

“Other” title includes privatised or private lignite-fired power plants. Most of the capacity (620 MW) belongs to Park Termik-Cayirhan power plant which was privatised from EGIC. The lignite combustion of “other” sector was calculated with using fuel consumption data obtained from TETC Statistics [28].

Categorised power plants and their lignite consumption amounts are given in Table 5.1.

5.1.1.1. First step calculations for CO₂ emissions (before SO₂ abatement)

CO₂ emissions were calculated within two steps, because SO₂ abatement technology. increases the amount of the CO₂ emissions.

Fuel consumption amount was calculated as TJ by using following methodology; fuel consumption amount, low heating values and carbon oxidation ratios were obtained from EGIC [36] for each of the plant except private ones. For the private ones, Tier 1 default values of IPCC [32] are used as carbon oxidation ratio. Private power plants’ fuel combustion amount was calculated by deducting from the lignite consumption amount given in MENR Energy Balance Table [8]. Finally CO₂ emissions were calculated and indicated in Table 5.1.

For preventing double counting, the final lignite consumption amount which are given in both energy balance table of MENR [8] and TETC [28] were compared. Unfortunately values of TETC and MENR are not perfectly compatible with each other, but acceptable. TETC 2010 lignite consumption value is 56,689,392 ton and MENR value is 55,436,000 ton. TETC value was accepted for further calculations.

Carbon weight in the fuel was derived from literature [25]. Carbon emission factor (C-EF) is calculated by dividing carbon weight to low heating value (LHV), the formula is given below;

$$\text{Carbon Emission Factor (C-EF)} = \text{wt carbon} / \text{LHV} \quad (3.1)$$

wt carbon : Carbon weight in the fuel (%)

LHV : Low heating value (MJ/kg)

Then CO₂ emissions were calculated by using Formula 3.2.

$$\text{Pre-calculated CO}_2 \text{ emission} = (44/12) \cdot \text{FC} \cdot \text{C-EF} \cdot \text{OCR} \quad (3.2)$$

44/12 : Carbon – carbon dioxide conversion factor

FC : Fuel consumption (TJ)

C-EF : Carbon emission factor (ton/ TJ)

OCR : Oxidized Carbon Ratio (%)

Pre-calculated emission factors were derived from above equations with using Formula 3.3.

$$\text{Pre-calculated CO}_2 \text{ emission factor} = \text{Emission} / \text{Fuel consumption} \quad (3.3)$$

Emission : CO₂ emission calculated above (ton/yr)

Fuel consumption: (TJ)

Regarding to IPCC guideline [32], calculated emission factors should be in a range, which is 90900-115000 kg/TJ. If calculated emission factor is above or under of these values, then emission factor should be adjusted and emissions should be calculated again. Therefore emission factors were adjusted in Table 5.1.

The final stage was calculating final- adjusted CO₂ emissions of lignite fired power plants by using adjusted emission factors. Finally total emissions were calculated as 45,195,429 ton in 2010 without the effect of abatement technology.

Table 5.1 : Calculation steps for CO₂ emissions of lignite-fired thermal power plants before SO₂ abatement.

	Fuel Consumption	Carbon weight in the fuel	Low Heating Value	Carbon EF	Oxidized C Ratio	CO ₂ /C	Pre- calculated Emission	Pre- calculated EF	Adjusted EF	Adjusted Emissions
	TJ	%	MJ/kg	ton/TJ	%		ton/yr	kg/ton	kg/TJ	ton/yr
Afsin Elbistan A	25,587	19.53	4.94	40	0.986	44 / 12	3,655,082	142,849	115,000	2,942,511
Afsin Elbistan B	78,297	16.87	4.74	36	0.976	44 / 12	9,980,326	127,467	115,000	9,004,183
18 Mart	21,611	33.52	12.30	27	0.960	44 / 12	2,072,956	95,920	95,920	2,072,956
Kangal	24,342	18.23	4.97	37	0.968	44 / 12	3,170,075	130,228	115,000	2,799,385
Orhaneli	11,917	23.00	9.04	25	0.993	44 / 12	1,104,365	92,672	92,672	1,104,365
Seyitomer	40,482	23.52	7.39	32	0.959	44 / 12	4,529,478	111,890	111,890	4,529,478
Tuncbilek A+B	18,450	48.31	12.02	40	0.980	44 / 12	2,664,399	144,413	115,000	2,121,728
Kemerkoş	28,888	24.49	7.67	32	0.998	44 / 12	3,374,313	116,805	115,000	3,322,162
Soma A + B	71,365	40.08	15.18	26	0.985	44 / 12	6,802,029	95,314	95,314	6,802,029
Yatagan	30,462	20.89	9.13	23	0.998	44 / 12	2,549,961	83,711	90,900	2,768,952
Yenikoş	13,820	29.00	8.32	35	0.996	44 / 12	1,759,653	127,327	115,000	1,589,294
Other	53,377	40.00	10.04	40	0.980	44 / 12	7,640,309	143,138	115,000	6,138,386
Total	418,598						49,302,946			45,195,429
Average								117,644	107,641	

According to Ari I. (2010) [25] average emission factor for lignite is 1080 kg CO₂/MWh electricity produced. In this study it is calculated that, 0.01171 TJ lignite combustion is required to produce 1 MWh electricity. This value was obtained by using total electricity production of EGIC [36] power plants in MWh unit and calculated calorific values of the lignite used in these power plants, therefore this value was not certain and gives only an approximate value to convert units. Finally, lignite combustion related CO₂ emission factor was found as 92,228 kg/TJ. It is compatible with the range given by IPCC guideline [32] but this value can not be compared with the value calculated in this study.

Table 5.2 : Lignite-fired thermal power plant CO₂ Emission factor comparison

Reference Year:	Emission Factors (kg/TJ)	
	This study 2010	Ari I [25] 2001-2008
Afsin Elbistan A	115,000	115,000
Afsin Elbistan B	115,000	115,000
18 Mart	95,920	96,892
Kangal	115,000	110,441
Orhaneli	92,672	96,762
Seyitomer	111,890	107,835
Tuncbilek A+B	115,000	93,505
Kemerkoy	115,000	107,405
Soma A + B	95,314	96,111
Yatagan	90,900	100,019
Yenikoy	115,000	104,578
Other	115,000	90,900

Yearly changes in low heating value of the lignite causes the differences between two studies. The biggest difference is in ‘other’ category, because only Park Termik power plant was considered in the thesis of Ari I, however all private power plants including Park Termik were considered in this study, under ‘other’ category.

5.1.1.2. Other emissions (before SO₂ and PM abatement)

NO_x, CO, NMVOC, SO_x, N₂O and CH₄ emissions were calculated in this section to prevent confusion between CO₂ emissions calculations which were given in Section 5.1.1.3, because CO₂ emissions were calculated by applying an approach to acquire plant specific emission factors and emissions.

SO_x emissions were calculated by considering specific sulphur content of the fuel for each of the plant. SO₂ emission factors were given in Table 5.3.

Table 5.3 : SO₂ Emission factor calculation and emissions.

	S in fuel (%)	EF kg/ton	SO ₂ Emissions ton/yr
Afsin Elbistan A	1.4	21	108,669
Afsin Elbistan B	1.4	21	346,926
18 Mart	4.5	67.5	118,510
Kangal	1.9	28.5	139,480
Orhaneli	1.5	22.5	29,649
Seyitomer	0.9	13.5	73,871
Tuncbilek A+B	1.5	22.5	34,511
Kemerkoş	2.2	33	124,220
Soma A + B	0.8	12	56,379
Yatağan	1.6	24	79,988
Yenikoş	1.7	25.5	42,340
Other	2.6	39	207,170
			1,361,714

Sulphur percentages were derived from Vardar N et.al. [37]. Emission factor was calculated by using the methodology recommended by EPA [38].

Other emissions were calculated by using emission factors given in Table 5.4.

Table 5.4 : Emission factors of lignite-fired thermal power plants.

	EF (kg/TJ)
NO _x	360
CO	113
NM VOC	1.7
SO _x	820
N ₂ O	1.5
CH ₄	1

NO_x, CO, NM VOC emission factors were taken from EMEP [40], N₂O and CH₄ emission factors were taken from IPCC Tier 1 [32]. Emissions which were calculated by using these emission factors were given in Table 5.5.

Table 5.5 : Other emissions of lignite-fired thermal power plants.

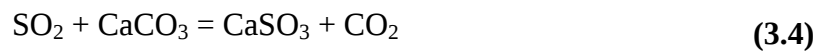
	Emissions (ton/year)											
	NO _x	CO	NMVOC	SO _x	Controlled			Uncontrolled			N ₂ O	CH ₄
					TSP	PM ₁₀	PM _{2.5}	TSP	PM ₁₀	PM _{2.5}		
Afsin Elbistan A	9,211	2,891	43	108,669	7,762	1,941	291	452,789	97,026	14,554	38	26
Afsin Elbistan B	28,187	8,848	133	346,926	24,780	6,195	929	1,445,526	309,756	46,463	117	78
18 Mart	7,780	2,442	37	118,510	2,634	658	99	153,625	32,920	4,938	32	22
Kangal	8,763	2,751	41	139,480	7,341	1,835	275	428,227	91,763	13,764	37	24
Orhaneli	4,290	1,347	20	29,649	1,977	494	74	115,302	24,708	3,706	18	12
Seyitomer	14,573	4,574	69	73,871	8,208	2,052	308	478,793	102,599	15,390	61	40
Tuncbilek A+B	6,642	2,085	31	34,511	2,301	575	86	134,209	28,759	4,314	28	18
Kemer koy	10,400	3,264	49	124,220	5,646	1,412	212	329,372	70,580	10,587	43	29
Soma A + B	25,691	8,064	121	56,379	7,047	1,762	264	411,094	88,092	13,214	107	71
Yatagan	10,966	3,442	52	79,988	4,999	1,250	187	291,624	62,491	9,374	46	30
Yenikoy	4,975	1,562	23	42,340	2,491	623	93	145,283	31,132	4,670	21	14
Other	19,216	6,032	91	207,170	7,968	1,992	299	464,805	99,601	14,940	80	53
Total	150,695	47,302	712	1,361,714	83,154	20,789	3,118	4,850,650	1,039,425	155,914	628	419

PM emissions of lignite-fired thermal power plants were calculated for uncontrolled and controlled conditions by using emission factors of EPA [38]. Emission factors of TSP are 87.5 kg/ton for uncontrolled condition and 1.5 kg/ton for controlled condition. Uncontrolled PM₁₀ is 22kg/ton and PM_{2.5} is 3.28 kg/ton. Abatement technology efficiency was accepted as approximately 98%.

5.1.1.3. Second step calculations for CO₂ and SO₂ emissions (after SO₂ abatement)

Flue Gas Desulphurization (FGD) is the technology or process which is used to remove sulphur oxides and sulphur dioxides (SO₂) from the products of combustion or flue gases at power plants (biomass or coal fuelled) that are produced in boilers. FGD removes the pollutants before discharge to the atmosphere and is also referred to as a scrubber. Commonly used chemicals or natural materials include lime as the "scrubbing" media [33].

[34] Wet scrubbers are the most widely used FGD technology for SO₂ control throughout the world. Calcium, sodium and ammonium-based sorbents have been used in a slurry mixture, which are injected into a specially designed vessel to react with the SO₂ in the flue gas. The preferred sorbent in operating wet scrubbers is limestone followed by lime. These are favoured because of their availability and relative low cost. The overall chemical reaction, which occurs with a limestone or lime sorbent, can be expressed in a simple form as:



As it is clear from the Equation 3.4, CO₂ is revealed from the process, therefore CO₂ and SO₂ emissions were calculated and adjusted in this section again.

In Turkey FGD system is used in 18 Mart, Kemerkoş, Yatagan, Yeniköy and Park Termik (evaluated in 'other' category), Kangal and Orhanlı power plants [35].

In Equation 3.4, it is shown that 1 mol CO₂ occurs for each of the SO₂ mol reduced. It can be said that 44 gr CO₂ occurs for the reduction of each 64 gr SO₂ with considering molecular weights. However more than needed amount lime is added to the process, therefore CaCO₃ amount was taken as 115 gr. In this case, 50.6 ton CO₂ occurs.

50.6 ton CO ₂ occurs	----->	for the reduction of 64 ton SO ₂
x ton CO ₂ occurs	----->	for the reduction of 1 ton SO ₂
= 0.79 ton CO ₂ / ton SO ₂ reduced		

Wet scrubbers can achieve removal efficiencies as high as 99% [34]; however in this study it was accepted 85% to reach an average value for all of the plants. Therefore only 85% of SO₂ amount was accepted as removed in the above mentioned power plants.

Before FGD SO_x emissions were calculated in Section 5.1.1.2 and CO₂ emissions were calculated in Section 5.1.1.1. After abatement emissions were summarized for each of the plant in Table 5.6.

Table 5.6 : Lignite-fired power plants' after abatement CO₂ and SO₂ emissions

	After abatement Emissions (ton/yr)	
	CO ₂	SO ₂
18 Mart	2,142,210	17,777
Kangal	2,880,893	20,922
Orhaneli	1,121,691	4,447
Kemer koy	3,394,753	18,633
Yatagan	2,815,695	11,998
Yenikoy	1,614,036	6,351
Park Termik	3,394,753	18,633
Total	17,364,031	98,761

Regarding to EGIC Annual Report [30], Park Termik power plant (included in 'other' category) has nearly equal installed capacity with Kemer koy power plant, therefore SO₂ and CO₂ amount of Park Termik was accepted as same with Kemer koy power plant.

5.1.1.4. Final emissions

Final emissions of lignite-fired thermal power plants were summarized in Table 5.7 for 'before and after SO₂ abatement'.

Up to now, CO₂ and SO₂ emissions were calculated for 'before and after FGD treatment'. Table 5.7 includes final emission amounts of these two pollutants.

NO_x, CO, NMVOC, N₂O, CH₄ emissions were calculated for only controlled conditions directly by using the related emission factors.

TSP, PM₁₀ and PM_{2.5} emissions were calculated for both controlled and uncontrolled conditions.

Table 5.7 : Overall emissions of lignite-fired thermal power plants.

	Emissions (ton/yr)	
	Before SO ₂ Abatement	After SO ₂ Abatement
NO _x	150,695	150,695
CO	47,302	47,302
NM VOC	712	712
SO _x	1,361,714	802,067
PM	83,154	83,154
N ₂ O	628	628
CH ₄	419	419
CO ₂	45,195,429	45,580,186
Total	46,840,052	46,665,163

Regarding to results of this study, CO₂ emissions accounts 97,6% of all emissions, other emission percentages were explained in Figure 5.3.

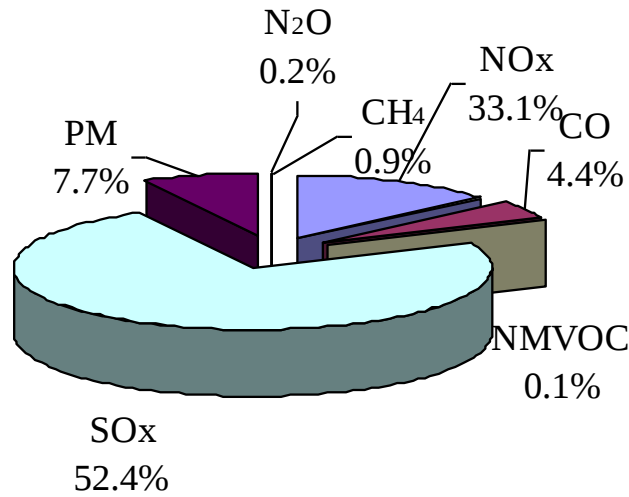


Figure 5.3 : Non-CO₂ emission distribution of lignite-fired thermal power plants.

SO_x emissions still account 52.4% of non-CO₂ emissions after SO₂ abatement, and then NO_x comes with 33.1% of non- CO₂ emissions.

Lignite-fired thermal power plants were not separated under a unique title in NIR 2010 Turkey [26] and included in solid fuels category of public energy production activities. Also lignite combustion related emission factors were calculated by using overall lignite consumption of Turkey and not separated for power plants. Therefore there is no direct comparison data from NIR 2010 Turkey [26] for lignite-fired thermal power plants.

5.1.2. Hard coal-fired thermal power plants

In 2010, there was only one hard coal-fired thermal power plant in Turkey; Catalagzı Power Plant which produced 10.6% of the electricity produced by all thermal power plants [8].

Table 5.8 : CO₂ emissions of hard coal-fired power plants.

Fuel Amount ton	LHV kcal/kg	Fuel Amount TJ	EF kg/TJ	Emissions ton/yr
7,582,000	6,100	193,640	196,600	19,034,845

Low heating value of hard coal was taken from EIE [41] and emission factor was taken from IPCC Tier 1 [32]. Also this emission factor was used in NIR 2010 Turkey [26].

Table 5.9 : Other emissions of hard coal-fired power plants.

	EF	Emission
Pollutant	kg/TJ	ton/yr
NO _x	310.0	60,029
CO	150.0	29,046
NM VOC	1.2	232
SO _x	820.0	158,785
TSP	30.0	5,809
PM ₁₀	20	3,873
PM _{2.5}	9	1,743
N ₂ O	2	290
CH ₄	1	194

NO_x, CO, NM VOC, SO_x, PM emission factors were taken from EMEP [40], N₂O and CH₄ emission factors were taken from IPCC Tier 1 [32].

5.1.3. Imported lignite- fired thermal power plants

The number of imported lignite-fired power plants is not known exactly, however the amount of total imported coal is taken from TETC [28] and used in calculations.

Table 5.10 : CO₂ emissions of imported lignite-fired power plants.

Fuel Amount ton	LHV kcal/kg	Fuel Amount TJ	EF kg/TJ	Emissions ton/yr
5,388,911	3,000	67,687	97,500	6,599,471

Low heating value of brown coal was taken from EIE [41] and emission factor was taken from IPCC Tier 1 [32]. Also this emission factor was used in NIR 2010 Turkey [26].

The other emissions were calculated in Table 5.11.

Table 5.11 : Other emissions of imported lignite-fired power plants.

Pollutant	EF kg/TJ	Emission ton/yr
NO _x	360.0	24,367
CO	113.0	7,649
NMVOC	1.7	115
SO _x	820.0	55,503
TSP	30.0	2,031
N ₂ O	2	102
CH ₄	1	68
PM ₁₀	20	1,354
PM _{2.5}	9	609

NO_x, CO, NMVOC, SO_x, PM emission factors were taken from EMEP [40], N₂O and CH₄ emission factors were taken from IPCC Tier 1 [32].

5.1.4. Asphaltite-fired thermal power plants

The number of asphaltite -fired power plants is not known exactly; however the amount of total consumed asphaltite was taken from MENR [8] and used in calculations.

Table 5.12 : Calculation steps for CO₂ emissions of asphaltite-fired power plants.

Fuel Amount ton	LHV kcal/kg	Fuel Amount TJ	EF kg/TJ	Emissions ton/yr
467,000	4,300	8,408	97,500	819,733

The other emissions were calculated in Table 5.13.

NO_x, CO, NMVOC, SO_x, PM emission factors were taken from EMEP [40], N₂O and CH₄ emission factors were taken from IPCC Tier 1 [32].

Table 5.13 : Other emissions of asphaltite-fired power plants.

Pollutant	EF kg/TJ	Emission ton/yr
NO _x	360.0	3,027
CO	113.0	950
NMVOC	1.7	14
SO _x	820.0	6,894
TSP	30.0	252
N ₂ O	2	13
CH ₄	1	8
PM ₁₀	20	117
PM _{2.5}	9	53

5.1.5. Natural gas-fired thermal power plants

The number of natural gas-fired power plants is not known exactly, however the amount of total natural gas consumption was taken from MENR [8] and used in calculations.

The details of the calculations for each of the known plant was not given here, total amount was given in Table 5.14.

Table 5.14 : Calculation steps for CO₂ emissions of natural gas-fired power plants.

Fuel Amount Sm ³	LHV kJ/m ³	Fuel Amount TJ	EF kg/TJ	Emissions ton/yr
21,783,414,596	34,541	752,423	56,100	42,210,936

Natural gas-fired thermal power plants' CO₂, CH₄ and N₂O emissions were given separately (gaseous fuels) in NIR as indicated in Table 5.15.

Table 5.15 : Emissions of natural gas-fired power plants in NIR Turkey 2010 [26].

Fuel Consumption TJ	Emission Factors (kg/TJ)			Emissions (ton)		
	CO ₂	CH ₄	N ₂ O	CO ₂	CH ₄	N ₂ O
Natural Gas 762,097	56,000	1	0.1	42,744,124	762	79

The difference between CO₂ emissions mainly because of the selected low heating value.

The other emissions were calculated in Table 5.16.

Table 5.16 : Other emissions of natural gas-fired power plants.

	EF g/GJ=kg/TJ	Emissions ton/yr
NO _x	88.01	66,222
CO	38.91	29,277
N ₂ O	0.10	75.2
PM	0.90	677.2
SO ₂	0.30	225.7
CH ₄	1.00	752.4
NMVOC	1.50	1,128.6

NO_x emission factor was taken from EPA [39], CO, PM, SO₂, NMVOC emission factors were taken from EMEP [40], and N₂O and CH₄ emission factors were taken from IPCC Tier 1 [32].

5.1.6. Fuel oil-fired thermal power plants

The amount of total fuel oil consumption was taken from MENR [6] and used in calculations. The details of the calculations for each of the known plant was not given here, total amount was given in Table 5.17.

Table 5.17 : Calculation steps for CO₂ emissions of fuel oil-fired power plants.

Fuel Amount ton	LHV kcal/kg	Fuel Amount TJ	EF kg/TJ	Emissions ton/yr
891,782	9,828	36,696	73,300	2,689,830

Table 5.18 : Other emissions of fuel oil-fired power plants.

Pollutant	EF kg/TJ	Emission ton/yr
NO _x	215.0	7,890
CO	5.0	183
NMVOC	0.8	29
SO _x	485.0	17,798
TSP	25.0	917
N ₂ O	1	22
CH ₄	3	110
PM ₁₀	2	73
PM _{2.5}	1	37

NO_x, CO, NMVOC, SO_x, PM emission factors were taken from EMEP [40], N₂O was taken from EPA [50] and CH₄ emission factor was taken from IPCC Tier 1 [32].

5.1.7. Diesel-fired thermal power plants

The amount of total diesel consumption was taken from MENR [6] and used in calculations. The details of the calculations for each of the known plant was not given here, total amount was given in Table 5.19.

Table 5.19 : Calculation steps for CO₂ emissions of diesel-fired power plants.

Fuel Amount ton	LHV kcal/kg	Fuel Amount	EF kg/TJ	Emissions ton/yr
		TJ		
20,354	10,200	869	74,100	64,410

The other emissions were calculated in Table 5.20.

Table 5.20 : Other emissions of diesel-fired power plants.

Pollutant	EF	Emission
	kg/TJ	ton/yr
NO _x	180.0	156
CO	15.0	13
NM VOC	0.8	1
SO _x	460.0	400
TSP	3.0	3
N ₂ O	1	1
CH ₄	3	3
PM ₁₀	2	2
PM _{2.5}	1	1

NO_x, CO, NM VOC, SO_x, PM emission factors were taken from EMEP [40], N₂O and CH₄ emission factors were taken from IPCC Tier 1 [32].

5.1.8. Naphtha-fired thermal power plants

The amount of total naphtha consumption was taken from MENR [6] and used in calculations. The details of the calculations for each of the known plant was not given here, total amount is given in Table 5.21.

Table 5.21 : Calculation steps for CO₂ emissions of naphtha-fired power plants.

Fuel Amount ton	LHV kcal/kg	Fuel Amount	EF kg/TJ	Emissions ton/yr
		TJ		
13,140	10,400	572	73,300	41,939

The other emissions were calculated in Table 5.22.

Table 5.22 : Other emissions of naphtha-fired power plants.

Pollutant	EF kg/TJ	Emission ton/yr
NO _x	180.0	103
CO	15.0	9
NMVOC	0.8	0.5
SO _x	460.0	263
TSP	3.0	2
N ₂ O	1	0.3
CH ₄	3	2
PM ₁₀	2	1
PM _{2.5}	1	1

NO_x, CO, NMVOC, SO_x, PM emission factors were taken from EMEP [40], N₂O and CH₄ emission factors were taken from IPCC Tier 1 [32].

5.1.9. Biomass-fired thermal power plants

The combustion of biomass (straw, wood, landfill gas, etc.) is increasingly relevant for countries to meet the drive for renewable or sustainable energy sources. In Turkey, 31,000 ton wood and 362,000 ton animal and plant residue were fired for electricity production purposes in 2010 [6].

Table 5.23 : Calculation steps for CO₂ emissions of biomass-fired power plants.

	Fuel Amount ton	LHV kcal/kg	Fuel Amount TJ	EF kg/TJ	Emissions ton/yr
wood	31,000	3,000	389	112,000	43,610
plant and animal residue	362,000	2,300	3,486	100,000	348,593

The other emissions were calculated in Table 5.24.

NO_x, CO, NMVOC, SO_x, PM emission factors were taken from EMEP [40], N₂O and CH₄ emission factors were taken from IPCC Tier 1 [32].

5.1.10. Overall evaluation

In this section, fuels were classified into four groups to ease the comparison with NIR 2010 Turkey [26]. these groups are; solid fuels (include lignite, hard coal, brown coal and asphaltite), liquid fuels (include fuel oil, diesel and naphtha), gaseous fuels include only natural gas.

Table 5.24 : Other emissions of biomass-fired power plants.

Pollutant	EF	Emission (ton/yr)	
	kg/TJ	Wood Plant	Animal Residue
NO _x	211	82	736
CO	258	100	899
NM VOC	7	2.8	25.4
SO _x	11	4	38
TSP	51	19.9	177.8
N ₂ O	4	1.6	13.9
CH ₄	30	11.7	104.6
PM ₁₀	38	14.8	132.5
PM _{2.5}	33	12.8	115.0

PM emission was not calculated in NIR 2010.

As a result, CO₂ and other emissions were calculated higher than NIR 2010 Turkey, except gaseous fuels.

Biomass CO₂ emissions were not calculated in NIR 2010 Turkey and co-incinerated biomass by cement plants by gathering licence were included under ‘energy’ category. Therefore total volume of biomass used as fuel is high in NIR 2010 Turkey. Thus N₂O and CH₄ emissions might be calculated higher than this study.

Table 5.25 : Public electricity production sector results comparison with NIR 2010 Turkey [26].

	SOLID FUELS		LIQUID FUELS		GASEOUS FUELS		BIOMASS		TOTAL	
	this study	NIR 2010	this study	NIR 2010	this study	NIR 2010	this study	NIR 2010	this study	NIR 2010
NO _x	238,118		8,149		66,222		818		313,306	316,136
CO	84,946		205		29,277		1,000		115,428	115,826
NMVOC	1,073		31		1,129		28		2,261	11,482
SO _x	1,023,250		18,461		226		43		1,041,979	413,784
PM	91,246		922		677		198		93,043	
N ₂ O	1,032	865	23	21	75	79	16	350	1,146	1,315
CH ₄	688	642	114	108	752	762	116	2,625	1,671	4,137
CO ₂	72,034,234	61,533,381	2,796,178	2,546,454	42,210,936	42,744,124	392,203	N.A.	117,433,551	106,823,958

Blank cells show uncalculated emissions for the related category.

5.2. Oil Refineries

Crude oil refineries (hydrocarbon processing industry) separate crude oil into useful hydrocarbon fractions and purify or convert these fractions into oil products.

TUPRAS (Turkey Petroleum Corporation) has four refineries in Turkey which are located in Batman, Izmir, Izmit and Kirikkale, and have totally 28,100,000 ton refining capacity per year [42].

Petroleum refinery activities start with receipt of crude for storage at the refinery, include all petroleum handling and refining operations, and they terminate with storage preparatory to shipping the refined products from the refinery [43].

The petroleum refining industry employs a wide variety of processes. A refinery's processing flow scheme is largely determined by the composition of the crude oil feedstock and the chosen slate of petroleum products. The arrangement of these processes will vary among refineries, and few, if any, employ all of these processes.

Oil refinery processes are summarized below [44];

The first process is separation by distillation of crude oil into various fractions in order to decreasing volatility; gases, LPG, gasoline, naphtha, kerosene, gasoil and diesel oil and fuel oil. The two methods used for distillation are topping and vacuum distillation. Generally vacuum distillation is used in Turkish refineries.

The second process is conversion of petroleum fractions comes from the first process into by thermal cracking, catalytic cracking, reforming, isomeration, alkylation, hydrogenation, dehydrogenation, polymerisation methods. Thus longer molecules of heavy oil fractions are cracked and consequently split into several smaller molecules and raising the yield of components. Thermal catalytic cracking or fluid catalytic cracking methods are used in Turkish refineries.

The third process is purification of petroleum fractions like light oils, lubrication oils and dewaxing. Sulphuric acid treatment, sweetening by catalytic desulphurisation, solvent extraction and other processes (washing, clay treatment etc.) are applied for purification.

The fourth and last process is extraction of components like aliphatics/aromatics and blending.

5.2.1. Process emissions

Emissions from petroleum refining industries are PM, SO₂, CO, HC and others.

During calculations, all processes were accepted as “Uncontrolled”. Only blowdown unit emissions were sent to Flare, thus Hydrocarbon (HC) emissions were accepted as “Controlled”. Emissions from the blowdown system can be effectively controlled by combustion of the noncondensables in a flare.

Operating time was accepted 330 days, 24 hours per year. Rent of the time was left for repair and maintenance.

There is an extra process in Turkish Refineries except Batman Refinery which is sulphur recovery with Claus Process. Sulphur recovery refers to the conversion of hydrogen sulphide (H₂S) to elemental sulphur. Hydrogen sulphide is a by-product of processing natural gas and refining high-sulphur crude oils. Approximately 90 to 95 percent of recovered sulphur is produced by the Claus process [45].

Uncontrolled SO₂ emissions include Claus plant. Also Total HC (hydrocarbon) represents an approximate value for VOC emissions and it was flared in uncontrolled conditions. There was no control technology employed for SO₂ and NH₃ emissions.

Table 5.26 : Petroleum refining industry process emissions.

	Uncontrolled Emissions ton/yr	Controlled Emissions ton/yr
PM	36,827	1,841
SO ₂	32,403	4,860
CO	57,805	2,890
Total HC	43,762	2,301
NO ₂	729	510
Aldehydes	42	
NH ₃	201	20

Emission factors were not given in Table 5.26. There are two reasons; first, each of the refineries has its specific flowchart and it requires choosing emission factors with considering these specific conditions. Therefore there is a unique emission factor for each of the refinery for each of the pollutant. Second, these factors were mainly given as kg pollutant/ m³ of product of the related process. As it is clear, unlike conventional emission factors (kg pollutant/ton product), these were given in

volumetric basis. Therefore the density of the oil was calculated (Equation 5.1 [46]) and volume based emission factors are converted to mass base.

$$\text{Oil Density} = \frac{141,5}{131,5 \times \text{API Gravity}} = \frac{141,5}{131,5 + 31,64} = 0,867 \text{ ton/m}^3 \quad (5.1)$$

API (American Petroleum Institute) Gravity [42] is calculated and published by TUPRAS each year for Turkey and depends on the type of crude oil imported and extracted.

Controlled emissions were calculated by considering controlling of HC emissions by flare with approximately 95% abatement efficiency and staged combustion for NO_x emissions with 30% abatement efficiency and Flue Gas Desulphurisation (FGD) for SO₂ emissions with 85% reduction efficiency.

5.2.2. Fugitive emissions

Fugitive emissions are attributable to the evaporation of leaked or spilled petroleum liquids and gases [43]. Fugitive emissions include valves, flanges, pump seals, compressor seals, relief valves, drains, cooling towers and oil water separators and calculated for both uncontrolled conditions and given in Table 5.27. Controlled conditions were applied only for cooling towers and oil water separators.

Table 5.27 : Petroleum refining industry fugitive emissions (except storage).

	Uncontrolled Emissions ton/yr	Controlled Emissions ton/yr
HC	19,920	3,051

The emission factor was given as an average value in Table 5.27, because emissions were calculated for each of the process with different activated data.

Control technology was selected as minimisation of hydrocarbon leaks into cooling water system, monitoring of cooling water for hydrocarbons, covered separators and/or vapour recovery system for oil/water separators.

In NIR 2010, the calculations of fugitive emissions that occur during the exploration, production (processing), transport (transmission), refining and storage of domestic oil, are calculated first time for the year 2010 [26]. The result of the calculation was totally 2,180 ton CH₄ and 109,766 ton CO₂ from refining, storage, venting and

flaring of oil. In this study, only production, refining, storage, venting, flaring VOC emissions are calculated only.

5.2.2.1. Storage tanks' emissions

In the refineries, there are storage tanks for the crude oil and processed oil / raw materials to keep organic liquids in the tanks before processing or using. Horizontal, vertical, and underground fixed roof tanks, and internal and external floating roof tanks are the types of the used tanks.



Figure 5.4 : Floating roof tank construction in Tupras Izmir-Aliaga Refinery [47].

EPA has TANKS model for calculation of emissions emitted from organic liquid storage tanks. TANKS is a Windows-based computer software program that estimates volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions from fixed- and floating-roof storage tanks [48]. TANKS is based on the emission estimation procedures from Chapter 7 of EPA's Compilation of Air Pollutant Emission Factors (AP-42) and developed by API.

TANKS model was not used in this study however EPA's Chapter 7 methodology was used. This study covers only emissions emitted from storage tanks of TUPRAS, not from other industries' because of data deficit from other sectors.

The equation was mainly consisted with following factors; dimensions of tanks, vapour pressure, molecular weight and other specific specialities of contained chemical(s), daily vapour temperature, ambient temperature, tank paint solar absorption, daily solar insolation factor, atmospheric pressure, annual net throughput, turnover rate. Finally total VOC emissions emitted per year was calculated and given in Table 5.28. It should be noted that, emission factor which was given in

Table 5.28 was selected only for the values of the specific the conditions listed above.

Table 5.28 : Petroleum refining industry storage tanks' emissions.

	EF (kg/ton)	Emission (ton/yr)
VOC	4,97	26,903

Uncontrolled emissions are not calculated. NMVOC emission was calculated by Simsir S [49] in 2010 as 3,250 ton/yr, however in this study NMVOC emissions were calculated within VOC emissions as 26,903 ton/yr.

5.2.3. Fuel combustion emissions

The fuel combusted within petroleum refineries to produce the heat and steam needed to run the refinery processes typically amounts to 6 to 10 percent of the total fuel input to the refinery, depending on the complexity and vintage of the technology [32].

Fuel combustion data was taken from the General Energy Balance Table (2010) of Ministry of Energy and Natural Resources (MENR) [8]. Petroleum refineries consumed electricity, petrol and natural gas for the usage in the processes and residential purposes in the refinery in 2010.

5.2.3.1. Natural gas combustion

Natural gas utilization was taken from MENR 2010 general energy balance table for petroleum refineries as 1,103,000,000 Sm³.

First of all combustor type was decided with using hourly heat input data which was derived from MENR tables' [46] data with considering the number of the boilers for each of the refineries. Finally, combustor type was found as large wall fired which has more than 100 MMBtu heat input per hour.

PM Emission factor was selected from EMEP [40] as 0.89 g/GJ. It was 4 g/GJ in AP42 [39] as the sum of filterable and condensable PM. This pollutant was not calculated in NIR 2010.

SO₂ emission factor was selected from EMEP [40] as 0.3 g/GJ; however it was 0.278 g/GJ in AP42 [39] with considering 100% conversion of sulphur to SO₂.

CO emission factor was given same in both of AP42 [39] and EMEP [40] as 39 g/GJ.

NO_x emission factor was chosen from AP42 [39] for uncontrolled post NSPS conditions as 88 g/GJ; however it was recommended 60 g/GJ in EMEP.

CO₂ emission factor was selected from IPCC- Tier 1 as 56,100 g/GJ.

N₂O emission factor was taken from AP42 [39] for uncontrolled conditions as 0,3 g/GJ. There is no recommendation in EMEP [40]. It was taken in NIR 2010 as 2.2 g/GJ.

NMVOC emission factor was selected as 2.6 from EMEP [40]. There was no recommendation for NMVOC in EMEP [40], however NMVOC parameter was calculated in some of the studies and also NIR 2010, therefore it was calculated here.

All of these emission factors were summarized in Table 5.29. Also these results were compared with former studies in Table 5.31.

5.2.3.2. Fuel oil combustion

Two major categories of fuel oil are burned by combustion sources: distillate oils and residual oils; with Nos. 1 and 2 being distillate oils; Nos. 5 and 6 being residual oils; and No. 4 being either distillate oil or a mixture of distillate and residual oils which are produced from the residue remaining after the lighter fractions (gasoline, kerosene, and distillate oils) have been removed from the crude oil, they contain significant quantities of ash, nitrogen, and sulphur.

Table 5.29 : Unabated natural gas combustion emissions for petroleum refineries.

Pollutant	EF g/GJ	Reference	Emissions ton/yr
PM	0.89	[40]	33.9
SO ₂	0.30	[40]	11.4
CO	38.91	[39], [40]	4.5
NO _x	88.01	[39]	3,353
CO ₂	56,100	[32]	2,137,345
N ₂ O	0.30	[39]	11.3
NMVOC	2.60	[40]	99.1

Residual oils are used mainly in utility, industrial, and large commercial applications [50]. No 6 Oil was assumed to be used in refinery for combustion however in NIR Turkey 2010 refinery gas was assumed to be used in refineries [26].

Emission factors used in calculations and final emissions for refinery fuel oil combustion were given in Table 5.30. Fuel oil consumption of oil refineries was 925,000 ton [8] in 2010.

Table 5.30 : Fuel oil combustion emissions of petroleum refineries.

Pollutant	EF g/GJ	Reference	Emissions ton/yr
PM	20	[40]	821
SO _x	653	[50]	26,810
SO ₂	630		25,871
SO ₃	23		939
CO	14	[50]	589
NO _x	194	[50]	7,947
CO ₂	73,300	[50]	3,007,530
N ₂ O	1.52	[50]	62
CH ₄	3	[32]	123
NMVOC	2.3	[40]	94

PM emission factor was chosen from EMEP [40] as 20 g/GJ. However it was given by EPA [50] as approximately 385 g/GJ for filterable PM (particulate collected on or prior to the filter of an EPA Method 5 or equivalent sampling train and calculated by Sulphur content of the fuel) and approximately 4.3 for condensable emissions. To reach more realistic results, and for the information deficit about the specific filter of EPA Method 5, EMEP emission factor was used.

SO₂ emission factor 485 g/GJ in EMEP [40] and considers SO₂ abatement and is based on 1% mass sulphur content. There was no information about SO₂ abatement, therefore SO₂ emission factor was chosen from EPA [50] as 630.53 g/GJ. Average weight percentage of the sulphur in the oil is 1.4% as announced by Tupras [42]. This value was directly used for calculations.

NO_x emission factor is given as 125 g/GJ in EMEP [40] but it was taken from EPA [50] as 194 g/GJ which was expressed as NO₂. Fuel nitrogen conversion is the more important NO_x -forming mechanism in residual oil boilers. It can account for 50 percent of the total NO_x emissions from residual oil firing. The percent conversion of fuel nitrogen to NO_x varies greatly, however; typically from 20 to 90 percent of

nitrogen in oil is converted to NO_x. Except in certain large units having unusually high peak flame temperatures, or in units firing a low nitrogen content residual oil, fuel NO_x generally accounts for over 50 percent of the total NO_x generated. [50].

$$\text{NO}_x \text{ emission} = (20,54 + 104,39 \times N) \times 0,12 \quad (5.2)$$

NO_x emission factor was calculated with the Equation 5.2 which was taken from AP42 [50].

NO_x emission: calculated as 5.64 kg NO_x /m³

N: weight percentage of Nitrogen in the fuel (0.45 [51])

CO₂ emission factor was given as 73,300 g/GJ in IPCC Guideline Tier 1 Method [32] and 72,600 g/GJ value was used in NIR Turkey 2010 [26]. This value was directly related with the carbon content of the fuel combusted. No 6 fuel oil was accepted to be used in oil refineries and specific emission factor of this fuel was given in EPA [50] as 71,716 g/GJ. However, this value is not certain for Turkish refineries' fuel oils and can be updated with the certain information about carbon content of the fuel used in refineries.

N₂O emission factor was taken from EPA [50] as 1,52 g/GJ, however it was given as 6 g/GJ in IPCC Guideline [32] and same value was used in NIR Turkey 2010 [26]. Formation of N₂O is minimized when combustion temperatures are kept high (above 801.67 °C) and excess air is kept to a minimum (less than 1 percent). Emissions can vary widely from unit to unit, or even from the same unit at different operating conditions. Average emission factors based on reported test data have been developed for conventional oil combustion systems [50]. NO_x emission factor of EPA [50] was high when compared to other sources. Therefore N₂O emission factor was chosen from AP42 too, despite of being lower when compared to other sources with considering internal conversions between NO_x could be considered in emission factor determining by EPA.

CH₄ emission factor was taken from IPCC Guideline [32] as 3 g/GJ, it was given by EPA [50] as 2.87 g/GJ.

NMVOC emission factor of EPA [50] interacted with VOC emissions under Total Organic Carbons title and there is no clear distinction between these parameters. Therefore NMVOC emission factor was taken from EMEP [40] as 2.3 g/GJ.

5.2.4. Overall emissions of petroleum refining industry

Regarding to the calculations given in the above sections, overall emissions are listed in Table 5.31 as comparative to another studies and evaluated below.

Petroleum refining emissions were calculated by Tier Method of IPCC Guideline [32] in NIR Turkey 2010 [26].

Table 5.31 : Overall emissions of petroleum refineries and comparisons

Pollutant	Emissions (ton/yr)			
	this study reference year : 2010	NIR Turkey reference year : 2010	Agacayak T. reference year : 2004	Elbir T. et al. reference year : 1995
PM	37,681		2,904	20,500
SO _x	59,225		21,780	57,500
CO	5,238		1,510	67,500
NO _x	11,810	15,220	7,260	7,750
CO ₂	5,144,874	5,690,770		
N ₂ O	74	30		
CH ₄	164	2,350		
VOC	44,374		56,628	
NMVOC	99		430	

PM emission was calculated as 37,861 ton/yr and higher than other studies. Regarding to Agacayak T. [24], the total PM emission is 2,904 ton in 2004; this value can be reached only when high technology abatement technologies are applied to Fluid catalytic cracking and fluid coking units like electrostatic precipitator and CO boiler. PM emission was also calculated by Elbir T. et al. [52] as 20,500 ton in 1995, such an increase in 15 years, from 1995 to 2010, seems realistic.

SO_x emissions generally come from processes include Claus plant and fuel oil combustion and differ seriously up to selected sulphur contents of the fuels. Also knowledge about the amount of each type and specialities of the fuel used in refineries is very important to calculate specific emission factor. In 2010 only petroleum and natural gas were used for combustion in oil refineries, there was no information about the amount of the refinery gas or fuel type. Under this

circumstance total SO_x emission was calculated as 59,225 ton for year 2010 which was generally compatible with the result of Elbir T. et. al. [52].

CO emission was calculated as 60,670 ton/ yr in 2010 with considering combustion of blowdown emissions in flare.

NO_x emission generally comes from catalytic cracking units and compressor engines. Agacayak T. [24] and Elbir T. et al. [52] calculated same for NO_x emission for the years 2004, 1994 and 2004. Also it was calculated in NIR Turkey 2010 [26] as two times of these two studies.

CO₂ emission was calculated lower than NIR Turkey 2010 [26]. This result is mainly because of the selected fuel type. In this study fuel oil No 6 was selected, but in NIR 2010, mixture of some fuels was used in calculations; for liquid fuels petroleum and other, gasoline, gas/diesel oil, LPG; for gaseous oils natural gas and refinery gas were considered.

N₂O emission was a little bit high when considered to NIR Turkey 2010 [26]. This was because of the selected liquid fuel type.

CH₄, NMVOC and VOC emissions have a strong relation. Normally VOC emission should be nearly equal to the sum of NMVOC and VOC emissions but in this study there seems no relation. This is mainly because of the emission factor chosen in the calculation period. In guidelines there was no distinction between these three parameters and each of them was given separately and individually, not together. Therefore comparison between these three parameters and with other studies will be meaningless.

Consequently, final emissions from four petroleum refineries (Batman, Izmir, Izmit and Kirikkale) are calculated with all assumptions and with a margin of error.

5.3. Organic Chemicals Industry

Huge variety of organic chemicals is produced in a stepwise manner from natural sources of carbon.

The initial step in the oil refineries (hydrocarbon processing industry) covers the production of high volume “*raw materials*” (e.g. naphtha) for the chemical industry from three natural sources of carbon which are crude oil, natural gas and the coal.

Organic chemicals industry starts from this point by using these raw materials. Refineries export raw materials to petrochemical plants where they are transformed by a complex combination of physical and chemical operations into a variety of “*base materials*” (e.g. ethylene, BTX aromatics). The base materials then subjected to further sequences of processing which introduce functional groups to produce “*intermediates and monomers*” (e.g. alcohols, aldehydes, ketons, acids, chlorides). Also base materials and intermediate and monomers are totally named as “Commodity Organic Chemicals”. The intermediates are converted into a large variety of “*fine products and polymers*” with have high level of functualisation and high commercial value (e.g. solvents, detergents, plastics, dyes and drugs) [53]. All of these products are summarized in Figure 5.5.

PETKIM petrochemical industry is the major producer of petrochemicals in Turkey with two production plants in Kocaeli-Yarimca and Izmir-Aliaga. Also Tupras in Kocaeli-Yarimca, Sasa in Adana and iron-steel producers manufacture petrochemicals as by-product or product.

5.3.1. Synthetic rubber

There are different types of synthetic rubbers; SBR (styrene Butadiene rubber), CBR (Cis Polybutadiene Rubber), Synthetic Latex, Other Synthetic Latexes. Production technologies have established in Turkey for all of aforementioned synthetic rubbers, except CBR. There were six companies produce synthetic latex in Turkey in 2010 and fourteen companies produce crumb and other synthetic rubbers (e.g. nitrile) [62].

Copolymers containing less than 45 weight per cent styrene are known as styrene-butadiene rubber (SBR). As the styrene content is increased over 45 weight per cent, the product becomes increasingly more plastic. Two types of polymerization reaction are used to produce styrene-butadiene copolymers; the emulsion type and the solution type. The emulsion products can be sold in either a granular solid form, known as crumb, or in a liquid form, known as latex.

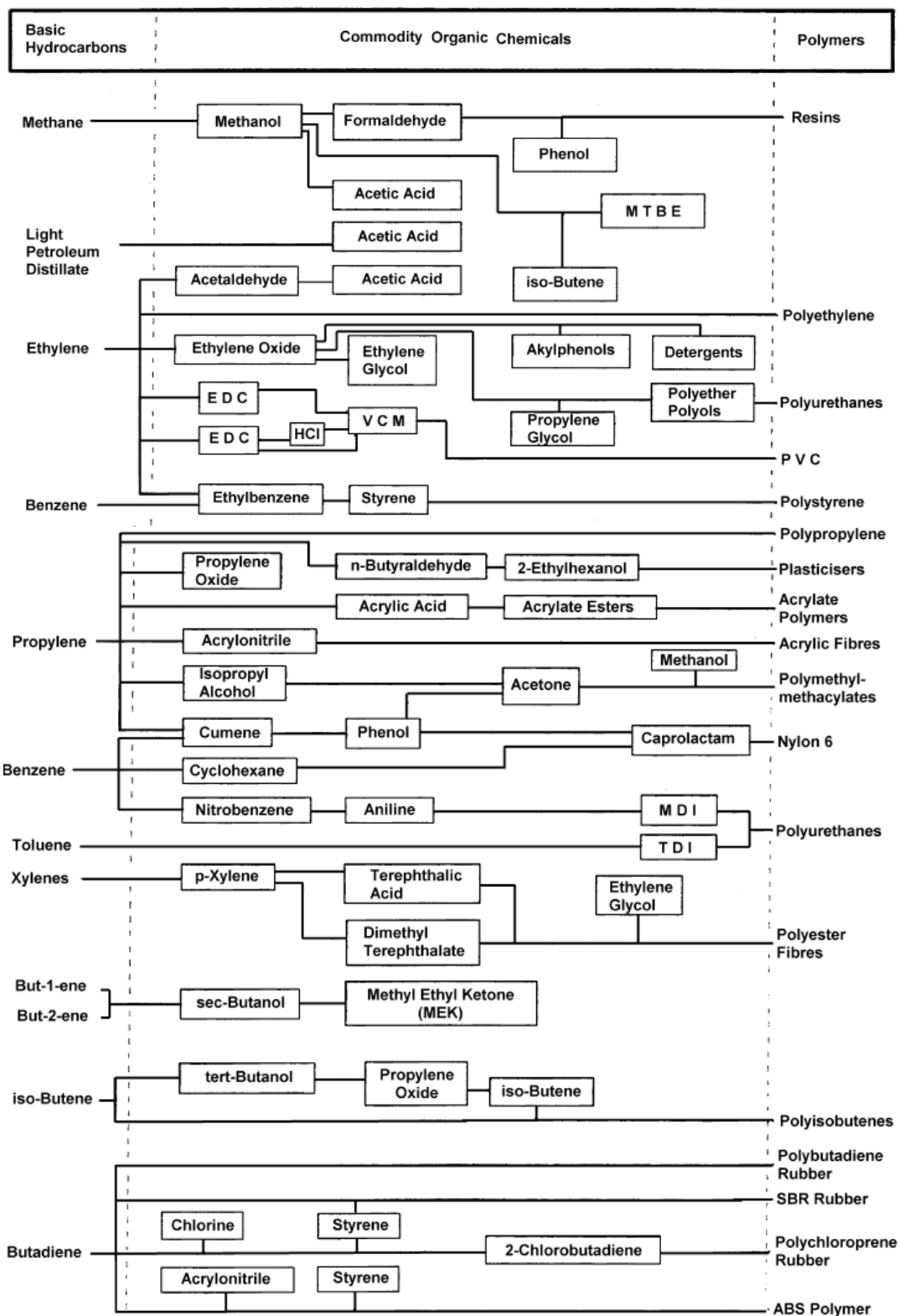


Figure 5.5: Pathways in the organic chemical industry [53].

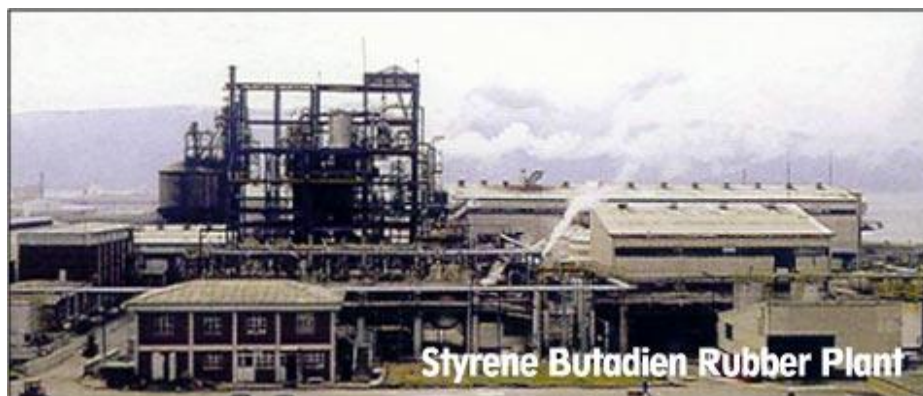


Figure 5.6 : Inactive SBR plant in Izmir-Aliaga [58].

The main producer of SBR and CBR in Turkey is Tupras which is privatised from Petkim, sold again to Koc Group and inactive since 2007 because of economic and structural reasons [60]. However Synthetic Latex and other synthetic rubbers are produced in Turkey and the emissions of these sectors are calculated in this section.



Figure 5.7 : Inactive CBR plant in Izmir-Aliaga [58].

Polybutadiene (BR or CBR) is the second largest volume synthetic rubber produced, next to styrene-butadiene rubber (SBR) [59].

[63] Emulsion crumb production process start with fresh styrene and butadiene piping separately to the manufacturing plant from the storage area and taking through reactors for reaction. The reaction product formed in the emulsion phase of the reaction mixture is a milky white emulsion called latex. The latex emulsion is introduced to flash tanks where, using vacuum flashing, the unreacted butadiene is removed and then compressed, condensed, and pumped back to the tank farm storage area for subsequent reuse.

The condenser tail gases and noncondensables pass through a butadiene adsorber/desorber unit, where more butadiene is recovered. The latex stream from

the butadiene recovery area is then sent to the styrene recovery process, usually taking place in perforated plate steam stripping columns. From the styrene stripper, the latex is stored in blend tanks. The latex is pumped from the blend tanks to coagulation vessels, where dilute sulphuric acid and sodium chloride solution are added. The acid and brine mixture causes the emulsion to break, releasing the styrene-butadiene copolymer as crumb product. The coagulation vessels are open to the atmosphere. Leaving the coagulation process, the crumb and brine acid slurry is separated by screens into solid and liquid. The crumb product is processed in rotary presses that squeeze out most of the entrained water. The liquid (brine/acid) from the screening area and the rotary presses is cycled to the coagulation area for reuse. The partially dried crumb is then processed in a continuous belt dryer that blows hot air at approximately 93°C across the crumb to complete the drying of the product. The dried product is baled and weighed before shipment.

Emulsion polymerization can also be used to produce latex products. As in emulsion crumb polymerization, the monomers are piped to the processing plant from the storage area. The polymerization reaction is taken to near completion (98 to 99 percent conversion), and the recovery of unreacted monomers is therefore uneconomical. After discharge from the blowdown tank or the styrene stripper, the latex is stored in process tanks. Stripped latex is passed through a series of screen filters to remove unwanted solids and is stored in blending tanks, where antioxidants are added and mixed. Finally, latex is pumped from the blending tanks to be packaged or bulk loaded.

5.3.1.1. Process emissions

The main emission of production process is VOC which is mainly occurs from uncontrolled monomer recovery, absorber vents, uncontrolled blend/coagulation tank and dryers. Only VOC emissions were calculated.

Table 5.32 : Process VOC emissions of styrene-butadiene copolymer production.

	Uncontrolled		Controlled	
	EF	Emission	EF	Emission
	kg/ton	ton/yr	kg/ton	ton/yr
Crumb production	5.53	124	3.19	71
Latex production	8.55	48	8.55	48

In the emulsion crumb process, uncontrolled noncondensed tail gases (VOCs) pass through a butadiene absorber control device, which is 90 percent efficient, to the atmosphere or, in some plants, to a flare stack. No controls are presently employed for the blend tank and/or coagulation tank areas, on either crumb or latex facilities. Emissions from dryers in the crumb process and the monomer removal part of the latex process do not employ control devices [63]. Therefore there is no strong difference between controlled and uncontrolled VOC emissions of SBR production.

Emission factors were taken from EPA [63]. There was no emission data about this sector in NIR 2010 Turkey [26] for comparison of the calculation results.

5.3.1.2. Fuel combustion emissions

Fuel combustion emissions of SBR/CBR production sector were not given separately but included in final emissions calculated in Section 5.4.13, because there was no specific information for the fuel consumption details of this sector.

5.3.2. Ethylene – propylene

Ethylene is a raw material used in petrochemical industry. Worldwide almost all ethylene is made by way of steam cracking of petrochemical feedstock. Ethylene may be produced from steam cracking of petrochemical feedstock in a petrochemical plant, and may also be produced from cracking and other processes operated at petroleum refineries. Steam cracking for ethylene production also produces secondary products including propylene and butadiene [65].

In Turkey Ethylene is produced mainly by thermal cracking of ‘Naphtha’ (also known as Light Distillate Fraction or crude gasoline) fractions. Feedstock is preheated to 750–850 °C by adding hot products and steam to the reaction furnace. Additional steam is added to dilute the reaction mixture. After the reaction the gas mixture is quenched with cold oil, which in turn is used to produce steam. The oil gas steam mixture is separated in different fractions in a rectification section. In several steps the most important products of the mixture are separated. The low boiling products ethylene, propylene and the butylenes are separated after drying, compression and distillation [61].

In Turkey, in 2010, Ethylene was produced in only Aliaga, Izmir Plant of Petkim by using liquid naphtha from oil refining as feedstock by steam cracking method.

Produced Ethylene was not sold in the market, only used as a feedstock in other factories of Petkim.



Figure 5.8 : Petkim Ethylene Plant [64].

5.3.2.1. Process emissions

Ethylene – propylene production is the source of CO₂, CH₄ and NMVOC emissions, but only NMVOC emission was considered in this study due to the reasons explained below.

Steam cracking process consumes feedstock and supplemental energy which are both the source of CO₂ emissions. Actually, it was hard to separate ethylene production emissions into two parts as “process emissions” and “fuel combustion emissions” because this industry uses naphtha which is a fuel as a feedstock in the process and supplemental fuel to meet energy demand for cracking furnace.

Regarding to IPCC Guideline [65] entire of fuel combustion emissions should be reported under industrial process emissions. However, in this study, the amount of consumed fuels by this sector were included in national energy statistics of Turkey and calculated in Section 5.4.13 within the fuel combustion emissions of all chemical industry.

CH₄ is emitted primarily from leakage losses and from cracking of naphtha and there is only one emission factor without any distinction between these two CH₄ sources [65]. Therefore entire of the CH₄ emissions emitted from ethylene production was

accepted as occurred from cracking of naphtha and evaluated under fuel combustion emissions of ethylene production.

Finally only NMVOC emission was evaluated under ‘process emissions of ethylene production’ title.

Table 5.33 : Process emissions of ethylene production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
NMVOC	4.5	2,246	0.6	300

Controlled NMVOC emission factor was taken from EMEP [61] and corroborated with IPPC [53], uncontrolled one was taken from IPPC [53] too.

[53] All crackers are provided with flare gas systems to allow safe disposal of any hydrocarbons or hydrogen that can not be recovered in the process. Except this, during normal operation there are very few VOC emissions from the cracking process because they are recycled into the process, used as a fuel or routed to associated processes on an integrated site. Elevated VOC emissions from ethylene plants are intermittent but occur during plant start-up and shutdown, process upsets and emergencies. VOCs may be emitted from pressure relief devices, intentional venting of off-specification materials or depressurising and purging of equipment for maintenance. Crack gas compressors and refrigeration compressor outages are potential sources of short term, high rate VOC emissions.

The emissions calculated in Table 5.33 were considered without flaring for uncontrolled conditions.

Propylene production emissions from propylene production processes were not considered in this study and all calculations were made with considering Ethylene production because there is no separation between these two lower olefins. Also they were accepted to be produced in one cycle in a production chain and propylene was accepted as a by-product of Ethylene. However propylene production related NMVOC emission factor was taken as 1.4 kg/ton in NIR 2010 Turkey [26], there was no information about the calculation of other emissions of Propylene production.

5.3.2.2. Fuel combustion emissions

The steam cracking olefins process is highly endothermic, and requires large quantities of energy at high temperature ($>800\text{ }^{\circ}\text{C}$) to achieve feedstock dissociation, whilst at the same time requiring the application of cryogenic separation processes (involving deep refrigeration to temperatures as low as $-150\text{ }^{\circ}\text{C}$) to separate and purify the products. Steam crackers are therefore designed to be highly energy-integrated units, recovering as much as possible of the energy required to be input at the front-end of the process to convert to the work required for the separation processes. This is usually accomplished by raising high-pressure steam in the furnace area, which is then used to drive turbines for cracked gas compression and refrigeration systems [53].

The major emissions to air are CO_2 , NO_x , CO , CH_4 produced during the combustion of fuel gases in the reaction furnace and hydrocarbons. The first three compounds are produced during the combustion of fuel gases in the reaction furnace [61].

Table 5.34 : Combustion emissions of ethylene production.

	EF kg/ton	Emissions ton/yr
CO_2	1730	863,616
NO_x	0.54	270
CH_4	3	1,498
PM	0.4	200

CO_2 and NO_x emission factor is calculated by some statistical approaches in IPPC [53]. The emission factor was derived from this statistics without considering any abatement technologies. CO_2 emission factor is recommended as 1730 kg/ton in IPCC [65] by Tier 1 methodology; however it was taken as 1900 kg/ton with considering statistics given in IPPC [53].

There was no specific PM emission factor for fuel combustion, which separates fuel combustion and process emissions. Therefore all PM emission was accepted to be emitted from fuel combustion even though it is known that some of the PM emissions were emitted from processes.

Only CH_4 emissions of Ethylene production was calculated in NIR Turkey 2010 [26] by using emission factor as 1 kg/ton by Tier 1 methodology and included in “other”

sector. Nevertheless it is given as 3 kg/ton by IPCC [65] and this value was used in this study.

Fuel combustion emissions of this sector included under final emissions calculated in Section 5.4.13. Above calculated emissions were given for only individual industry comparison purposes.

5.3.3. Aromatics – BTX

The term ‘aromatics’ is used to describe benzene, toluene, mixed xylenes, ortho-xylene, para-xylene and meta-xylene (commonly known as BTX - Benzene, Toluene, Xylene). The BTX aromatics are produced from three main feedstocks; refinery reformates, steam cracker pyrolysis gasoline (pygas) and benzol from coal tar processing [53]. In Turkey, it is produced from Naphtha by Petkim, also BTX is produced as a coke oven by-product in steel production but has a small production capacity, and therefore it was not calculated.

The first step of the process is ‘Refining’. The aim of the process is hydrogenation of diolefins and desulphurization. This process is done in 200-250 °C with Hydrogen with a catalyst or solvent such as Co, Mo, Ni, and Pd. In Petkim pygas and naphtha are processed as feedstock. The second step is extraction and non aromatic compounds separation. The third step is distillation which Benzene and Toluene are separated. In the transalkylation process Benzene and C8 aromatics are produced from Toluene in 350-530°C with Zeolite as a catalyst separation of reformers in a splitter column. Then in the isomerisation process, Xylene types are produced. Finally, the 5th step aims the enrichment of Benzene and Toluene [53].

These are not all of the processes in an aromatics plant but a general summary of it. All of these processes are included in Petkim Aromatics plant.



Figure 5.9 : Petkim Aromatics Plant [66].

5.3.3.1. Process emissions

Emissions from aromatics plants are to a large extent due to the use of utilities (e.g. heat, power, steam, and cooling water) needed by the aromatics separation processes. A relatively minor component of the emissions are related to the core process but there may be arising due to the elimination of certain impurities, inherent waste streams generated during processing and emissions from equipment. Some chemical reactions take place at high pressures and temperatures, but these are inherent to the processes. There are no particular process parameters that lead to a higher than normal emission patterns [53].

CH₄ emissions are emitted mainly from various fugitive sources especially when producing from naphtha. VOC emissions occur from process and fugitive sources as tanks. Emission factors used in calculations and emissions emitted from processes were given in Table 5.35.

Table 5.35 : Process emissions of aromatics production.

	Uncontrolled		Controlled	
	EF kg/ton	Emission ton/yr	EF kg/ton	Emission ton/yr
VOC	2.4	513	0.2	51
CH ₄	0.9	222	0.1	22

Emission factors were derived from IPPC [53].

5.3.3.2. Fuel combustion emissions

The heating furnaces give rise to following combustion gases; SO₂ because of the sulphur content of the fuel, NO_x and PM as flare stack releases.

Table 5.36 : Combustion emissions of aromatics production.

	EF g/GJ	Emissions ton/yr
CO ₂	71,716	184,392
PM	20	51
SO _x	653	1,680
CO	14	37
NO _x	194	498
N ₂ O	2	4
CH ₄	3	8
NMVOG	2	6

Emission factors were decided by comparing the guidelines of EPA [50], EMEP [40] and IPCC [123]. Additionally fuel combustion emissions of this sector included under final emissions calculated in Section 5.4.13. Above calculated emissions were given for only individual industry comparison purposes as indicated in Materials and Method, Section 3.

5.3.4. Vinyl chloride monomer (EDC/VCM)

[53] Vinyl Chloride Monomer (VCM) is used almost exclusively in the manufacture of the commercially important plastic Polyvinyl Chloride (PVC) and the associated homo-polymers / copolymers.

VCM is produced in the Ethylene based process; 1,2 Dichloroethane (EDC-Ethane Dichloride) is synthesised by the chlorination of Ethylene (Direct Chlorination) or by the chlorination of ethylene with Hydrochloric Acid (HCl) and oxygen (oxychlorination) [53] at high temperatures. The final step is the pyrolysis of EDC to produce VCM.

VCM is produced in Turkey in only Petkim Aliaga, Izmir.

[61] The main process used for VCM production is the balanced process. When all the HCl generated in 1,2-Dichloroethane cracking is re-used in an oxychlorination section, and when no 1,2-dichloroethane or HCl is imported or exported, then the VCM unit is called a ‘balanced unit’. The balanced process consists of two routes operated simultaneously; in the direct chlorination route, chlorine is added to ethylene to form 1,2-dichloroethane; in the oxychlorination route, ethylene reacts with hydrogen chloride under oxidative conditions (presence of oxygen) also to form 1,2-dichloroethane.



Figure 5.10 : Petkim VCM Plant [67].

5.3.4.1. Process emissions

VCM, as a carcinogen, is the gaseous pollutant of most concern, but other pollutants include EDC and chlorinated hydrocarbons such as carbon tetrachloride [53]. These pollutants were not determined as key parameters in this study and were not evaluated.

However, VOC emissions emitted mainly from maintenance of the process and fugitive sources were calculated in Table 5.37. VOC emissions include chlorinated hydrocarbons, Ethane and Vinyl Chloride occurs in the process.

The CO₂ emission from the process includes noncombustion CO₂ emissions from the ethylene dichloride process vent. Non-combustion CH₄ emissions from ethylene dichloride/vinyl chloride monomer production are negligible [65].

Table 5.37 : Process emissions of VCM production.

	Uncontrolled		Controlled	
	EF	Emission	EF	Emission
	kg/ton	ton/yr	kg/ton	ton/yr
<i>EDC Production</i>				
NMVOC	2.5	560	0.5	112
VOC	12.1	2718	2.4	544
CO ₂	5.7	1276		
<i>VCM Production</i>				
NMVOC	2.5	354	0.5	112
VOC	7.1	1001	1.4	317
CO ₂	8.3	1176		

NM VOC and VOC emission factors were taken from IPPC [53], CO₂ emission factor was taken from IPCC [65] for uncontrolled conditions. VOC and NM VOC emissions were calculated individually as indicated by IPPC [53].

NM VOC and VOC abatement technologies include sophisticated types of seals or same technologies as indicated by EMEP [61]. 80% abatement efficiency was accepted.

5.3.4.2. Fuel combustion emissions

Combustion emissions mainly occur from natural gas and or hydrogen combustion in the EDC cracking furnace and contain NO_x, CO, CH₄ and CO₂, except chlorinated compounds.

Fuel combustion CO₂ emission factors include combustion of both process waste gas and auxiliary fuel in the process waste gas thermal incinerator [65].

Table 5.38 : Combustion emissions of VCM production.

	EF kg/ton	Emission ton/yr
NO _x	0.24	34
CO	15.4	2.2
CO ₂	477	83,270
CH ₄	0.023	3.2
Total	493	83310

Additionally fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13. Above calculated emissions were given for only individual industry comparison purposes. CO₂ and CH₄ emission factor source was IPPC [53], NO_x and CO emission factor source was IPPC [53].

5.3.5. Ethylene oxide – Ethylene glycol (EO/EG)

Ethylene oxide (EO-C₂H₄O) is a key chemical intermediate in the manufacture of many important products. Most ethylene oxide product is converted into glycols, detergent ethoxylates etc.

Ethylene glycols are produced by reacting EO with water. EO is formed by reacting gaseous ethylene and oxygen over a solid, silver containing catalyst. The exothermic reaction is carried out at elevated temperature (200-300 °C) and pressures (15-25

bar) with a residence time of one second. The main by-products are CO₂ and water, which results from the highly exothermic full oxidation of ethylene.

Monoethylene Glycol (MEG) is formed by the hydrolysis of EO with water at elevated temperature and pressure and is the most important outlet for EO. The main co-product in the MEG manufacturing process is di ethylene Glycol (DEG), which is formed by the reaction of MEG with EO.

Above-mentioned process description was derived from IPPC [53].



Figure 5.11: Petkim EO/EG Plant [67].

MEG and DEG were produced in integrated plant of Petkim [68] which was the only producer in Turkey in 2010 [69].

5.3.5.1. Process emissions

In air-based plants both NMVOC and VOC emissions (prior to treatment) from ethylene oxide plants mainly arise from the secondary absorber vent and the fractionating tower vent [61]. Cooling towers are the another source of VOC emissions [53] and it was accepted that there was no direct treatment of the gas stream leaving the cooling tower and cooling tower vapours are vented to the atmosphere for uncontrolled conditions. Storage tanks are another source of VOC and contribute to plant emissions with emitted EO emissions. Also fugitive/non-channelled emissions arise from reactor analyser vents and from maintenance activities [53]. CH₄ emissions arise from purification process exhaust gas steam, process vents and fugitive emission sources [65]. CO₂ is a by-product of the process

and depends on catalyst selectivity. There was no information about catalyst selectivity of the Petkim process therefore default values were used in calculations.

Table 5.39 : Process emissions of EO/EG production.

	Uncontrolled		Controlled	
	EF	Emission	EF	Emission
	kg/ton	ton/yr	kg/ton	ton/yr
VOC	21	1,612	0.03	2.36
CH ₄	1.79	141	0.79	62
CO ₂	863	67,878		

CO₂ emission factor was developed by IPCC [65] by using stoichiometric principles and assuming that emissions of CH₄ and NMVOC from the process were negligible and that all of the carbon contained in the ethylene feedstock was converted either into ethylene oxide product or to CO₂ emissions and does not include emissions from flares. However CH₄ and VOC emissions were calculated in this study because they are not separated into two or more sub-categories as emitted from feedstock or other fugitive sources in emission factor sources. Thermal treatment was accepted for the control technology of CH₄ emissions.

NMVOC emission factor is given as 2 kg/ton by EMEP [61]. However this emission factor seems inadequate for uncontrolled emissions, therefore VOC emission factor was taken from IPPC [53] and CH₄ emission factor was taken from IPCC [65]. CO₂ emission factor was taken from IPCC [65] for the air based plants and default emission factor without abatement.

CO₂ emissions were not calculated for uncontrolled conditions because there was no information for reuse of ‘after CO₂ stripping’ emissions. In Petkim, CO₂ emissions are absorbed with K₂CO₃ and this aqueous solution is boiled, thus CO₂ emissions were eliminated [69]. There was no information about reuse, therefore it was accepted that CO₂ emissions were not controlled.

5.3.5.2. Fuel combustion emissions

The EO/EG process is both a consumer and a producer of energy. The EO section typically a net energy producer and this is used to generate steam. The EG section is a net consumer of energy. Apart from generating steam, the process also generates a number of gaseous and liquid effluent streams that may be recovered as fuel for

furnaces, power plants and steam boilers [53]. There is no site specific information about fuel recovery in Petkim.

Fuel combustion emissions of this sector included under final emissions calculated in Section 5.4.13. Above calculated emissions are given for only individual industry comparison purposes as indicated in Materials and Method, Section 3

There was no information about EO/EG production emissions in NIR 2010 Turkey [26].

5.3.6. Acrylonitrile (Vinyl Cyanide)

Acrylonitrile is made either by way of direct ammoxidation of propylene with ammonia (NH_3) and oxygen over a catalyst or by ammoxidation of propane or directly from reaction of propane with hydrogen peroxide [65]. First process was used in Petkim which is the only producer in Turkey in 2010; nearly the entire of the produced ACN was used for acrylic fibre production [69].



Figure 5.12 : ACN Plant of Petkim in Aliaga, Izmir [67].

The process involves a fluidized bed reaction of chemical-grade propylene, ammonia, and oxygen over a catalyst. The catalyst is a mixture of heavy metal oxides (including bismuth and molybdenum). The process produces acrylonitrile as its primary product and acetonitrile (methyl cyanide) and hydrogen cyanide (HCN) as secondary products. The ammoxidation process also produces by-product CO_2 , CO, and water from the direct oxidation of the propylene feedstock, and produces other hydrocarbons from side reactions in the ammoxidation process [65].

Hydrogen cyanide that is not used or sold may be burned for energy recovery or flared. The acetonitrile may be also recovered for sale as a product, but more often the acetonitrile is burned for energy recovery or flared [65].

5.3.6.1. Process emissions

Main process emissions are NMVOC, CH₄, CO₂ and NH₃. The off gas can be treated by flare.

Acrylonitrile and other non-methane hydrocarbons are released from miscellaneous process vents, including storage tanks [65].

The emission factors were derived from the catalyst selectivity using stoichiometric principles and were based on the assumption that emissions of CH₄ and NMVOC from the process were negligible and that all of the carbon contained in the ethylene feedstock was converted either into ethylene oxide product or to CO₂ emissions [53].

In many cases the vent stream are flared, oxidised (thermally or catalytically), or sent to boiler or power plant (either attached to the core plant or a central site facility).

Table 5.40 :Process emissions of ACN production.

	Uncontrolled		Controlled	
	EF	Emissions	EF	Emissions
	kg/ton	ton/yr	kg/ton	ton/yr
VOC	50	4,702	1	94
CO	125	11,756	6.25	588
CO ₂	1,000	94,045		
CH ₄	3.6	339	0.18	17
NH ₃	0.2	19	0.03	3

CO₂ emission factor was selected with considering secondary products burned for energy recovery and/or flared, which was default emission factor in IPCC [65]. Controlled CO emissions were selected with considering thermal treatment with 95% reduction efficiency. NH₃ controlling technology was accepted as scrubber with 85% abatement efficiency.

VOC emission factor was taken from IPCC [53] and EMEP [61], CH₄ emission factor was taken from IPCC [65] and NH₃ emission factor was taken from both Reinders [44] and IPCC [53], CO emission factor was taken from Reinders [44].

5.3.6.2. Fuel combustion emissions

Propylene ammoxidation is a highly exothermic reaction. ACN plants are net exporters of energy as the heat of reaction is used to generate high pressure steam, which in turn can be used to drive air compressors, exported and provide energy to downstream separation and purification units. The energy export range is 340 to 5700 MJ/t ACN [65]. In Petkim, the generated heat is used to obtain high-pressure steam.

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.3.7. Phthalic anhydride

Phthalic Anhydride (PAN) is used for plasticizers, alkyd resin, unsaturated polyester resins etc. and produced by catalytic oxidation of either orthoxylene or naphthalene [70]. Petkim was the only producer of PAN in 2010 in Turkey, and used o-xylene as the main feedstock [69].



Figure 5.13 : PA Plant of Petkim in Aliaga, Izmir [71].

In PAN production by using o-xylene as the basic feedstock, filtered air is preheated, compressed, and mixed with vaporized o-xylene and fed into the fixed-bed tubular reactors. The reactors contain the catalyst, vanadium pentoxide, and are operated at 340 to 385°C. Small amounts of sulphur dioxide are added to the reactor feed to maintain catalyst activity. Exothermic heat is removed by a molten salt bath circulated around the reactor tubes and transferred to a steam generation system [70].

5.3.7.1. Process emissions

The major contributor of emissions is the reactor and condenser effluent which is vented from then condenser unit. Particulate, sulphur oxides, and carbon monoxide make up the emissions, with carbon monoxide comprising over half the total. The most efficient (96 percent) system of control is the combined usage of a water scrubber and thermal incinerator. A thermal incinerator alone is approximately 95 percent efficient in combustion of pollutants [70]. SO₂ is used to keep the catalyst active, therefore exists in emissions [44].

Table 5.41 :Process emissions of PAN production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	120.4	4,784	6.4	254
SO _x	4.7	187	4.7	187
NMVOC	1.2	48	0.1	4
CO	151	6,000	8	318

In the calculations, abatement technology is accepted as ‘thermal incineration’ for the main process stream, pre-treatment and distillation units. Emission factor source was EPA [70].

5.3.7.2. Fuel combustion emissions

The reactions are exothermic. In the catalyst space there are cooling pipes to carry of the heat produced. This heat is used to produce high-pressure steam [44].

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.3.8. Polyethylene

Polyethylene is produced in low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE). In this section LDPE and LLDPE are considered.

[61] Polyethylene is a polymer of ethylene and has the general empirical formula (-CH₂CH₂-). Manufacturing process depends upon the type of polymer produced.

5.3.8.1. Low density polyethylene

LDPE is a tough waxy polymer, with approximately 2 % branching between polymer chains and a density of about 0.92 t/m^3 . LDPE is generally produced by high pressure and high temperature catalytic polymerisation of ethylene in a tubular or autoclave reactor.

A low pressure method is generally used in which ethylene and a co-monomer such as butene or hexane is catalytically polymerised [61]. The special name of the process is 'Extrusion Coating' or 'Autoclave Reactor'.



Figure 5.14 : LDPE Plant of Petkim in Aliaga, Izmir [74].

In Turkey, in 2010 it was produced by only Petkim which has a factory at Izmir, Aliaga which was purchased after privatisation in 2003.

5.3.8.1.1. Process emissions

The major emissions to air are NMVOC unreacted monomer (i.e. ethylene), some partially reacted monomer (alkenes and alkanes) together with small amounts of additives. NMVOCs are emitted primarily through leakages [61].

Table 5.42 : Process emissions of LDPE production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
VOC	16	3032	2.4	455
PM	0.31	59	0.031	4

VOC emissions include all hydrocarbons and other organic compounds including fugitive emissions. However regarding to Barlow A., et. al. [73] VOC emissions do not include CH₄, therefore they can be assumed as equal to NMVOC emissions. It should be noted that, this assumption should be considered only for separately comparison of NMVOC or VOC emissions with other sectors or studies.

Controlled conditions include 85% VOC abatement and 90% PM abatement assumptions. VOC emission factors are taken from EMEP- Tier 2 [61] and PM emission factors are taken from Barlow et.al. [73].

5.3.8.1.2. Fuel combustion emissions

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.3.8.2. Linear low density polyethylene

LLDPE is a crystalline polymer with no chain branching and a density comparable to that of LDPE. A low pressure method is generally used in which ethylene and a co-monomer such as butene or hexane is catalytically polymerised [61]. The special name of the process is ‘Blown Film or ‘Tubular Reactor’.



Figure 5.15: LLDPE Plant of Petkim in Aliaga, Izmir [72].

In Turkey LLDPE was only produced by Petkim in 2010.

5.3.8.2.1. Process emissions

The emission is depends on the temperature and selected emission factors were listed in Table 5.43.

Table 5.43 :Process emissions of LLDPE production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
VOC	16	3032	2.4	332
TSP	0.25	47	0.025	3

Controlled conditions include 85% VOC abatement and 90% PM abatement assumptions.

VOC emission factors were taken from EMEP-Tier 2 [61] and PM emission factors were taken from Barlow et.al. [73].

5.3.8.2.2. Fuel combustion emissions

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.3.8.3. High density polyethylene

HDPE is a crystalline polymer with no chain branching and a density of about 0.96t/m³. HDPE is produced by low pressure polymerisation of ethylene in a reactor containing a liquid hydrocarbon diluent and in the presence of Ziegler catalysts. The polymer produces slurry as it forms and is filtered from the solvent.



Figure 5.16 : HDPE Plant of Petkim in Aliaga, Izmir [75].

HDPE was only produced by Petkim which is the only producer of the Turkey and produces 25% of the HDPE need of the country in 2010 [69].

5.3.8.3.1. Process emissions

The main emissions emitted from HDPE production process are VOC and particulate. VOC emission factor includes all HC and other organic compounds including fugitive emissions.

Table 5.44 :Process emissions of HDPE production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
NMVOC	15.3	1259	2.3	189
TSP	0.6	53	0.097	8

VOC and NMVOC emission factors were taken from EMEP-Tier 2 [61] and IPPC [53] as the Europe average values. Controlled conditions include 85% VOC abatement and 90% PM abatement assumptions.

5.3.8.3.2. Fuel combustion emissions

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.3.9. Polypropylene

Polypropylene (PP) is one of the most economically important thermoplastic materials.

PP is produced by polymerisation of propylene. Most of the applied processes for the production of polypropylene are very similar to the ones used to produce high density polyethylene. The most important and most widely used processes for the production of polypropylene are gas phase processes and suspension processes [61].

The traditional suspension processes using an organic diluent are known within the PP nomenclature as ‘slurry’ processes. Modern suspension processes use a liquid monomer instead of a solvent, known as ‘bulk’ processes. The major emission to air is propylene [61].



Figure 5.17 : PP Plant of Petkim in Aliaga, Izmir [76].

The only PP producer in Turkey is Petkim which is located in Aliaga, Izmir and uses slurry process [69].

5.3.9.1. Process emissions

Traditional PP suspension (slurry) process emissions and consumption levels can be considered comparable with the HDPE slurry process [69]. The major sources of air contamination in plastics manufacturing are the raw materials or monomers, solvents, or other volatile liquids emitted during the reaction; sublimed solids such as phthalic anhydride emitted in alkyd production, and solvents lost during storage and handling of thinned resins [78]. PP process causes VOC and PM emissions as HDPE process.

Table 5.45 :Process emissions of PP production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
NMVOC	4	201	0.6	80
TSP	1.5	535	0.15	20

VOC emissions include all hydrocarbons and other organic compounds including fugitive emissions. However regarding to Adams K., et. al. [77] VOC emissions do not include CH₄, therefore they can be assumed as equal to NMVOC emissions. It should be noted that, this assumption should be considered only for separately comparison of NMVOC or VOC emissions with other sectors or studies.

[78] Much of the control equipment used in this industry is a basic part of the system serving to recover a reactant or product. These controls include floating roof tanks or vapour recovery systems on volatile material, storage units, vapour recovery systems (adsorption or condensers), purge lines venting to a flare system, and vacuum exhaust line recovery systems.

Controlled conditions include 85% VOC abatement and 90% PM abatement efficiency assumptions.

VOC emission factor was taken from EMEP-Tier 2 [61] and compatible with other emission factor sources. PM emission factor was taken from EPA [78].

5.3.9.2. Fuel combustion emissions

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.3.10. Polystyrene

Polystyrene (PS) belongs to the group of standard thermoplastics that also includes PE, PP, and PVC. Because of its special properties, PS can be used in an extremely wide range of applications [59].

[59] The process of producing polystyrene requires one reactor or a series of reactors controlled by a set of parameters such as temperature, pressure and conversion rate. The process requires the addition of several raw materials, i.e. solvent, initiator (optional), and chain transfer agents, into the reactors under well defined conditions. The reaction heat is removed by transfer to the new incoming feed and/or by the evaporation of solvent and/or by heat transfer medium, i.e. circulating oil. The crude product coming out of the reactor train has a solid content of between 60 and 90 %. To remove the unconverted monomer and solvent from the crude product, it is heated to about 220–260 °C and led through a high vacuum. This is called the devolatilisation step and can have one or two stages. Finally, the cleaned, high purity polymer is granulated. The monomer and solvent are stripped in the devolatilisation section and recycled within the process.



Figure 5.18 : PS Plant of Petkim in Aliaga, Izmir [81].

In Turkey PS production is made by private sector. Yarimca factory is privatised from Tupras in 2004 and manufacturing is stopped in 2005 because of the economic reasons [69]. The other one is a private company, Basic Petrochemicals, and the only producer of PS in Turkey in 2010. Also there are some other producers but they produce end-product from PS by using it as semi-finished product, therefore they were not considered in calculations.

5.3.10.1. Process emissions

The major emissions to air are styrene and other hydrocarbons. The losses due to leakage can be limited by using certain types of seals and application of double seals near pumps.

Table 5.46 :Process emissions of PS production.

	Uncontrolled		Controlled	
	EF	Emissions	EF	Emissions
	kg/ton	ton/yr	kg/ton	ton/yr
NMVOC	3.207	385	0.044	5.28
PM	0.02	2.4	0.002	0.24

Although PM emission is negligible for PS manufacturing industry, PM emission was calculated by taking emission factor from IPPC [59]. NMVOC emission factor was taken from EPA [79] and compatible with the emission factor range given in IPPC [59]. Controlled conditions include 85% VOC abatement and 90% PM abatement efficiency assumptions.

5.3.10.2. Fuel combustion emissions

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.3.11. Polyvinyl Chloride

Polyvinyl chloride (PVC) is used in most industrial sectors (e.g. packaging, automotive, building, agriculture, medical care) [59] and PVC is made by polymerising vinyl chloride. Several processes are available, which are mass polymerisation (which accounts for 8 % of PVC production in Europe), emulsion polymerisation (E-PVC) (12 %) or suspension polymerisation (S-PVC) (80 %) [61]. S-PVC method is used in Petkim.

Suspension polymerisation is a batch process. Vinyl chloride monomer (VCM) is dispersed in water by agitation. Polymerisation starts by adding monomer-soluble initiators and addition of suspension stabilisers and suspending agents minimises coalescence of the grains. The reaction temperature is used for the control of the polymer molecular weight and varies between 45 and 75°C. Reactor pressure is between 800 and 1200 kPa. Reaction is carried out until 85% conversion is reached. After polymerisation most unreacted monomer is recovered in a dump tank. The remaining monomer is stripped from the polymer with steam. The waste water is separated in a centrifugator. The PVC resin is dried with hot air and stored [59].

Only producer was Petkim in Turkey, in 2010. This factory consumes all VCM produced in VCM factory of Petkim [69].



Figure 5.19 : PVC Plant of Petkim in Aliaga, Izmir [82].

5.3.11.1. Process emissions

The major emissions to air are vinyl chloride due to leakage and storage loss. The losses due to leakage can be limited by use of certain types of seals and application of double seals near pumps [59].

Table 5.47 :Process emissions of PVC production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
NMVOC	2.3	341	0.35	51
TSP	2.9	433	0.26	39
PM ₁₀	1.1	165	0.1	15
PM _{2.5}	0.1	8	0.01	1

According to Reinders [44], NMVOC emissions from PVC plants should be between 2.3-21.2 kg/ton however it depends on the process and can be abated by the application of gas purification technology. This NMVOC emission factor was compatible with AP42 [87]. Also it was given in EMEP [61] as 0.263 kg/ton. With considering all of these recommendations, emission factor was chosen 2.3 kg/ton which is the lower value of Reinders [44]. PM emission factor was taken from EMEP [61]. Controlled conditions include 85% VOC abatement and 90% PM abatement assumptions.

5.3.11.2. Fuel combustion emissions

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.3.12. Synthetic fibre and yarn

Fibres are formed by forcing a viscous fluid or solution of the polymer through the small orifices of a spinnerette and immediately solidifying or precipitating the resulting filaments. There are two types of synthetic fibre products [86]. First one is the “semi-synthetics” or cellulosics; viscose rayon and cellulose acetate. Second one is the “true synthetics” or non-cellulosic; polyester polymer, polyamide Polymer (Nylon), Acrylic-Modacrylic and Polypropylene (Polyolefin). True synthetics are products of the polymerization of smaller chemical units into long-chain molecular polymers.

Synthetic fibres (both semi-synthetic and true synthetic) are produced typically by two easily distinguishable methods, melt spinning and solvent spinning. Melt spinning process uses heat to melt the fibre polymer to a viscosity suitable for extrusion through the spinnerette. Solvent spinning process uses large amounts of organic solvents, which usually are recovered for economic reasons, to dissolve the fibre polymer into a fluid polymer solution suitable for extrusion through a spinneret [86]. Generally melt spinning method is used in Turkey [69].

Polyamide Polymers (Nylon 6, Nylon 66 staple and yarn), Polyester Polymer staple and yarns, Acrylic staple, Polyolephin staple and yarns were produced in Turkey in 2010 [69].

5.3.12.1. Process emissions

VOC is emitted by synthetic fibres industry generally because of the organic solvent use to dissolve the polymer for extrusion or that use an organic solvent in some other way during the filament forming step [86]. However in yarn plants, PM emissions are higher than VOC emissions.

Table 5.48 : Process emissions of synthetic staple and yarn production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
NMVOC	32.2	4,814	4.8	722
PM	252.6	23,952	1.4	132

Emission factors were derived from EPA [86]. The most NMVOC emission emitting subsectors were respectively; acrylic fibre and yarn production, polypropylene fibre and yarn production, polyamide polymer (nylon 6 and 66) fibre production, polyester polymer fibre production and other yarn productions. NMVOC emission abatement efficiency was accepted as 85%. Generally bag filter is used in synthetic fibre and yarn industry therefore bag filter was accepted for the controlling technology of this industry [29].

The largest source of PM is polyester polymer fibre production which accounts nearly all of the PM emitted from synthetic fibre and yarn industry. The emission factor for this sector was chosen with considering after control extrusion parts cleaning operations.

5.3.12.2. Fuel combustion emissions

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.3.13. Formaldehyde

Formaldehyde (Formic Aldehyde, Metil Aldehyde) is produced from methanol, either by catalytic oxidation under air deficiency ('silver process') or air excess ('oxide process') [53]. There was no technology specific information about the process type; therefore all formaldehyde plants were accepted to produce with silver process with overall methanol conversion.

In the initial step of silver process, methanol is dehydrogenated. In the second stage there is a secondary combustion of hydrogen resulting the overall reaction. The process for total methanol conversion consists of four main unit operations, namely; methanol vaporisation, catalytic methanol conversion to formaldehyde, formaldehyde absorption and emission control. The reaction off-gas contains 18-23% hydrogen and has a calorific value that makes it suitable for thermal incineration with energy recovery, either in a dedicated thermal oxidiser, a gas engine (with the production of electricity) or a conventional boiler.

There were five formaldehyde production plants in Turkey in 2010.

5.3.13.1. Process emissions

The off-gas from the formaldehyde absorption column is the only continuous waste gas stream. The main pollutants are formaldehyde, methanol, CO and dimethyl ether. Further emissions may arise from storage breathing and fugitives [53].

Table 5.49 : Process emissions of formaldehyde production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
CO	12	436	0.2	7
NMVOC	7	255	0.0016	0.06
TSP	0.5	18	0.0005	0.02

Emission factors were taken from EMEP [61]. Abatement technology was thermal or catalytic incineration for controlled conditions.

5.3.13.2. Fuel combustion emissions

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.3.14. Isopropyl alcohol

Isopropyl Alcohol (Dimethyl Carbinol, 2-Propanol, Isopropanol) was produced by three companies in Turkey in 2010 [62] (as by-product and product), however this sector's emissions were not calculated because of the activity data deficit.

5.3.15. Methanol

Methanol (Methyl Alcohol) is a by-product of Ethanol (Ethyl Alcohol). There were three companies producing methanol in Turkey [62] (as by-product and product), however this sector's emissions were not calculated because of the activity data deficit.

5.3.16. Ethanol

Ethanol (Ethyl Alcohol) is used as a raw material for the manufacturing of alcoholic drinks and used in sugar factories; therefore generally produced by alcoholic drinks and sugar producers. Regarding to TurkStat [62] in Turkey there were three producers; two of them were from sugar industry and one of them was from alcoholic drinks industry. However regarding to TOBB [12] there were 15 companies.

Additionally there were no specific emission factors and process configuration information in the literature for the production of Ethanol; therefore this sector's emissions were not calculated.

5.3.17. Crude terephthalic acid

Terephthalic acid (TPA) is primarily used in the manufacture and production of polyester fibres, films, polyethylene terephthalate solid-state resins and polyethylene terephthalate engineering resins [83]. Crude terephthalic acid (C-TPA) was produced only by Petkim in Turkey, in 2010.



Figure 5.20: PTA Plant of Petkim [84].

Terephthalic acid is typically produced by liquid-phase air oxidation of p-xylene in the presence of manganese and cobalt acetate catalysts and a sodium bromide promoter to form C-TPA. Crystalline C-TPA is collected as wet cake and dried. It is purified by dissolving in hot water under pressure and selectively hydrogenating contaminants catalytically [83].

5.3.17.1. Process emissions

A general characterization of the atmospheric emissions from the production of C-TPA is difficult because of the variety of processes. Emissions vary considerably, both qualitatively and quantitatively [85]. Generally NMVOC emissions occur from reactor vents, crystallisation separation and dryer vents, distillation and recovery vents and product transfer vent. However CO emissions occur from mainly reactor vent and product transfer vent.

Table 5.50 : Process emissions of crude teraphthalic acid production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
CO	19	1400	0.19	14
NMVOC	19.8	1459	0.198	15

Emission factors were taken from EPA [85]. There was no more emission factor related with this factory.

Typically thermal oxidation results in >99% reduction of VOC and CO [13]. Therefore controlled emission factors were calculated by using this reduction efficiency value.

5.3.17.2. Fuel combustion emissions

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.3.18. Soap

The term "soap" refers to a particular type of detergent in which the water-solubilised group is carboxylate and the positive ion is usually sodium or potassium [88].

Soap market and production is very large in Turkey and 60% of the produced soap is exported beyond selling in internal market. Additionally there are numerous family businesses and exact production amount cannot be identified [89].

The main atmospheric pollution problem in soap manufacturing is odour. The storage and handling of liquid ingredients (including sulfonic acids and salts) and sulphates are some of the sources of this odour. Vent lines, vacuum exhausts, raw material and product storage, and waste streams are all potential odour sources. Control of these odours may be achieved by scrubbing exhaust fumes and, if necessary, incinerating the remaining volatile organic compounds (VOC) [88].

Blending, mixing, drying, packaging, and other physical operations may all involve dust emissions. The production of soap powder by spray drying is the single largest source of dust in the manufacture of synthetic detergents. Dust emissions from other finishing operations can be controlled by dry filters such as bag houses [88].

All of the guidelines were investigated in terms of availability of emission factors for soap production. Currently, no emission factors are available for soap manufacturing. No information on hazardous air pollutants (HAP), VOCs, ozone depleters, or heavy metal emissions information was found for soap manufacturing. Therefore soap manufacturing emissions were not calculated within this study.

5.3.19. Detergents

The term "synthetic detergent products" applies broadly to cleaning and laundering compounds containing surface-active (surfactant) compounds along with other ingredients [88].

The process flow described in this section is derived from EPA [88].

The manufacture of spray-dried detergent has three main processing steps: (1) slurry preparation, (2) spray drying, and (3) granule handling. The 3 major components of detergent are surfactants (to remove dirt and other unwanted materials), builders (to treat the water to improve surfactant performance), and additives to improve cleaning performance. Additives may include bleaches, bleach activators, antistatic agents, fabric softeners, optical brighteners, anti redeposition agents, and fillers.

The formulation of slurry for detergent granules requires the intimate mixing of various liquid, powdered, and granulated materials. Detergent slurry is produced by blending liquid surfactant with powdered and liquid materials (builders and other additives) in a closed mixing tank called a soap crutcher. Premixing of various minor ingredients is performed in a variety of equipment prior to charging to the crutcher or final mixer.

Liquid surfactant used in making the detergent slurry is produced by the sulfonation of either a linear alkylate or a fatty acid, which is then neutralized with a caustic solution containing sodium hydroxide (NaOH).

The blended slurry is held in a surge vessel for continuous pumping to a spray dryer. The slurry is atomized by spraying through nozzles rather than by centrifugal action. The slurry is sprayed at pressures in single-fluid nozzles. Steam or air is used as the atomizing fluid in the 2-fluid nozzles. The slurry is sprayed at high pressure into a vertical drying tower having a stream of hot air of from 315 to 400°C. The detergent granules are conveyed mechanically or by air from the tower to a mixer to incorporate additional dry or liquid ingredients, and finally to packaging and storage.

In Turkey there approximately 250 detergent manufacturers, 2 biggest companies are public and others are private companies [89]. Therefore there was no credible and detailed information about final production amount.

5.3.19.1. Process emissions

The emissions from detergent production are mainly originated from spray drying towers and contain fine detergent particles. Organics vaporized in the higher temperature zones of the tower were not considered within this study.

Typically, dry cyclones and cyclonic impingement scrubbers are the primary collection equipment employed to capture the detergent dust in the spray dryer

exhaust for return to processing [88] and defined as primary treatment of PM. Also Secondary collection equipment is used to collect fine particulates that escape from primary devices.

Table 5.51 : Process emissions of detergents production.

	Uncontrolled		Controlled	
	EF	Emissions	EF	Emissions
	kg/ton	ton/yr	kg/ton	ton/yr
PM	45	62,226	0.54	747

In the calculations only primary treatment technology was selected as fabric filter and applied in the calculations of detergent industry emissions. Emission factor was taken from EPA [88].

5.3.19.2. Fuel combustion emissions

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.3.20. Paint, varnish and ink

Paint and ink are suspensions of finely separated pigment particles in a liquid that when spread over a surface in a thick layer will form a solid, cohesive, and adherent film [90].

Paint factories belong to the group of the ‘compounders’. A compounder is an industry that obtains basic materials from third parties and mixes them intensively in certain proportions. In general, it can be said that chemical processes do not play a part in the preparation of paint or printing ink [44]. Only physical processes are involved in the industry however some air pollutants are emitted from this processes. Another separated section was not opened for each of the paint, varnish and ink sectors. Also, these sectors were evaluated under ‘organic chemicals’ sector because of using organic chemicals as raw materials.

The manufacture of paint involves the dispersion of a coloured oil or pigment in a vehicle, usually an oil or resin, followed by the addition of an organic solvent for viscosity adjustment. Only the physical processes of weighing, mixing, grinding, tinting, thinning, and packaging take place. No chemical reactions are involved. These processes take place in large mixing tanks at approximately room temperature [91].

The manufacture of varnish also involves the mixing and blending of various ingredients to produce a wide range of products. However in this case, chemical reactions are initiated by heating. Varnish is cooked in either open or enclosed gas-fired kettles for periods of 4 to 16 hours at temperatures of 93 to 340°C (200 to 650°F).

Printing inks manufacturing process is in much the same way that regular varnish is made. The ink "varnish" or vehicle is generally cooked in large kettles at 93 to 315°C for an average of 8 to 12 hours [92].

5.3.20.1. Process emissions

The primary factors affecting emissions from paint manufacture are care in handling dry pigments, types of solvents used, and mixing temperature.

Varnish cooking emissions, largely in the form of volatile organic compounds, depend on the cooking temperatures and times, the solvent used, the degree of tank enclosure and the type of air pollution controls used.

Ink production emissions' largest source is varnish or vehicle preparation by heating. Cooling the varnish components — resins, drying oils, petroleum oils, and solvents — produces odorous emissions. At about 350°F (175°C) the products begin to decompose, resulting in the emission of decomposition products from the cooking vessel. Emissions continue throughout the cooking process with the maximum rate of emissions occurring just after the maximum temperature has been reached. Compounds emitted from the cooking of oleo resinous varnish (resin plus varnish) include water vapour, fatty acids, glycerine, acrolein, phenols, aldehydes, ketones, terpene oils, terpenes, and carbon dioxide [92]. However, only NMVOC and PM emissions were considered in this study.

Table 5.52 : Uncontrolled process emissions of paint, varnish, ink production.

	Uncontrolled					
	PAINT		VARNISH		INK	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	3.5	2114			1	48
NMVOC	15	9059	45	8987	58.75	2791

Controlled emissions were calculated by accepting controlling technology as after burners for VOC emissions with 99% abatement efficiency. Water spray and oil filter

system, after burners were accepted for PM emissions with 90% abatement efficiency.

Table 5.53 : Controlled process emissions of paint, varnish, ink production.

	Controlled					
	PAINT		VARNISH		INK	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	0.4	211			0.1	5
NMVOC	0.15	91	0.45	90	0.59	28
Total	0.5	302		90	0.69	33

Paint pigment rate was accepted as 35% [93] when calculating PM emission factor of paint industry. All of these emission factors were derived from EPA [91,70].

5.3.20.2. Fuel combustion emissions

Fuel combustion emissions of this sector are included under final emissions calculated in Section 5.4.13

5.4. Inorganic Chemicals Industry

5.4.1. Boron compounds

Boron has the chemical symbol B is a semi-conductive metallic and ametallic element. Boron does not exist by itself in nature but can be found in over 230 kinds of borate minerals. The different features of the compounds it forms with various metallic or ametallic elements enable it to be used as a range of boron compounds in industry. A rising star in the world with its wide range of use and product diversity, 85% of borate is used in the glass, glass-wool, detergents, agriculture and ceramics sectors, and it is an important raw material in many branches of industry. About 69.7% of the world [94] borate reserves are located in Turkey.

The most commercially important are tincal, colemanite, kernite and ulexite. The most abundant boron minerals in Turkey are tincal, colemanite and ulexite. These minerals are respectively sodium, calcium and sodium+calcium based boron compounds. These minerals are first concentrated with physical processes to obtain concentrated boron and later refined and transformed into a variety of boron chemicals [94].



Figure 5.21 : Eti Maden Boron Oxide plant, Bandirma [95].

In Turkey Boron chemicals are produced by Eti Maden. This company produced 39.6% of the Boron produced in the world in 2010 and has 69.7% of world Borate reserves [94]. There are five production plants; Bigadic, Emet, Bandirma, Kirka and Kestelek. Most of them have open pits, concentrator plants, milling and enrichment plants.

5.4.1.1. Process emissions

Boron chemicals production was evaluated as a whole, by including both mining of Boron mineral and processing of pulverised Boron mineral.

Rock and crushed stone products generally are loosened by drilling and blasting and then are loaded by power shovel or front-end loader into large haul trucks that transport the material to the processing operations. Techniques used for extraction vary with the nature and location of the deposit. Processing operations may include crushing, screening, size classification, material handling and storage operations. All of these processes can be significant sources of PM emissions if uncontrolled [96].

Table 5.54 : Process emissions of boron production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
Total PM	1.16	2559	0.06	122
PM ₁₀	0.65	1439	0.03	73
PM _{2.5}	0.25	550	0.01	28

The PM emission factor was taken from EPA [96] and generated / updated for tertiary and fines crushing, screening, conveyor transfer, wet drilling, truck unloading and truck loading, grinding, dry classifying, flash drying and storage. Controlled emission factors include wet suppression in crushed stone processing and fabric filter in pulverized mineral processing.

5.4.1.2. Fuel combustion emissions

Energy data was taken from Annual report of Eti Maden [94] and combustion emissions were calculated with considering a scenario which assumes approximately 50% of the steam is generated by using gaseous fuels and rest of it was generated by using solid fuels.

Emission factors were taken from EPA [96]. Firing configuration was accepted as spreader stocker and for uncontrolled conditions.

Table 5.55 : Combustion emissions of boron production.

	EF Gaseous Fuels ton/m ³	EF Solid Fuels kg/ton	Emissions Overall ton/yr
NO ₂	4.48	2.63	1,369
CO	1.34		8
CO ₂	1920	2300	1,188,208
N ₂ O	0.04		0.21
PM	0.12		0.72
SO _x	0.01	40.8	20,860
NMVOC		0.014	7
CH ₄	0.04		0.22
VOC	0.09		0.52

NMVOC, VOC and CH₄ emission factors are given separately, however VOC emission = CH₄ + NMVOC equation can be used for comparisons.

It should be noted that, fuel combustion emissions of this sector were included under chemical industry overall final emissions calculated in Section 5.4.13. Above calculated emissions were given for only individual industrial comparison purposes.

5.4.2. Soda ash

Sodium carbonate (Na₂CO₃), commonly referred to as soda ash, is one of the largest volume mineral products in Turkey.

Soda ash is used in a variety of applications, including glass production, soaps and detergents, flue gas desulphurisation, chemicals, pulp and paper and other common consumer products [97]. Soda ash may be manufactured synthetically or from naturally occurring raw materials such as ore (Trona).

Natural soda ash production can be produced from trona and nahcolite. Also trona can be produced either from underground as dry or from trona lakes as solution. Production from trona from underground deposits were summarised here because of its concern with Turkish industry. Natural Soda ash is produced by Eti Soda in Turkey.

Underground ‘dry’ trona processing consists of several steps; mechanical mining by the ‘room and pillar’ or ‘long wall’ method. As trona is an impure sodium sesquicarbonate mineral ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), it has firstly to be calcined to produce a soda ash still containing all the impurities from the ore. Next, the calcined trona is dissolved, and the solution is settled and filtered to remove impurities (inorganic and organics). The purified liquor is sent to evaporators where sodium carbonate monohydrate crystals precipitate. The monohydrate slurry is concentrated in centrifuges before drying and transformation into dense soda ash [57].

Synthetic production of Soda ash is applied when natural trona deposits are not available or current trona ore is not in a good quality for production. Synthetic soda production is made with Solvay process also called the ammonia soda process by using the locally available natural raw materials of salt brine and limestone of the required purity [97, 98]. About 75 percent of the world production of soda ash is synthetic ash made from sodium chloride [65].

The Solvay process uses salt (NaCl) and limestone (CaCO_3) as raw materials. Ammonia, which is also used in the process, is almost totally regenerated and recycled. The main advantage of this process is the availability of the relatively pure (depending on local conditions) raw materials, which can be found almost everywhere in the world and, therefore, allows operating production units close to the market. Synthetic production method of soda ash is used in Turkey by Sisecam Soda Sanayii with using imported trona despite of trona abundance and because of the low quality.

The Solvay process produces ‘light soda ash’ with a pouring density of about 500 kg/m³. It is used in that form mainly for the detergent market and certain chemical intermediates. Light soda ash is transformed by recrystallization firstly to sodium carbonate monohydrate, and finally to ‘dense soda ash’ after drying (dehydration). Dense soda ash has a pouring density of about 1000 kg/m³. It is used mainly in the glass industry. Dense soda ash can also be produced by compaction [57].

In the Solvay process, the first reaction occurs in the salt solution (brine). First of all, ammonia is absorbed and then, the ammoniated brine is reacted with CO₂ to form successive intermediate compounds; ammonium carbonate ((NH₄)₂CO₃) then ammonium bicarbonate (NH₄HCO₃). By continuing CO₂ injection and cooling the solution, precipitation of sodium bicarbonate (NaHCO₃) is achieved and ammonium chloride (NH₄Cl) is formed. The mother liquor is treated to recover ammonia. The ammonium chloride filtrate is reacted with alkali, generally milk of lime (CaCl₂), followed by steam stripping to recover free gaseous ammonia. NH₃ is recycled to absorption step. CO₂ and calcium hydroxide originate from limestone calcination followed by calcium oxide (CaO) hydration. Finally, brine is treated to remove impurities; calcium and magnesium [57].

5.4.2.1. Process emissions

Soda ash production and consumption (including sodium carbonate, Na₂CO₃) results the release of pollutants.

Synthetic soda ash production is the source of CO₂, CO, NH₃ and PM emissions. The main pollutant is carbon dioxide (CO₂). . In addition, dust is emitted from soda ash production in limited quantities, arising from handling and also from limestone conversion in kilns. It is common to use bag filters or wet scrubbers, which significantly reduce the levels of dust emitted to the atmosphere. During the oxidation of nitrogen in the kiln, NO_x and SO_x are emitted. The formation of NO_x is limited due to the moderate temperature of the combustion (approximately 1100 °C). The formation of SO_x depends on the sulphur in the compounds and in the fuel. These pollutants were not evaluated in this study.

Particulate emissions consist ore mining, crushing, screening, transfer, monohydrate process (rotary ore calciner), rotary soda ash dryers, soda ash screening, and storage

loading and unloading. Total particulate matter includes filterable particulate and inorganic condensable particulate.

Table 5.56 : Process emissions of soda ash production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
<i>Natural Soda Ash Production</i>				
Total PM	131	148,816	0.39	442
CO ₂	263	298,768		
<i>Synthetic Soda Ash Production</i>				
CO ₂	300	300,000		
CO	12	12,000	0.12	120
NH ₃	1	1,000	0.05	50
Dust	0.1	100	0.001	1

The CO₂ emissions calculated here was related with fuel combustion activities, therefore included in process emissions as advised in IPCC guidelines [65].

CO₂ emissions factor was taken from EPA [97] as 263 kg/ton which was emitted from Monohydrate Process, rotary ore calciner and rotary soda ash dryers. 76% of CO₂ emissions are emitted from rotary ore calciners in natural soda ash production. IPCC [65] recommends CO₂ emission from natural soda ash production as 300 kg/ton within the context of Tier 1 method and changeable regarding to local conditions. Synthetic soda ash production emission factors were derived from IPCC [57].

Cyclone / Electrostatic filters were selected for controlled PM emissions. CO emissions were accepted to be controlled by thermal incineration. NH₃ emissions control efficiency was accepted as 95%.

Emissions from combustion sources such as boilers, and from evaporation of hydrocarbon fuels used to fire these combustion sources, were not covered in process emissions section.

5.4.2.2. Fuel combustion emissions

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.4.3. Chromium oxides

Chromium chemicals find a wide usage area in different industries. The main chromium chemicals produced in Turkey are; base chromium sulphate, chromic acid, sodium bichromate, chromium nitrate, chromium Chlorur, chromium hydroxide sulphate and sodium sulphate as a by-product. The main feedstock is Chromite ore which is common in Turkey [98].

Chromium chemicals production includes primary processing, effluent treatment, & residue disposal plant: chromite ore is dried and milled, then mixed with sodium carbonate and process residues. The mixture is then calcined, oxidising insoluble trivalent chromium to soluble hexavalent sodium chromate. After quenching, the sodium chromate is separated and purified, then acidified to form sodium dichromate liquor and a sodium sulphate by-product. The sodium dichromate is evaporated to form either concentrated liquors for use elsewhere on site or for sale.



Figure 5.22: Kromsan chromium chemicals factory [99].

Chromic sulphate is produced by the reduction of sodium dichromate solution with sulphur dioxide, produced by the combustion of molten sulphur in a furnace. Excess sulphur dioxide in the outlet from the reactor is absorbed in fresh sodium dichromate and a candle filter is used to remove sulphur trioxide droplets. The chromic sulphate is then dried in a spray drier as is or used as a feedstock to produce further products.

The manufacture of chromic oxides consists of two stages, the first is being the between ammonium sulphate and sodium dichromate dehydrate solution. The resulting slurry of ammonium dichromate and sodium sulphate is thermally decomposed in a rotary kiln to form chromic oxide. This product can either be

quenched, filtered and dried for sale or can be further processed by calcining in a rotary kiln before quenching, filtering and drying.

Chromic acid is produced by reacting sodium dichromate with sulphuric acid. The resulting slurry is centrifuged, washed and dried in a gas fired drier. The final powder is compacted, granulated and sieved to remove fines before being packaged for sale.

Potassium dichromate is produced by the reaction of chromic acid produced on site with potassium hydroxide solution. The potassium dichromate product is dried in a thermal Venturi drier after various treatments to remove impurities. Ammonium dichromate is also produced on the same plant by reacting chromic acid and ammonia.

The processes summarized above are derived from UK Department for Environment Industrial Report [100]. However it may not be compatible in the details with the processes used in Turkey.

The biggest chromium chemicals manufacturer is Sisecam Soda Sanayii Corporation and was the biggest base chromium sulphate producer in the world in 2010 [98].

5.4.3.1. Process emissions

Emissions of both particulate matter and chromium can occur from various stages of the processes but particularly from drying, handling and packaging of feedstock and products [100]. These emissions do not cover chromium ore mining emissions.

Table 5.57 : Process emissions of chromium chemicals production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	306.62	22,690	2.08	154
Chromium	0.39	29	0.39	29

PM and chromium emission factors were derived from UK Department for Environment Industrial Report [100]. PM emissions were accepted to be controlled by fabric filter/ESP with 99% efficiency.

5.4.3.2. Fuel combustion emissions

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13.

5.4.4. Magnesium oxide (Magnesia)

Turkey was the 6th bigger magnesium oxide producer in the world in 2010 and represented 3.54% of world magnesium production. Two magnesium oxide (MgO) commercial forms produced in Turkey; Dead Burned Magnesia (DBM) which has 86% of production rate and Caustic Calcined Magnesia (Light burned magnesia) which has 14% production rate in Turkey [57].

Magnesium Oxide (MgO = Magnesia) is the most important industrial magnesium compound with its main application in the steel and refractory industry. The melting point of magnesia is at around 2800 °C which gives an advantage for the usage as a raw material for refractory products which are used in high temperature process for the steel, cement, lime, glass and non-ferrous metals industries [124]. The raw materials for the production of MgO are both natural magnesium carbonate and brucite or magnesium chloride from seawater and brines. In Turkey only Magnesite (MgCO_3) is used as raw material.

There are three major categories of magnesia (MgO) products which are produced from Magnesite: Caustic Calcined Magnesia (CCM), dead burned magnesia (DBM or sintered magnesia) and fused magnesia (FM).

Calcined magnesia is used in many agricultural and industrial applications (e.g., feed supplement to cattle, fertilisers, electrical insulations and flue gas desulphurisation). Dead burned magnesia is used predominantly for refractory applications, while fused magnesia is used in refractory and electrical insulating markets.

At high temperatures MgCO_3 is thermally decomposed to magnesia (MgO) and CO_2 . Therefore CO_2 emissions are significant for this process.

5.4.4.1. Process emissions

Unfortunately, there are no separated emission factors for each of the magnesium oxide production. Therefore some of the plants' [57] emission factors which were published for public use and they were applied to this study.

NO_x and CO₂ emissions were emitted from calcining and sintering sections.

Table 5.58 : Process emissions of MgO production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	32	11,368	0.3	108
CO ₂	1000	360,000		
NO _x	5.2	1,872	3.64	1,310

Dust emission factor was taken from IPPC [57], CO₂ and NO_x emission factors were taken from IPPC [124]. Fabric filter/ESP was accepted as the control technology of PM emissions with 99% abatement efficiency. Staged combustion was accepted as the control technology of NO_x emissions with 30% abatement efficiency.

5.4.4.2. Fuel combustion emissions

Due to combustion processes of natural gas and air, in both calcining and sintering, there are emissions of nitrogen oxides as well as carbon oxides.

Table 5.59 : Fuel combustion emissions of MgO production.

	EF kg/ton	Emissions ton/yr
CO	9	3,240
CO ₂	450	162,000
NO _x	2	720

Emission factors were taken from IPPC [57].

The emissions calculated for fuel combustion in magnesium oxide production are given only for individual sectorial comparisons. Final emissions of this sector were included in Chapter 5.4.13.

5.4.5. Fertilizer

Any natural or manufactured material that contains at least 5% of one or more of the three primary nutrients - nitrogen (N), phosphorous (P), or potassium (K) - can be considered a fertilizer. Industrially manufactured fertilizers are sometimes referred to as "mineral" fertilizers [101].

The fertilizer industry helps ensure that farmers have the nutrients they need to grow enough crops to meet the world's requirements for food, feed, fibre and energy. The

nutrients supplied by the industry supplement on-farm sources of nutrients such as manure and legumes. Nutrients in manufactured fertilizers are in forms that can be absorbed by plants. All of these nutrients exist in nature, but the quantities are not sufficient to meet the needs of our growing, urbanized population [101].

Fertilizer production entails gathering raw materials from nature; treating them in order to purify them or increase their concentration; converting them into plant-available forms; and often combining them into products that contain more than one nutrient.

Common fertilizer products and intermediates are listed below [101];

Nitrogen fertilizers: Ammonia, Ammonium sulphate (AS), Ammonium nitrate (AN), Calcium ammonium nitrate (CAN), Urea

Phosphate fertilizers: Single superphosphate (SSP), Triple superphosphate (TSP), Diammonium phosphate (DAP), Monoammonium phosphate (MAP), Ground phosphate rock

Potash fertilizers: Muriate of potash (MOP), also called potassium chloride, Sulphate of potash, Sulphate of potash magnesia, Magnesium fertilizers, Kieserite, Epsom salts

Complex fertilizers: NPK fertilizers, NP fertilizers, NK fertilizers, PK fertilizers

Only some of them were produced in Turkey in 2010, which were ammonium sulphate, ammonium nitrate, urea, triple super phosphate, diammonium phosphate, Potassium phosphate, compose fertilizers [102].

5.4.5.1. Ammonium sulphate

Ammonium sulphate ($[\text{NH}_4]_2\text{SO}_4$) is an inorganic chemical which is commonly used as a fertilizer.

About 90 percent of ammonium sulphate is produced by 3 different processes: (1) as a by-product of caprolactam production, (2) from synthetic manufacture, and (3) as a coke oven by-product. After formation of the ammonium sulphate solution, manufacturing operations of each process are similar. Ammonium sulphate crystals are formed by circulating the ammonium sulphate liquor through a water evaporator,

which thickens the solution. Ammonium sulphate crystals are separated from the liquor in a centrifuge [103].

Ammonium Sulphate was produced in Turkey in 2010 as both by-product and main product. There was a factory produces AS (ammonium sulphate) as the main product, and iron and steel industry produced it as a by-product [102].

5.4.5.1.1. Process emissions

Ammonium sulphate particulate is the principal emission from ammonium sulphate manufacturing plants. The gaseous exhaust of the dryers contains nearly all the emitted ammonium sulphate. Other plant processes, such as evaporation, screening and materials handling, are not significant sources of emissions [103].

Table 5.60 : Process emission of Ammonium Sulphate production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	23	4648	0.02	4
VOC	0.74	150	0.11	22

For PM emissions, control technology was accepted as wet scrubber on the rotary dryers. Emission factors were taken from EPA [103].

5.4.5.2. Ammonium nitrate

Ammonium nitrate (NH_4NO_3) is produced by neutralizing nitric acid (HNO_3) with ammonia (NH_3). Ammonium nitrate is marketed in several forms, depending upon its use. Liquid ammonium nitrate may be sold as a fertilizer, generally in combination with urea.

The manufacture of ammonium nitrate involves several major unit operations including solution formation and concentration; solids formation, finishing, screening and coating; and product bagging and/or bulk shipping. In some cases, solutions may be blended for marketing as liquid fertilizers. The number of operating steps employed depends on the end product desired. For example, plants producing ammonium nitrate solutions alone use only the solution formation, solution blending and bulk shipping operations. Plants producing a solid ammonium nitrate product may employ all of the operations [104].

All ammonium nitrate plants produce an aqueous ammonium nitrate solution through the reaction of ammonia and nitric acid in a neutralizer.

Prilling and granulation are the most common processes used to produce solid ammonium nitrate. To produce prills, concentrated melt is sprayed into the top of a prill tower. In the tower, ammonium nitrate droplets fall counter current to a rising air stream that cools and solidifies the falling droplets into spherical prills. Prill density can be varied by using different concentrations of ammonium nitrate melt [104].

Since the solids are produced in a wide variety of sizes, they must be screened for consistently sized prills or granules. Cooled prills are screened and off size prills are dissolved and recycled to the solution concentration process. Granules are screened before cooling. Undersize particles are returned directly to the granulator and oversize granules may be either crushed and returned to the granulator or sent to the solution concentration process [104].

Ammonium Nitrate is named with adding the percentage of the nitrogen in the ammonium nitrate. For example means of AN26 is an ammonium nitrate contains 26% nitrogen.

In Turkey the types of ammonium nitrate fertilizers; AN20.5, AN26, AN33 which were produced by several companies.

5.4.5.2.1. Process emissions

Emissions from ammonium nitrate production plants are particulate matter (ammonium nitrate and coating materials), ammonia, and nitric acid. Ammonia and nitric acid are emitted primarily from solution formation and granulators. Particulate matter (largely as ammonium nitrate) is emitted from most of the process operations and is the primary emission. Specific plant operating characteristics, however, make these emissions vary depending upon use of excess ammonia or acid in the neutralizer [104].

Table 5.61 : Process emission of Aluminium Nitrate production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	4.47	5503	0.45	553
NH ₃	1.3	1548	0.06	77
HNO ₃	N.E.	N.E.	0.05	61

Factors for controlled emissions were not presented by EPA due to conflicting results on control efficiency [104]. However in this study, abatement technology was accepted as wet scrubber for particulate matter and granulator recycle scrubber for NH₃ abatement with 95% recovery rate. Uncontrolled emissions were calculated by using emission factors of EPA [104] and Reinders [44].

5.4.5.3. Urea

Urea [CO(NH₂)₂], also known as carbamide or carbonyl diamide, is marketed as a solution or in solid form. Most urea solution produced is used in fertilizer mixtures, with a small amount going to animal feed supplements. Most solids are produced as prills or granules, for use as fertilizer or protein supplement in animal feed, and in plastics manufacturing [105].

The process flow mentioned in this section was derived from EPA [105].

The process for manufacturing urea involves a combination of up to 7 major unit operations; solution synthesis, solution concentration, solids formation, solids cooling, solids screening, solids coating and bagging, and/or bulk shipping. The combination of processing steps is determined by the desired end products. For example, plants producing urea solution use only the solution formulation and bulk shipping operations. Facilities producing solid urea employ these 2 operations and various combinations of the remaining 5 operations, depending upon the specific end product being produced.

In the *solution synthesis* operation, ammonia (NH₃) and carbon dioxide (CO₂) are reacted to form ammonium carbamate (NH₂CO₂NH₄). The carbamate is then dehydrated to yield 70 to 77 percent aqueous urea solution

The 3 methods of *concentrating the urea* solution are vacuum concentration, crystallization, and atmospheric evaporation. The most common method of solution concentration is evaporation.

The concentration process furnishes urea "melt" for *solids formation*. Urea solids are produced from the urea melt by two basic methods: prilling and granulation. Prilling is a process by which solid particles are produced from molten urea. Molten urea is sprayed from the top of a prill tower. As the droplets fall through a counter current air flow, they cool and solidify into nearly spherical particles.

The *solids screening* operation removes off size product from solid urea. The off size material may be returned to the process in the solid phase or be redissolved in water and returned to the solution concentration process.

Urea was produced only by a privatised company in Turkey in 2010.

5.4.5.3.1. Process emissions

Emissions from urea manufacture are mainly ammonia and particulate matter. Formaldehyde and methanol, hazardous air pollutants, may be emitted if additives are used [105]. Ammonia is emitted during the solution synthesis and solids production processes. Particulate matter is emitted during all urea processes.

Table 5.62 : Process emission of Urea production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	7.1	823	0.49	57
NH ₃	9.3	1074	0.46	53
NO ₂	1	116	0.7	81

Controlled condition NH₃ emission factor was selected for entrainment scrubber. Fabric filter/ESP was accepted as the control technology of PM emissions with 99% abatement efficiency. Staged combustion was accepted as the control technology of NO₂ emissions with 30% abatement efficiency.

5.4.5.4. Triple super phosphate

Triple superphosphate (TSP), also known as double, treble, or concentrated superphosphate, is a fertilizer material with a phosphorus content of over 40 percent, measured as phosphorus pentoxide (P₂O₅) [106].

Two processes have been used to produce triple superphosphate: run-of-the-pile and granular. Granular method usage is common in Turkey, therefore only this method was described in this section.

In this process, ground phosphate rock or limestone is reacted with phosphoric acid in 1 or 2 reactors in series. A small side stream of slurry is continuously removed and distributed onto dried, recycled fines, where it coats the granule surfaces and builds up its size. Pug mills and rotating drum granulators have been used in the granulation process. A rolling bed of dry material is maintained in the unit while the slurry is introduced through distributor pipes set lengthwise in the drum under the bed. Slurry-wetted granules are then discharged onto a rotary dryer, where excess water is evaporated and the chemical reaction is accelerated to completion by the dryer heat. Dried granules are then sized on vibrating screens. Oversize particles are crushed and recirculated to the screen, and undersize particles are recycled to the granulator. Product-size granules are cooled in a counter current rotary drum, and then sent to a storage pile for curing. After a curing period of 3 to 5 days, granules are removed from storage, screened, bagged, and shipped [106].

TSP was mainly produced by three companies in Turkey in 2010.

5.4.5.4.1. Process emissions

Emissions of TSP production mainly occur from rock unloading, feeding, reactor, granulator, dryer, cooler and screens, curing building.

Table 5.63 : Process emission of TSP production.

	Uncontrolled		Controlled	
	EF	Emissions	EF	Emissions
	kg/ton	ton/yr	kg/ton	ton/yr
PM	126	15,494	1.26	155
Fluoride	0.1	17		

Controlled emission factor was selected for the bag houses with 99% collection efficiency. Emission factors were taken from EPA [106].

5.4.5.5. Diammonium phosphate

Ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) is produced by reacting phosphoric acid (H_3PO_4) with anhydrous ammonia (NH_3). Ammoniated superphosphates are produced by adding normal superphosphate or triple superphosphate to the mixture. The production of liquid ammonium phosphate and ammoniated superphosphates in fertilizer mixing plants is considered a separate process [107].

DAP is produced mainly by two companies in Turkey in 2010.

5.4.5.5.1. Process emissions

Sources of air emissions from the production of ammonium phosphate fertilizers include the reactor, the ammoniator-granulator, the dryer and cooler, product sizing and material transfer, and the gypsum pond. The reactor and ammoniator-granulator produce emissions of gaseous ammonia, gaseous fluorides such as hydrogen fluoride (HF) and silicon tetrafluoride (SiF₄), and particulate ammonium phosphates.

[107] Exhaust streams from the reactor and ammoniator-granulator pass through a primary scrubber, in which phosphoric acid is used to recover ammonia and particulate. Exhaust gases from the dryer, cooler, and screen first go to cyclones for particulate recovery, and then to primary scrubbers. Materials collected in the cyclone and primary scrubbers are returned to the process. The exhaust is sent to secondary scrubbers, where recycled gypsum pond water is used as a scrubbing liquid to control fluoride emissions. The scrubber effluent is returned to the gypsum pond.

Table 5.64 : Process emission of DAP production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	6.8	3,372	0.34	168.6
NH ₃	1.4	694	0.07	34.7
SO ₂	4.0	1,983	0.04	19.8
Fluoride			0.02	9.9

SO₂ emission factor was dubious in EPA [107] because it was based on only limited data from a plant, nevertheless it was included in the calculations. All other emission factors were derived from EPA [107]. Uncontrolled emission factors were calculated for following abatement efficiencies; 95% for PM and NH₃, 90% for SO₂.

5.4.5.6. Compose fertilizer

Compose fertilizers, named as NPK, are produced in the same production line with DAP by mixing nitrogen, phosphorus and potassium in pre-identified ratios.

When manufacturing compose fertilizer the following compounds are mixed in the proper ratios: NH₄NO₃, (NH₄)₂SO₄, NH₂CONH₂, CaHPO₄, Ca(H₂PO₄)₂, KCl, (NH₄)H₂PO₄, (NH₄)₂HPO₄, K₂SO₄; sometimes magnesium salts and small amounts of trace elements are added to improve the mixture. The mixtures are granulated,

and, after screening the granules according to size, are treated with oil and then with powder in order to prevent caking. The product can then be sold [44]. There were 65 company produce compose fertilizers in Turkey in 2010 [12].

5.4.5.6.1. Process emissions

The emission consists of dust, the composition of which depends on the mixture produced. Ammonia is also emitted, depending on the method of manufacturing the ammonium salts. Flue gases, if any, are also emitted, these are used for drying the granules [12] .

Emission factors were taken from Reinders [12]. 95% abatement efficiency was accepted for controlled conditions.

Table 5.65 : Process emission of NPK production.

	Uncontrolled		Controlled	
	EF	Emissions	EF	Emissions
	kg/ton	ton/yr	kg/ton	ton/yr
PM	1	1309	0.05	65
NH ₃	3	3272	0.13	164
Fluoride	0.02	26.2		

5.4.5.7. Fuel combustion emissions of fertilizer industry

Fuel combustion emissions of this sector were included under final emissions calculated in Section 5.4.13

5.4.6. Inorganic Phosphates

The main applications of inorganic phosphates (volume wise) are in fertilizers, animal feeds, detergents, human food or pharmaceutical ingredients [57].

In this study, inorganic phosphates which were used as fertilizers are investigated in Chapter 5.4.5.

Detergent Phosphates: Inorganic phosphate which is used in detergents mainly includes sodium tripoliphosphate (STPP) and investigated in Section 5.4.6.1. Also STPP is used as *food phosphate* at human food and pharmaceutical ingredients.

Feed Phosphate: Inorganic phosphate which is used for animal foods and named as calcium phosphate, in particular dicalcium phosphate (DCP), and other phosphates are investigated in Section 5.4.6.2.

In general terms, all inorganic phosphates can be seen as mostly derived from phosphate rock, $\text{Ca}_5(\text{PO}_4)_3\text{F}$.

The process from phosphate rock to final product may schematically be seen to involve four major steps [57] ; (1) dissolution of phosphate from the rock to yield phosphoric acid, (2) purification of phosphoric acid to a varying degree of purity, (3) neutralisation of phosphoric acid by reaction with sodium, calcium, ammonium and/or other ions to produce the required inorganic phosphate, (4) dehydration, drying or calcination plus optional finishing to give a product in the required form (e.g. dry powder).

Although strong mineral acids, such as sulphuric, hydrochloric and nitric acid can be used for the dissolution of the phosphate from the phosphate rock, by far the most commonly used is sulphuric acid [57].

Unpurified (merchant grade), usually called ‘green’, phosphoric acid is a market commodity used by many producers as the starting point for further processing.

5.4.6.1. Sodium tri poli phosphate

Sodium poli phosphate (STPP) is most commonly used detergent phosphate. However it causes excessive moss in the waters therefore usage of STPP in the detergents is banned in some countries such as Switzerland. Now it is under usage in Turkey, thus the sector is included in this study.

Sodium phosphates are a family of salts prepared from phosphoric acid and sodium hydroxide or sodium carbonate. Worldwide, STPP is used as a detergent builder more than zeolites [57].

For the production of STPP, it is vital to have a low amount of impurities present in the starting materials. Caustic soda and soda ash are normally pure, but the most widely available form of phosphoric acid, the so-called green acid, is contaminated to a considerable to a considerable extent with fluoride and metals such as magnesium, iron and aluminium. It also contains excess sulphuric acid from the production stage. Green acid is produced from phosphate rock by sulphuric acid rock [57].

Impurities in green acid need to be removed before the STPP is produced. There are two ways of doing this, which give rise to two distinct production routes towards the

feedstock orthophosphate solution for the proper STPP process. This process flows are summarized in Figure 5.23. The process summary was derived from IPPC [57].

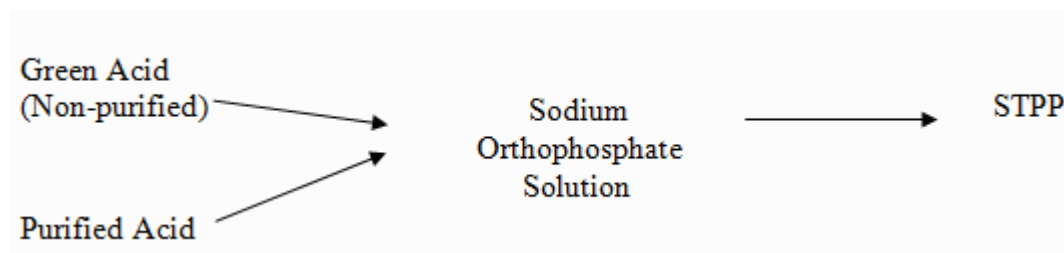


Figure 5.23 : STPP production process summary diagram.

In the first route (from green acid to STPP), following steps are applied;

Pre-treatment of green acid for purification to eliminate the sulphuric acid related impurities formed during the manufacture of phosphoric acid.

Neutralization of the pre-treated organic acid by adding sodium hydroxide or carbonate to the pre-treated green acid in order to obtain final proportion of Na, P elements. The phosphoric acid is converted into an orthophosphate solution with an adequate Na:P molar ratio that increases from the first step to the second.

Concentration of the sodium orthophosphate solution aims to eliminate water content of the solution. This is necessary to ensure a smooth operation in the next step (either in a calcination kiln or a spray tower).

In the second route (from purified acid to STPP), following steps are applied;

Purified acid is *neutralised* by the addition of sodium oxide in the form of hydroxide or carbonate in order to obtain Na, P molar ratio.

In the final route (from orthophosphate solution to STPP), following steps are applied;

Calcination is applied to dry the orthophosphate solution and form orthophosphate solids.

Cooling and hydration step is applied to produce final STPP product exist at a temperature of about 40-80 °C . Hydration step is optional by adding demineralised water for increasing the performance of STPP in the detergent applications.

Milling and screening is applied to obtain various particle sizes.

There is a company produces STPP in Turkey in 2010. There is no information about the process flow of this company; therefore the first route is accepted for the calculations.

5.4.6.1.1. Process emissions

The principal air pollutants from the processes are particulate, phosphate solution droplets, and CO₂ from the use of Na₂CO₃ as the neutralisation agent as opposed to the use of NaOH.

Table 5.66 : Process emission of STPP production.

	Uncontrolled		Controlled	
	EF	Emissions	EF	Emissions
	kg/ton	ton/yr	kg/ton	ton/yr
PM	700	21,420	0.7	21.4
Fluorine			0.3	9.2

5.4.6.1.2. Energy emissions

Energy consumption will depend directly on the concentration of green acid being used as a raw material and on the concentration of orthophosphate solution being produced as an output, and therefore varies widely.

Table 5.67 : Combustion emission of STPP production.

	EF	Emissions
	kg/ton	ton/yr
CO ₂	357.5	16,065
CO	5.1	156.1
VOC	1.2	36.7
NO _x	0.55	16.8
SO ₂	0.21	6.4

There is no information about energy recycling rate, therefore median of the range given by IPPC [57] is selected as the emission factor for CO₂.

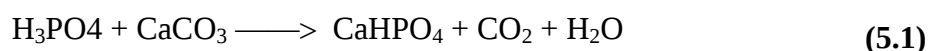
Additionally, fuel combustion emissions of this sector included under final emissions calculated in Section 5.4.13.

5.4.6.2. Dicalcium Phosphate

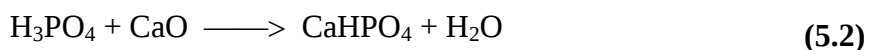
Dicalcium phosphate (DCP, calcium hydrogen orthophosphate) is a calcium salt of H_3PO_4 , produced by neutralisation with CaOH and drying. DCP is the most commonly used calcium phosphate feed for animals [57].

An adequate supply of phosphorus is essential if optimal livestock health and productivity are to be achieved. Without an adequate supply of phosphorus, an animal will suffer from a phosphorus deficiency, the consequences of which are varied, but in all cases affect the animal's physical well-being, as well as its economic performance.

In the phosphoric acid route (production method), purified phosphoric acid is reacted with quick lime and/or calcium carbonate under strictly controlled conditions. The main reactions are given in Equations 6.1 and 6.2.



and / or



DCP processing methods are the hydrochloric acid process route and the phosphoric acid process route. Only phosphoric acid route is described in this section because of the common usage of this process in Turkey.

There are numerous calcium phosphate types and processing methods. However, DCP is characterised by the highest production volume [57] and, therefore in this study, DCP production is indicated to represent all other products and emissions were calculated by the assumption of all feed phosphates (as calcium) are produced as DCP.

In 2010 there were 2 producers of DCP in Turkey [62]. These plants produce DCP, mono calcium phosphate (MCP), mono di calcium phosphate (MDCP) with 18, 20, 21, and 22.7% phosphorus in it.

5.4.6.2.1. Process emissions

Regarding to IPPC [57] only dust emissions are considerable for DCP production, however CO₂ should be emitted when the mass balances given in Equations 6.1 and 6.2. considered.

Table 5.68 : Process emission of DCP production.

	Uncontrolled		Controlled	
	EF	Emissions	EF	Emissions
	kg/ton	ton/yr	kg/ton	ton/yr
PM	61.3	3545	0.06	3.5

Uncontrolled emission factor was derived from controlled emission factor by assuming usage of a bag filter with 99% control efficiency. Emission factor was taken from IPPC [57].

5.4.6.2.2. Energy emissions

Fuel combustion emissions of this sector are included under final emissions calculated in Section 5.4.13.

5.4.7. Sulphuric Acid

Sulphuric acid (H₂SO₄) is a basic raw material used in a wide range of industrial processes and manufacturing operations. Almost 70 percent of sulphuric acid manufactured is used in the production of phosphate fertilizers. Other uses include copper leaching, inorganic pigment production, petroleum refining, paper production, and industrial organic chemical production [108].

H₂SO₄ production is summarized in Figure 5.24. The processes summarized in this section were derived from IPPC [109].

Only 3 SO₂ production methods were investigated here because of their usage by Turkish H₂SO₄ production industry.

First method is using elemental sulphur as SO₂ source. Elemental sulphur is derived from desulphurisation of natural gas or crude oil by the Claus process. Elemental sulphur is delivered to the plant preferably liquid but also solid and, if necessary, filtered prior to combustion. The combustion is carried out in one stage or two stage units between 900 and 1500°C. The combustion unit consists of a combustion chamber followed by a waste heat boiler. The SO₂ content of the combustion gases is

generally as much as 18% v/v and the O_2 content is low (but higher than 3%). The inlet gases content to the conversion process is generally between 7- 13% SO_2 , if necessary adjusted by dilution with air. There is one company in Turkey produces with this method.

In the second method, pyrite is used as SO_2 source. Pyrite is roasted to generate SO_2 . This process has 2 by-products; iron oxide and energy. Due to heterogeneous character of the pyrite, the SO_2 content in the gases is slightly variable over time (generally 6-14%, O_2 free). The gases are always treated in three to four cleaning steps with cyclones, bag filters, scrubbers and electronic precipitators. There were two companies in Turkey in 2010 which produce H_2SO_4 with this method.

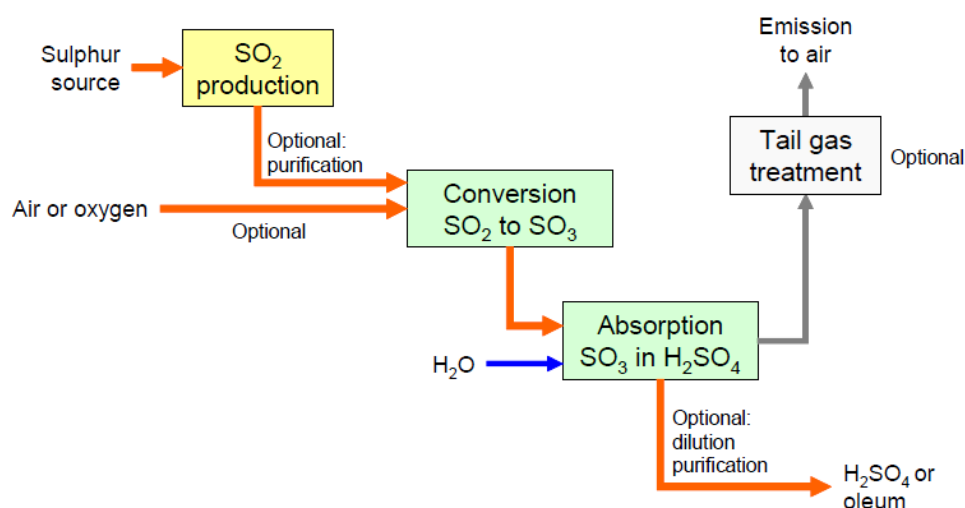


Figure 5.24 : Overview of the production of the H_2SO_4 [109].

The third SO_2 production technique is applied by non-ferrous metal producers. Examples of metallurgical processes like roasting, smelting or sintering of ores in order to yield metals such as Cu, Zn. Many metal sulphides when roasted during metallurgical processes produce gases containing SO_2 . The concentration of SO_2 in gases entering an acid plant, determines the amount of gas that must be treated per tonne of fixed sulphur. There was one company in Turkey in 2010 which produces H_2SO_4 with using this method.

SO_2 produced one of the above mentioned three methods is then converted into SO_3 in a gas phase chemical equilibrium reaction using a catalyst. At present, vanadium pentoxide is more widely used catalyst.

Finally H_2SO_4 is obtained from the absorption of SO_3 and water into H_2SO_4 (with a concentration of at least 98%).

5.4.7.1. Process emissions

Nearly all sulphur dioxide emissions from sulphuric acid plants are found in the exit stack gases. The mass of these SO_2 emissions is an inverse function of the sulphur conversion efficiency (SO_2 oxidized to SO_3). This conversion is always incomplete, and is affected by the number of stages in the catalytic converter, the amount of catalyst used, temperature and pressure, and the concentrations of the reactants (sulphur dioxide and oxygen) [108].

There was a difference between EMEP [61], AP42 [108] and IPPC [109] for SO_2 emission factors. In EMEP, SO_2 emission factor was given between 3-17 kg/ton for 100% H_2SO_4 . In AP42 it was given between 0-48 kg/ton for 93-100% SO_2 conversion to SO_3 . In IPPC it is given 0-8.6 kg/ton SO_2 in the tail gas for 98.7-100 % SO_2 conversion rates. Under this condition emission factors were chosen for each specific production technology and the average value of the selected factors is 3.88 kg SO_2 /ton and this value is compatible with all of the guidelines described above.

Table 5.69 : Process emissions of H_2SO_4 production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
SO_2	3.9	4,162	0.4	416.2
CO_2	4.1	4,345		
Acid Mist	0.6	687	0.064	69

Acid mist emission factor was taken from AP42 [108]. It is difficult to analyze SO_3 separately from H_2SO_4 , only one value [44] was given for the emission of these substances and named as 'acid mist'. Controlled emission factor was calculated from uncontrolled emission factor of SO_2 with 90% abatement efficiency. Acid mist emissions were accepted to be controlled by fibre mist eliminator control devices.

5.4.7.2. Fuel combustion emissions

Fuel combustion emissions of this sector are included under final emissions calculated in Section 5.4.13

5.4.8. Phosphoric Acid

Phosphoric acid, H_3PO_4 , is a colourless, crystalline compound that is readily soluble in water. The main product is H_3PO_4 with a commercial concentration of 52-54 / P_2O_5 . After sulphuric acid, phosphoric acid is the most important mineral acid in terms of volume and value [109].

Phosphoric acid (H_3PO_4) is produced by 2 commercial methods: wet process and thermal process. Wet process phosphoric acid is used in fertilizer production. Thermal process phosphoric acid is of a much higher purity and is used in the manufacture of high grade chemicals, pharmaceuticals, detergents, food products, beverages, and other nonfertilizer products [110]. In Turkey, generally wet process is used; therefore only wet process was described here.

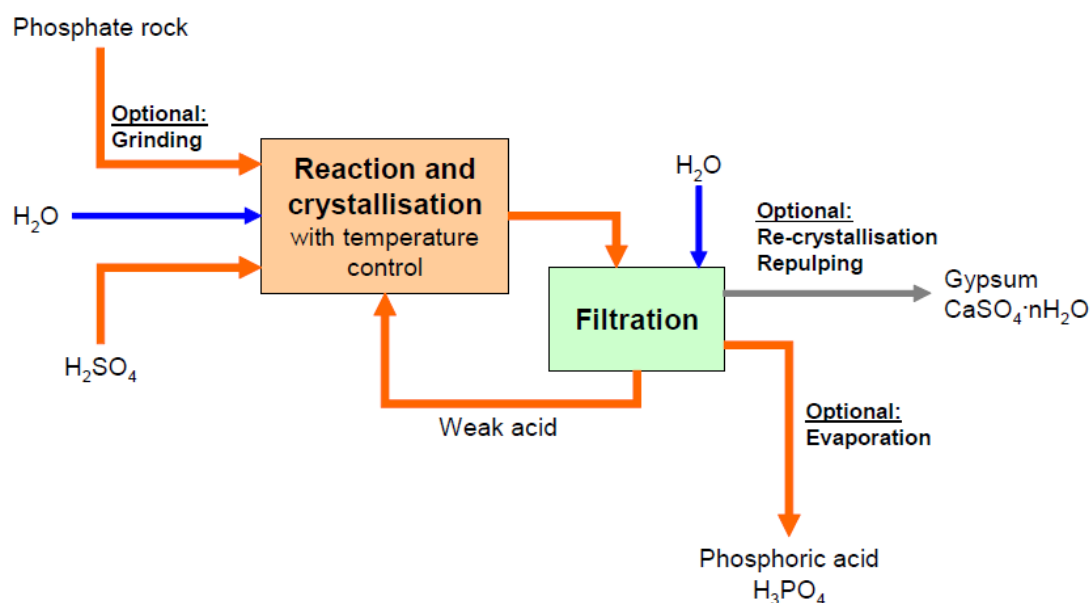


Figure 5.25: Overview of the production of the H_3PO_4 by wet process [109].

In a wet process, phosphoric acid is produced by reacting sulphuric acid (H_2SO_4) with naturally occurring phosphate rock. The phosphate rock is dried, crushed, and then continuously fed into the reactor along with sulphuric acid. The reaction combines calcium from the phosphate rock with sulphate, forming calcium sulphate (CaSO_4), commonly referred to as gypsum. Gypsum is separated from the reaction solution by filtration. Facilities in the U. S. generally use a dehydrate process that produces gypsum in the form of calcium sulphate with 2 molecules of water (H_2O) ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or calcium sulphate dehydrate). Japanese facilities use a hemihydrate process that produces calcium sulphate with a half molecule of water ($\text{CaSO}_4 \cdot \frac{1}{2}$

H₂O). This one-step hemihydrate process has the advantage of producing wet process phosphoric acid with a higher P₂O₅ concentration and less impurities than the dehydrate process.

During the reaction, gypsum crystals are precipitated and separated from the acid by filtration. The separated crystals must be washed thoroughly to yield at least a 99 percent recovery of the filtered phosphoric acid. After washing, the slurry gypsum is pumped into a gypsum pond for storage. Water is syphoned off and recycled through a surge cooling pond to the phosphoric acid process.

Considerable heat is generated in the reactor. In older plants, this heat was removed by blowing air over the hot slurry surface. Modern plants vacuum flash cool a portion of the slurry, and then recycle it back into the reactor. Wet process phosphoric acid normally contains 26 to 30 percent P₂O₅. In most cases, the acid must be further concentrated to meet phosphate feed material specifications for fertilizer production. Depending on the types of fertilizer to be produced, phosphoric acid is usually concentrated to 40 to 55 percent P₂O₅ by using 2 or 3 vacuum evaporators.

Process summary given above was derived from EPA [110].

5.4.8.1. Process emissions

Major emissions from wet process acid production include gaseous fluorides, mostly silicon tetrafluoride (SiF₄) and hydrogen fluoride (HF). Phosphate rock contains 3.5 to 4.0 percent fluorine. The reactor in which phosphate rock is reacted with sulphuric acid is the main source of emissions. Fluoride emissions accompany the air used to cool the reactor slurry. In general, part of the fluorine from the rock is precipitated out with the gypsum, another part is leached out with the phosphoric acid product, and the remaining portion is vaporized in the reactor or evaporator [110]. PM emissions are mainly occurs from process equipments.

Two of the plants (approximately covers half of the total production) have fluoride controlling technologies. PM controlling technology was accepted as wet scrubber. Emission factors were taken from EPA [110].

Table 5.70 :Process emissions of phosphoric acid production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
Fluoride	0.231	35	0.002	0.6
PM	10	2,485	0.2	49.7

5.4.8.2. Fuel combustion emissions

Additionally, fuel combustion emissions of this sector are included under final emissions calculated in Section 5.4.13

5.4.9. Chlor Alkali

The chlor-alkali industry is the industry that produces Chlorine (Cl_2) and alkali, sodium hydroxide (NaOH) or potassium hydroxide (KOH), by electrolysis of a salt solution. The main technologies applied for chlor alkali production are mercury, diaphragm and membrane cell electrolysis, mainly using sodium chloride (NaCl) as feed or to a lesser extent using potassium chloride (KCl) for the production of potassium hydroxide [111].

In Turkey, chlor alkali products are manufactured by private sector generally by Membrane cell electrolysis method [69].

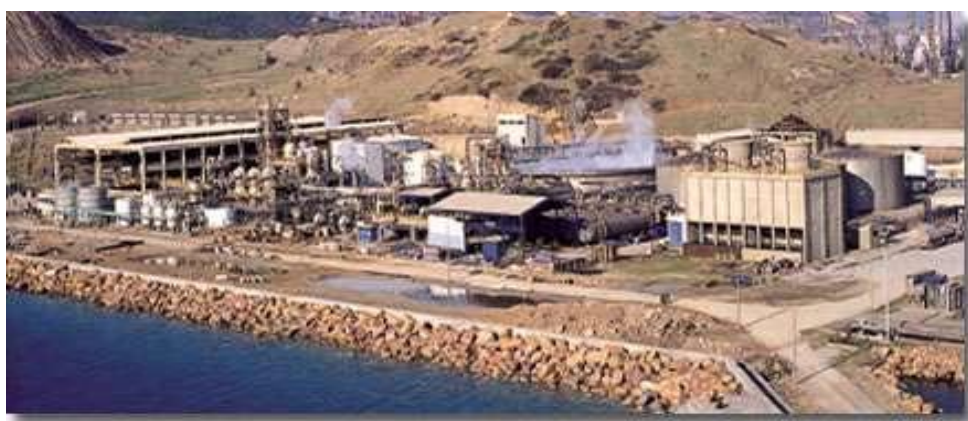


Figure 5.26: Chlor Alkali Plant of Petkim in Aliaga, Izmir [112].

5.4.9.1. Process emissions

Generally membrane cell electrolysis method was not clear in the sources in terms of emission factors. There were only large ranges for selection of emission factor.

H₂ (Hydrogen), Cl₂ and CO₂ emissions are emitted from chlorine alkali plants [111]. Emission factors are taken from IPPC [111] without including chlorine liquefaction and cooling systems emissions.

Table 5.71 :Process emissions of chlor alkali production.

	Emission factor	Emissions
	kg/ton	ton/yr
H ₂	3	537
Cl	0.08	14.3
CO ₂	3.1	555

Uncontrolled emission factors are taken from Reinders [44] and CO₂ emission factor was derived from IPPC [111]. Controlled emission factors were not calculated for this sector.

5.4.9.2. Fuel combustion emissions

Fuel combustion emissions of this sector included under final emissions calculated in Section 5.4.13

5.4.10. Hydrochloric Acid

Hydrochloric acid is a versatile chemical used in a variety of chemical processes, including hydrometallurgical processing (e. g., production of alumina and/or titanium dioxide), chlorine dioxide synthesis, hydrogen production, activation of petroleum wells, and miscellaneous cleaning/etching operations including metal cleaning (e. g., steel pickling) [113].

Hydrochloric acid may be manufactured by several different processes, although over 90 percent of the HCl produced in the U. S. is a by-product of the chlorination reaction [113]. In this section, HCl production was investigated producing as a by-product of chlorination in the production of vinyl chloride. However it can be produced in other chlorination processes e.g. dichloromethane, trichloroethylene, perchloroethylene [113].

In this section, only recycled HCl from VCM production in Petkim is considered.

5.4.10.1. Process emissions

The most important emission emitted during HCl production is HCl emission to the atmosphere as a by-product.

Table 5.72 : Process emission factors used for HCl production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
HCl	0.9	0.015	0.08	0.001

Emission factors were taken from EPA [113]. Controlling technology of HCl emission is final scrubber.

5.4.10.2. Fuel combustion emissions

Fuel combustion emissions of this sector are included under final emissions calculated in Section 5.4.13.

5.4.11. Ammonia

Ammonia (NH_3) is a major industrial chemical and most important nitrogenous material produced. Ammonia gas is used directly as a fertiliser and in heat treating, paper pulping, nitric acid and nitrates manufacture, nitric acid ester and nitro compound manufacture, explosives of various types, and as a refrigerant. Amines, amides, and miscellaneous other organic compounds, such as urea, are made from ammonia [65].

The process of ammonia production is based on the ammonia synthesis loop (also referred to as the Haber-Bosch process) reaction of nitrogen (derived from process air) with hydrogen to form anhydrous liquid ammonia. The hydrogen is derived from feedstock as natural gas (conventional steam reforming route) or sometimes uses other fuel feedstock as residual oil or coke (partial oxidation) that is being gasified and purified [61]. In Turkey natural gas is used as feedstock in all production facilities [143]. 77% of the world capacity use natural gas as feedstock and 83% of the world produce NH_3 by steam cracking method [109]. Therefore production technology is accepted as catalytic steam reforming method for all plants.

Six process steps are required to produce synthetic ammonia using the catalytic steam reforming method: (1) natural gas desulphurization, (2) catalytic steam reforming, (3) carbon monoxide (CO) shift, (4) carbon dioxide (CO_2) removal, (5) methanation, and (6) ammonia synthesis. The first, third, fourth, and fifth steps remove impurities such as sulphur, CO, CO_2 and water (H_2O) from the feedstock, hydrogen, and synthesis gas streams. In the second step, hydrogen is manufactured

and nitrogen (air) is introduced into this 2-stage process. The sixth step produces anhydrous ammonia from the synthetic gas. While all ammonia plants use this basic process, details such as operating pressures, temperatures, and quantities of feedstock vary from plant to plant [115].

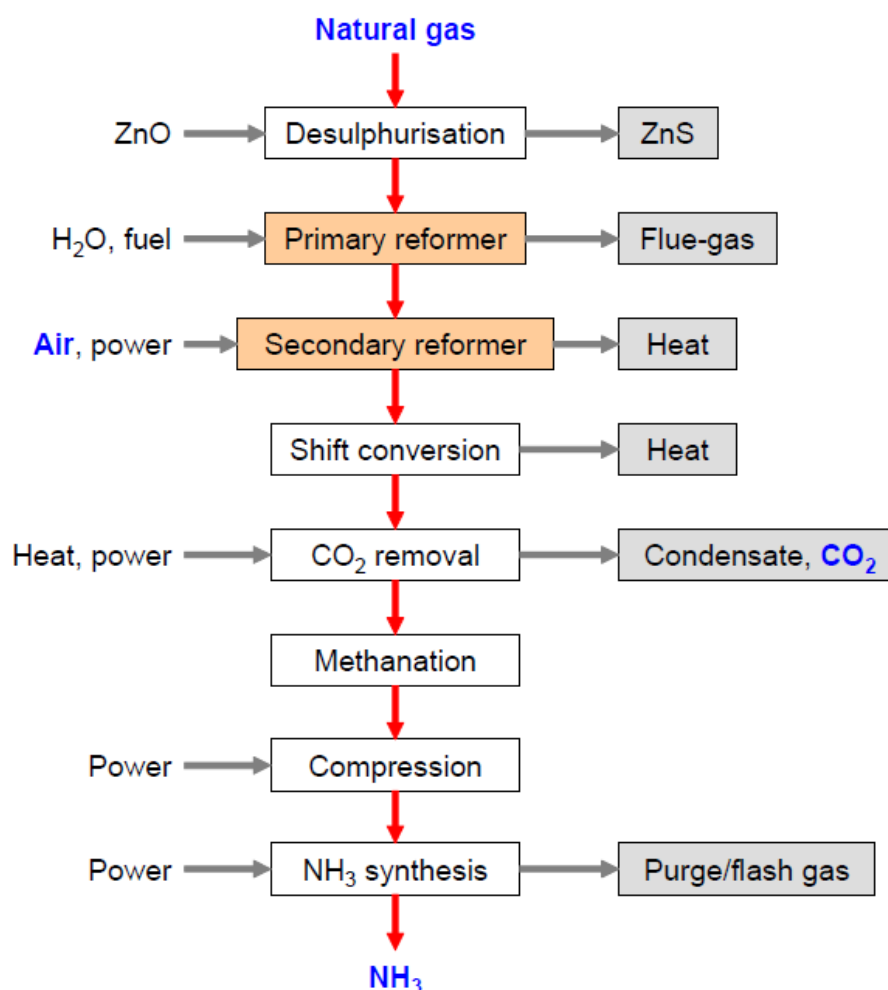


Figure 5.27 : Overview of the production of the NH₃ by steam cracking method [109].

5.4.11.1. Process emissions

CO₂ is produced in accordance with stoichiometric conversion and can be recovered for further use as feedstock for other products. There is, however, an inevitable excess of CO₂ which is released as an emission from the process [109]. The primary release of CO₂ at plants using the natural gas catalytic steam reforming process occurs during regeneration of the CO₂ scrubbing solution with lesser emissions resulting from condensate stripping [65]. Emission factor was decided by comparing IPCC [65] and EPA [115] guidelines. IPCC Tier 1 method was applied by NIR

Turkey 2010 [26] and CO₂ emission factor was selected as 1600 kg/ton. In this study it is selected as 1669 kg/ton. The other emission factors were given in Table 5.73.

Table 5.73 : Process emission of ammonia production.

	Uncontrolled		Controlled	
	EF	Emissions	EF	Emissions
	kg/ton	ton/yr	kg/ton	ton/yr
CO ₂	1669	861,410		
NH ₃	2.1	1,084	0.105	54
NO _x	1	516	0.7	361
CO	1	516	0.05	26
SO _x	0.03	46	0.0014	2

Condensate steam strippers are used to remove NH₃ and methanol from the water, and steam from this is vented to the atmosphere, emitting NH₃, CO₂, and CH₃OH. NH₃ emission factor was taken from IPPC [109] and Reinders [44] for controlled conditions.

NO_x and CO emission factors were taken from EMEP [61]. Natural gas combustion causes NO_x emission and 30% abatement efficiency was accepted for controlled conditions.

CO₂ is removed from the synthesis gas by scrubbing with some chemicals. Also CO, and SO_x emissions control efficiency is accepted as 99%.

5.4.11.2. Fuel combustion emissions

Fuel combustion emissions of this sector are included under final emissions calculated in Section 5.4.13.

5.4.12. Nitric Acid

Nitric acid is mainly used as a raw material in the manufacture of nitrogenous-based fertiliser. Nitric acid may also be used in the production of adipic acid and explosives (e.g., dynamite), in the processing of ferrous metals and for metal etching [65].

Nitric acid is produced by 2 methods. The first method utilizes oxidation, condensation, and absorption to produce a weak nitric acid. Weak nitric acid can have concentrations ranging from 30 to 70 percent nitric acid. The second method combines dehydrating, bleaching, condensing, and absorption to produce a high-strength nitric acid from a weak nitric acid. High-strength nitric acid generally

contains more than 90 percent nitric acid [116]. Following process descriptions were derived from EPA [116].

Weak HNO₃ Production: This process typically consists of 3 steps: (1) ammonia oxidation, (2) nitric oxide oxidation, and (3) absorption. Each step corresponds to a distinct chemical reaction.

Ammonia Oxidation first, a 1:9 ammonia/air mixture is oxidized at a temperature of 748.89°C to 798.89°C as it passes through a catalytic convertor. Higher catalyst temperatures increase reaction selectivity toward NO production. Lower catalyst temperatures tend to be more selective toward less useful products: nitrogen (N₂) and nitrous oxide (N₂O).

Secondly, the nitric oxide formed during the ammonia oxidation must be oxidized. The nitric oxide reacts noncatalytically with residual oxygen to form nitrogen dioxide (NO₂) and its liquid dimmer. This slow, homogeneous reaction is highly temperature- and pressure-dependent. Operating at low temperatures and high pressures promotes maximum production of NO₂ within a minimum reaction time.

The final step, absorption, introduces the nitrogen dioxide/dimmer mixture into an absorption process after being cooled.

High Strength HNO₃ Production: High-strength nitric acid (98 to 99 percent concentration) can be obtained by concentrating the weak nitric acid (30 to 70 percent concentration) using extractive distillation. The weak nitric acid can not be concentrated by simple fractional distillation. The distillation must be carried out in the presence of a dehydrating agent. Concentrated sulphuric acid (typically 60 percent sulphuric acid) is most commonly used for this purpose. Emissions from this process are relatively minor. A small absorber can be used to recover NO₂.

5.4.12.1. Process emissions

Emissions from nitric acid manufacture consist primarily of NO, NO₂ (which account for visible emissions), trace amounts of HNO₃ mist, and ammonia (NH₃). By far, the major source of nitrogen oxides (NO_x) is the tail gas from the acid absorption tower [116]. The NO_x emissions (nitrous gases) contain a mixture of nitric oxide (NO) and nitrogen dioxide (NO₂), dinitric oxide (N₂O₃) and dinitric tetroxide (N₂O₄)

[61]. Additionally a huge amount of N_2O emissions occurs mainly from weak acid production.

Ammonia and NH_3 occurs as trace amount therefore are not calculated in this study. However it is calculated in NIR Turkey 2010 [26] by using 0.01 kg/ton is used as emission factor. There is no information about NH_3 emissions of HNO_3 production in the emission factor sources.

Table 5.74 : Process emission of HNO_3 production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
N_2O	9.57	6,671	2.00	2,252
NO_x	15.43	10,762	0.90	1,013

N_2O emissions from HNO_3 production represents big portion emitted from chemical industry. Regarding to NIR Turkey 2010 [26], for the latest year, the plants have equipped with non-selective catalytic reduction (NSCR). for plants without NSCR, the N_2O emission factor was taken as 19 kg/t. However IPPC recommended N_2O emission factor between 10-19 kg/ton and 2 kg/ton for the plants using NSCR in all processes. In this study, 16 kg/ton is accepted for one outdated plant of Turkey. Finally weighted average of N_2O emission factor for all plants was calculated as 9.57 kg/ton for uncontrolled conditions. Medium pressure plant emission factor was applied for the controlled conditions of N_2O emissions.

NO_x emission factor was given by EMEP [61] between 0.4-12 kg/ton and it is used as 12 kg/ ton (average) in NIR Turkey 2010 [26]. Catalytic reduction is accepted to be used by all industries for the controlled conditions of NO_x emissions.

NO_x emission factors were selected with considering high/weak acid production, old/new plant etc. Finally weighted average of emission factors selected is 15,43 kg/ton. This value is compatible with all guidelines considered in this study.

5.4.13. Fuel combustion emissions of chemical industry

There was no information in the Energy Balance Table [46] about fuel combustion amounts of chemical industry sub-sectors. However, fuel combustion emissions were calculated in former sections for some of the sectors, but there is no chance to deduct formerly calculated emissions from the values in Table 5.75, therefore these results

should only be used for independent sectorial evaluation. Organic and inorganic chemicals industry fuel combustion emissions are given in Table 5.75.

5.5. Mineral Products Industry

5.5.1. Cement

[40] Portland cement can be produced either by dry or wet processes (there are also semi-dry and semi wet processes). In the wet process, the raw material is a chalk which is first slurried with water; this slurry is passed with other constituents into a rotary kiln for calcining and cement clinker formation. In the dry process, limestone is dry-mixed with other constituents, milled and typically passed to a pre-heater tower and/or a precalciner furnace before a rotary kiln. The dry process requires less energy than the wet process. In all processes the clinker is cooled after leaving the kiln, milled and blended with additives to form various grades of cement.

Turkey was the 2nd biggest producer in Europe and 6th in the world in 2010 [117]. In Turkey, about 98% of the cement kilns (not the plants) are based on dry systems (with or without pre-calciner). The remaining 2% covers semi-wet (Lepol) or wet systems [26].

There are 48 integrated cement plants in Turkey, which produce clinker and final product cement. There are also 19 cement plants in Turkey producing only cement from the clinker and final product cement [26]. The clinker production was around 55.6 million tonnes and cement production was around 66.2 million tonnes in 2010 (data consist of TCMA Members & estimations for non-members) [118].

During the production of clinker - is an intermediate product of cement were not grinded and not include additives - limestone, which is mainly calcium carbonate (CaCO_3), is heated, or calcined, to produce lime (CaO) and CO_2 as a by-product. The CaO then reacts with silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3) in the raw materials to make the clinker minerals (chiefly calcium silicates) [119].

Table 5.75 : Fuel combustion emissions of chemical industry.

Pollutant	Emission Factor (kg/TJ)				Emissions (ton/yr)				Total
	Hard Coal	Brown Coal	Petroleum	Natural Gas	Coal	Brown Coal	Petroleum	Natural Gas	
PM	124	124	27.5	0.50	266	760	686	3	1,715
SO ₂	916.2	900	140	0.50	1,966	5,517	3,491	3	10,976
CO	931	931	40	38.91	1,997	5,707	997	223	8,924
NO _x	173	173	100	88.01	371	1,060	2,493	505	4,430
CO ₂	98,300	101,000	73,300	56,100	210,885	619,077	1,827,680	321,667	2,979,309
N ₂ O	1.5	1.5	0.6	0.10	3	9	15	1	28
CH ₄	10.0	10.0	3.0	1.00	21	61	75	6	163
NMVOC	88.8	88.8	10.0	2.50	191	544	249	14	998

In this section, fuel combustion emissions of chemical industry is calculated totally, because the fuel consumption amounts are given totally for these 2 sectors sector in the Energy Balance Table [46] which is prepared by the MENR.

5.5.1.1. Process and fuel combustion emissions

Process and fuel combustion emissions are evaluated under a title because of it's hardness to separate emissions regarding to their sources. As a general, the main emissions emitted from the processes of cement industries are PM and CO₂. Other hand, emissions such as SO_x and NO_x are strongly dependent of the type and properties of the fuel used. Figure 5.28 shows a generalized mass balance of a cement factory.

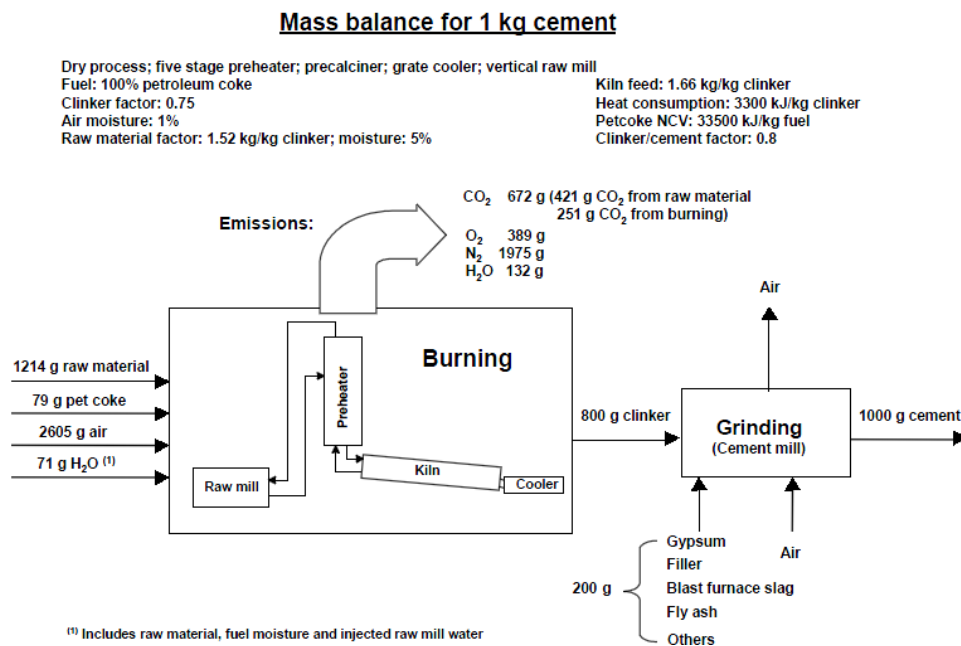


Figure 5.28: Mass Balance of 1kg cement production with dry process [119].

[120] Sulphur dioxide may be generated both from the sulphur compounds in the raw materials and from sulphur in the fuel. The sulphur content of both raw materials and fuels varies from plant to plant and with geographic location. However, the alkaline nature of the cement provides for direct absorption of SO₂ into the product, thereby mitigating the quantity of SO₂ emissions in the exhaust stream. Depending on the process and the source of the sulphur, SO₂ absorption ranges from about 70 percent to more than 95 percent. However, in systems that have sulphide sulphur (pyrites) in the kiln feed, the sulphur absorption rate may be as low as 70 percent without unique design considerations or changes in raw materials. Fabric filters on cement kilns are also absorb SO₂, but generally, substantial control is not achieved.

By using the values on Figure 5.27 it was calculated that, energy need to produce 1 kg clinker is 3.3-6.9 GJ, where it is given as 3.8 GJ/ton clinker [118] for Turkey for 2011 which hit upon 900,000 kcal/ton clinker. Additionally, regarding to the public announced information by cement factories, SO₂ concentration is approximately 50 mg/L in instant flue gas measurements which depends on the fuel used, the technology and the kiln and does not exceed 300 mg/Nm³ [121] which is the maximum permitted value by the local regulation. By using all of the values explained above, the SO₂ emission factor was calculated with following steps; flue gas amount for unit amount of clinker was calculated by considering 10% air excess as 2.5 m³/kg clinker, than current flue gas SO₂ measurement (approximately 50 mg SO₂ / m³ flue gas) was multiplied with flue gas amount which was resulted 0.125 kg SO₂ / ton clinker. This value corresponds to the emission factor which was used for emission calculations of this study. This value was 0.053 kg/ton cement (0.064 kg/ton clinker) [122] and 0.37 kg/ton clinker (Tier 2) [40] and 11.12 kg/ton [124] in other studies. Uncontrolled emissions were not calculated for SO₂.

PM emission is emitted from cement factories and milling/packaging factories. Controlled emission factor accepts 99.8% abatement efficiency for PM emissions with fabric filter/ESP and emission factor is taken from EPA [120] for preheater kiln. PM distribution between cement factories and milling and packaging factories are done by using the rate given by Canpolat B.R. et.al. [122]. PM₁₀ - PM_{2.5} emission factors were derived from EMEP [119] for controlled conditions and uncontrolled emission factors are calculated by using 99.8% reduction efficiency of PM emissions.

CO₂ emission factor is taken from IPCC [123] and adjusted regarding to personal communication with Alp K. [29].

Table 5.76 : Process emission of cement industry.

Pollutants	Uncontrolled		Controlled	
	EF kg/ton cement	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	130	7,186,267	0.203	14,373
* cement factories	95	6,726,062	0.19	13,452
* milling and packaging factories	7	460,204	0.013	920
PM ₁₀	100	5,422,294	0.2	10,845
PM _{2.5}	55	2,982,262	0.11	5,965
CO ₂	421	29,807,076		
SO ₂ (kg/ton clinker)			0.125	6,778

Only CO₂ and SO₂ emissions were calculated in NIR 2010 Turkey [26]. CO₂ emission was calculated 28,923,120 ton by taking CO₂ emission factor as 0.51 kg/ton in NIR 2010; however it was calculated as 29,807,076 ton in this study. This is mainly because of the activity data. Also SO₂ emission is calculated as 19,860 ton in NIR 2010.

Fuel combustion emissions of cement industry are given in Table 5.77. Fuel consumption values were taken from MENR 2010 Energy Balance Table [8].

Also emissions are compared with NIR 2010 Turkey [26] in Table 5.78.

Emission factors sources for coal and brown coal: NO_x, CO, NMVOC and PM emission factors were taken from EMEP [40]; CO₂, N₂O and CH₄ emission factors were taken from IPCC [123].

Emission factors sources for petroleum combustion: NMVOC and PM emission factors were taken from EMEP [40]; NO_x, CO, CO₂ and N₂O emission factors were derived from EPA [50] and CH₄ emission factor was taken from IPCC [123] with the acceptance of fuel oil No: 6 usage in the plants as fuel.

Emission factors sources for natural gas: NO_x emission factor was taken from EPA [39]; CO, PM, NMVOC emission factors were derived from EMEP [40]; CO₂, N₂O and CH₄ emission factors were taken from IPCC [123].

SO_x emissions were calculated in a different way by considering as process emission as explained within this section.

Blank cells in Table 5.78 show uncalculated emissions. Liquid fuels include petroleum; solid fuels include hard coal, brown coal, asphaltite and petroleum coke.

Gaseous fuels include only natural gas. Fuel consumption values were taken from MENR 2010 Energy Balance Table [8].

NO_x, NMVOC, N₂O, CH₄, CO emissions were evaluated under process emissions in the final evaluation despite they were calculated as fuel combustion emissions in this section, because it was impossible to separate these emissions as fuel combustion and process emissions.

The main difference between two studies is the liquid fuels which include only petroleum in the MENR Table and only 26,000 ton petroleum consumed in 2010 by cement industry. Under this condition, 6,386,546 ton CO₂ emission seems irrelevant. This situation can be understandable if TurkStat has different energy consumption table for cement industry of Turkey.

Table 5.77 : Fuel combustion emissions of cement industry.

Pollutant	Emission Factor (kg/TJ)					Emissions (ton/yr)					Total
	Hard Coal	Brown Coal	Petroleum Coke	Petroleum	Natural Gas	Coal	Brown Coal	Petroleum Coke	Petroleum	Natural Gas	
PM	N.E.	124.0	27.5	N.E.	0.50	N.E.	2,506	1,887		0.28	4,393
CO	2.0	931.0	40.0	2.0	38.91	108,446	18,815	2,744	2	22	130,029
NO _x	1.6	173.0	100.0	1.6	88.01	84,046	3,496	6,860	2	49	94,452
CO ₂	98,300	101,000	97,500	73,300	56,100	7,599,377	2,041,178	6,688,815	78,675	31,004	16,439,049
N ₂ O	1.5	1.5	1.5	0.6	0.10	116	30	103	1	0.06	250
CH ₄	10.0	10.0	10.0	3.0	1.00	773	202	686	3	1	1,665
NMVOC	0.1	88.8	10.0	0.1	2.50	5,422	1,795	686		1	7,904

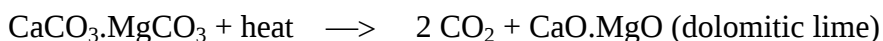
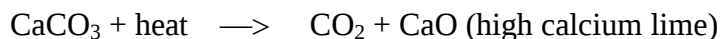
Table 5.78 : Cement industry fuel combustion emissions comparison between this study and NIR 2010 Turkey [26].

	LIQUID FUELS (ton/yr)		SOLID FUELS (ton/yr)		GASEOUS FUELS		TOTAL	
	This study	NIR 2010	This study	NIR 2010	This study	NIR 2010	This study	NIR 2010
CO ₂	78,675	6,386,546	16,329,370	9,935,302	31,004	34,020	16,439,049	16,355,867
CH ₄	3	682	1,661	1,049	1	3	1,665	1,734
N ₂ O	1	96	249	147	0.06	0.06	250	243
NO _x	2		94,402		49		94,452	52,187
CO	2		130,005		22		130,029	25,967
NMVOC	0.11		7,903		1		7,904	3,467

5.5.2. Lime

The raw material for lime production is limestone or dolomite or dolomitic limestone. 10% of the total's world volume of sedimentary rock is limestone.

Lime is manufactured in various kinds of kilns by one of the following reactions:



The process comprised of three sections. First one is handling of raw materials. This step includes preparation, cleaning and storage of raw materials, quarrying raw limestone, preparing limestone for the kilns by crushing and sizing, fuels. Second one is combustion in the kiln for the production for limestone calcining in different types of kilns which affect amount of air pollutants emitted. The final step is the after-treatment of the lime which includes processing the lime further by hydrating and miscellaneous transfer, storage, and handling operations [124].

There was more than 27 factories produce lime in Turkey in 2010 [62].

5.5.2.1. Process emissions

Released pollutants from lime production are sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (non-methane VOC and methane (CH₄)), carbon monoxide (CO), carbon dioxide (CO₂), nitrous oxide (N₂O) and particulate matter [125]. Only CO₂ and PM emissions were calculated and given in Table 5.79.

Table 5.79 : Process emissions of lime production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
CO ₂	750	2,743,421		
TSP	9	32,921	0.4	1,463
PM _{2.5}	0.7	2,561	0.2	732
PM ₁₀	3.5	12,803	0.03	110

It should be noted that this CO₂ emission only represents the emitted amount comes from converting of the CaCO₃ to CaO, not include fuel related CO₂ emission. In NIR Turkey 2010 [26], CO₂ emissions were calculated by IPCC Tier 1 [119] method with

using same emission factor as 2,817,000 ton for 2010. Controlled emission factor is taken from EMEP [119].

5.5.2.2. Fuel combustion emissions

The main environmental issues associated with lime production are air pollution and the use of energy. The lime burning process is the main source of emissions and is also the principal user of energy.

Table 5.80 : Fuel combustion emissions of lime industry.

	EF	Emissions
	kg/TJ	ton/yr
NO _x	80	1,434
CO	160	2,868
N ₂ O	1.5	27
SO _x	112	2,007
TSP	124	2,223
CO ₂	95,350	1,709,023
CH ₄	10	179.2
NMVOC	88.8	1,592
Total	95,926	1,719,352

The secondary processes of lime slaking and grinding can also be of significance in terms of energy usage, but subsidiary operations (namely crushing, screening, conveying, storage and discharge) are relatively minor in terms of both emissions and energy usage. Potentially significant emissions from lime plants include CO₂, CO, NO_x, SO₂ and dust [124].

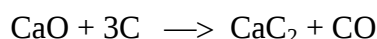
In the calculations, it is accepted that energy is mainly supplied from bituminous coal and coke. This assumption is compatible with the information supplied by KISAD [149]. Calorific values are derived from the annual publishing of EIE [41].

5.5.3. Carbide

There are two types of carbide products; silicon carbide and calcium carbide. Silicon carbide is a significant artificial abrasive. It is produced from silica sand or quartz and petroleum coke. Calcium carbide is used in the production of acetylene, in the manufacture of Cyanamid (a minor historical use), and as a reductant in electric arc steel furnaces. It is made from two carbon containing raw materials: calcium carbonate (limestone) and petroleum coke [119].

Only Calcium carbide was produced by a company in Turkey in 2010. Therefore only CaC₂ production process is described here.

Calcium carbide (CaC₂) is manufactured by heating a lime and carbon mixture to 2000 to 2100°C in an electric arc furnace. At those temperatures, the lime is reduced by carbon to calcium carbide and carbon monoxide (CO), according to the following reaction [126] :



Calcium carbide is used in the production of acetylene, in the manufacture of Cyanamid (a minor historical use), and as a reductant in electric arc steel furnaces [65].

5.5.3.1. Process emissions

The production of carbide can result in emissions of carbon dioxide (CO₂), methane (CH₄), carbon monoxide (CO) and sulphur dioxide (SO₂) [119] and dust. However, only CO₂, CH₄ and PM emissions were considered in this study.

The sources of carbon for the reaction are petroleum coke, metallurgical coke and anthracite coal [61]. Use of carbon-containing raw materials in the production processes results in emissions of CO₂ and CO.

Table 5.81 : Process emissions of Carbide production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
CO ₂	2620	37,419		
CH ₄	11.6	166	0.58	8
PM	1.78	25	0.089	1.27

CO₂ and CH₄ emission factors were taken from IPCC Tier 1 [119], PM emission factor as taken from EMEP [125]. There is no information for the control technology of this industry, therefore PM and CH₄ emissions were accepted to be controlled with 95% abatement efficiency when calculating controlled emissions.

5.5.3.2. Fuel combustion emissions

The presence of hydrogen-containing volatile compounds and sulphur (S) in the petroleum coke may cause formation and emission to the atmosphere of CH₄ and SO₂ [65]. Final emissions of this sector are included in Chapter 5.4.13.

5.5.4. Glass

The glass industry is characterised by wide variety of manufacturing facilities, from those firms engaged in primary glass manufacturing, to those that create products from purchased glass.

The glass fibre sector produces two main products and they are, textile glass fibres and insulation glass fibre. Textile glass fibre is used in the production of fireproof cloth, while insulation glass fibre is used in thermal and acoustic insulation, including tank and swimming pool shells.

5.5.4.1. Process emissions

The main emission from the production of glass is carbon dioxide (CO₂), originating mainly from the carbonisation process [127]. The major glass raw materials which emit CO₂ during the melting process are limestone (CaCO₃), dolomite ((Ca.Mg)(CO₃)₂) and soda ash (Na₂CO₃). Where these materials are mined as carbonate minerals for their use in the glass industry they represent primary CO₂ production and should be included in emissions estimates. Where carbonate materials are produced through the carbonation of a hydroxide they do not result in net CO₂ emissions and should not be included in the emissions estimate.

Minor CO₂-emitting glass raw materials are barium carbonate (BaCO₃), bone ash (3CaO₂P₂O₅ + xCaCO₃), potassium carbonate (K₂CO₃) and strontium carbonate (SrCO₃).

Additionally, powdered anthracite coal or some other organic material may be added to create reducing conditions in the molten glass, and will combine with available oxygen in the glass melt to produce CO₂ [119].

Table 5.82 : Process emissions of glass production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
<i>Float Glass</i>				
CO ₂	0.21	158,734	0.21	158,734
TSP	2.6	2208	0.13	110
PM ₁₀	2.4	204	0.12	10
PM _{2.5}	2	1699	0.1	85
<i>Others</i>				
CO ₂	0.2	181,090	0.2	181,090
TSP	6	5433	0.3	272
PM ₁₀	5.4	4889	0.27	244
PM _{2.5}	4.8	4346	0.24	217

CO₂ emission emitted from the glass production with float method was calculated by using IPCC [119] Tier 2 method as 339,824 ton, other glass types production were calculated by using emission factors of IPCC Tier 1 method. Controlled PM emission factors are taken from EMEP [125]. 95% abatement efficiency is accepted for PM emissions.

5.5.4.2. Fuel combustion emissions

The waste gases released from melting furnaces consist mainly of combustion gases generated by fuels and of gases arising from the melting of the batch or vapour released from the melt, which in turn depends on chemical reactions taking place in the furnace. The proportion of batch gases from exclusively flame-heated furnaces represents 3–5 % of the total gas volume [127].

Pollutants released during the manufacture of glass are sulphur oxides (SO_x), nitrogen oxides (NO_x), in very rare cases carbon monoxide (CO), carbon dioxide (CO₂) or nitrous oxide (N₂O). Also emissions of heavy metals are produced by the melting process. Emissions of particulate matter can also result from handling raw materials. Heavy metals can sometimes be present in the particulate matter [127].

The amount of SO₂ released during glass manufacturing is mainly determined by the sulphur content of the fuel, the sulphur content in the batch and the sulphur absorption ability of the glass produced.

The relevant NO_x emission process step within the production of glass is the melting stage. NO_x emissions released by glass furnaces are nitric oxides (NO to about 90 % due to the near stoichiometric operation of the furnaces, the remainder of the NO_x in the flue gases being nitrogen dioxide (NO₂)). The concentrations of nitrous oxide in glass furnace waste gases are in general below the detection limit.

Fuel combustion emission of glass production is calculated in 'Other Fuel Combustion Emissions'.

5.6. Metallurgical Industry

5.6.1. Iron and Steel Industry

Turkey was the 10th bigger iron and steel producer between 66 countries in the world in 2010 and produced 4.64% of world steel [128].

The consumption amount of final steel in domestic market corresponded to 89.67% of the manufacturing amount of Turkey in 2010 [129]. The active construction industry of Turkey has a significant effect in Turkish iron and steel industry.

Steel is produced from either iron ore in integrated steelworks or scrap in electrical arc furnaces. In Turkey, 71.2% of the steel is produced in electrical arc furnaces and 28.8% is produced in integrated steelworks in 2010 [129, 128].

5.6.1.1. Integrated steelworks

Integrated steelworks are large industrial complexes include sintering, pelleting, classic blast furnace, basic oxygen furnace route, also coking plants. In Turkey there are 3 integrated steelworks; Kardemir (established in 1939, in Karabuk), Erdemir (established in 1965, in Ereğli), Isdemir (established in 1977, in Iskenderun) [131]. All of these plants include coke production units.

The main air pollutants from integrated steelworks processes are PM, CO and SO₂. Selected emission factors and calculated emissions are given in Table 5.83. CO emissions emitted from blast furnace, SO₂ emissions emitted from scarfing operations. High carbon monoxide content may be used within the plant or flared. The efficiency of flares for the control of carbon monoxide and the reduction of VOCs has been estimated to be greater than 98 percent [152].

Table 5.83 : Process emissions of integrated steelworks.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	36	282,574	2.4	17,365
CO	37	255,723	0.74	5114
SO ₂	1.46	9744	0.4	3475
NO _x	0.45	2636	0.32	1845
CO ₂	1911	16,197,615		

PM emissions are accepted to be controlled by cyclone in sintering, by venturi scrubber at sinter discharge, roof monitor blast furnace and scrubber in basic oxygen furnaces (BOF). Hot metal desulphurization unit is accepted uncontrolled for PM emissions. BOF charging, tapping are accepted to be done at building monitor and hot metal transfer at source. PM emission factor is derived from EPA [132]. CO emission factor is derived from both EPA [132] and Reinders [44]. Controlled emission factor is calculated with assuming staged combustion with 30% reduction efficiency and calculated from the uncontrolled emission factor which was taken from EPA [132].

5.6.1.2. Metallurgical coke production

Metallurgical coke production is evaluated under the title of “process emissions of integrated iron and steel plants”.

Coke is produced by the destructive distillation of coal in coke ovens and used in iron and steel industry processes (primarily in blast furnaces) to reduce iron ore to iron. Most coke plants are collocated with iron and steel production facilities, and the demand for coke generally corresponds with the production of iron and steel [146].

85% of the metallurgical coke is mainly produced by 3 integrated steelworks in Turkey; Kardemir, Erdemir, İsdemir with the usage of coal as feedstock. Due to knowledge deficit for the rest of the production technology, other coke production facilities are not covered in this study.

Coke production process is the source of conventional pollutants as PM, CO, SO_x, NO_x, etc. and some other organic compounds such as VOCs and POM. Coal-handling operations may account for about 10% of the particulate load. Coal charging, coke pushing, and quenching are major sources of dust emissions.

Emission factors for each of the pollutant regarding to the processes are given in Table 5.84.

Table 5.84 : Process emission of coke production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	7.97	37,291	0.75	3519
CO	1.88	8,811	0.04	176
SO _x	0.40	1,869	0.20	919
VOC	6.03	22,059	0.06	252
NH ₃	0.01	28	0.0003	1.4
CH ₄	0.10	468	0.01	23
NO _x	0.83	3,886	0.58	2,720
CO ₂	560	2,045,989		

PM, CO, SO_x, VOC, NH₃ and NO_x emission factors are derived by comparing EPA [146] and IPCC [147] emission factor sources. Abatement technologies are applied for PM, SO_x and NO_x emissions; specific controlling technologies for PM (scrubber for coal charging, fabric filter for coke oven pushing; clean water, normal tower and/or proper maintenance for quenching; scrubber and cyclone usage for miscellaneous sources), lime injection dry scrubber for SO₂, and staged combustion for NO_x (30% reduction) were selected [29]. CO₂ and CH₄ emission factors were taken from IPCC-Tier 1 [133].

It should be noted that this subsector is not covered under “Fuel Combustion Emissions in Manufacturing Industries” title (IPCC Sector 1.A.2) in National Inventory Report of Turkey for 2009, 2010 while it is covered under “Fuel Combustion Emissions in Energy Production”. Therefore comparisons with other studies were evaluated with considering this detail, and explained as a deep note.

5.6.1.3. Electrical arc furnaces

Electrical arc furnaces (EAF) directly melt the materials which contain iron (mainly scrap) and don't need coke. Currently there are 21 electrical arc furnaces in Turkey [129]. In 2010, 71% of steel produced in Turkey is produced by EAFs.

[152] The input material for an EAF is typically nearly 100 percent ferrous scrap. An EAF is a cylindrical, refractory-lined container. Carbon electrodes can be raised and lowered through openings in the furnace roof. With electrodes retracted, the furnace

roof can be rotated aside to permit scrap metal to be placed (“charged”) into the EAF by overhead crane. Some furnaces are charged through a shaft or continuously charged from a conveyor without the removal of the furnace roof. Electric current generates heat between the electrodes and through the scrap to melt the scrap.

EAFs need considerable amounts of electrical energy and cause substantial emissions to air. The main EAF process air pollutants are respectively CO₂, CO, PM, NO_x, SO_x and NMVOC.

Table 5.85 : Process emission of EAFs.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
PM	25	522,623	0.15	3,136
CO	4	83,620	0.08	1,672
SO ₂	0.4	8,362	0.06	1,254
NO _x	0.19	3,882	0.13	2,718
NMVOC	0.92	19,233	0.05	962
CO ₂	80	1,672,393		

Controlled and uncontrolled PM emission factors were selected for melting, refining, charging, tapping, and slagging processes with building evacuation to bag house for alloy steel from EPA [152]. CO emission factor was taken from Reinders [44] by considering flare as the controlling technology with 98% reduction efficiency. SO₂, NO_x, NMVOC emission factors were derived from EMEP [132] and CO₂ emission factor was derived from IPCC [133].

5.6.1.4. Fuel combustion emissions

Iron and steel industry consumes 5 types of fuels; coal, brown coal, coke, petroleum and natural gas. Emission factors and emissions are given for each of the fuel type in Table 5.86.

Most of the coal is used for producing coke which is used for oxidation of iron ore. In this section coke production related coal consumption was not considered, (covered in metallurgical coke manufacturing, section 5.6.1.2 and considered as process emissions) only energy purpose coal consumption was considered here.

Fuel consumption data were taken from 2010 Energy Balance Table [46] which is prepared by the MENR.

Unfortunately iron and steel industry part of the MENR table includes only large scale iron and steel industry fuel consumption amounts where fuel consumption amounts of medium and small scale iron and steel industry are covered under ‘other’ category of MENR Table [26]. Therefore the emissions calculated in Table 5.86 do not represent entire of the iron and steel industry fuel combustion emissions.

5.6.2. Final emissions of iron and steel industry

Coke production is evaluated under Energy category in NIR 2010 Turkey [26]. Therefore calculations were given with/without coke production choices to ease evaluation. Only CO₂ emissions were calculated in NIR 2010 Turkey [26], other process emissions were not calculated. Overall PM, SO_x, NO_x, NMVOC and CO emissions were calculated by Elbir T. et.al. [52] by including fuel combustion and process emissions under a title. Also PM₁₀ emissions were calculated by Agacayak T.; 169,200 ton before abatement and 25,300 ton after abatement. Here ‘after abated’ emissions were considered, because abatement was considered in the calculations of this study especially for PM. PM emission of this study was given for uncontrolled conditions, however it was calculated as 20,723 ton for controlled conditions. The study of Elbir T. shows the emissions of 17 years ago, therefore the difference seems comprehensible.

Table 5.86 : Uncontrolled emissions comparison of iron and steel industry.

	Process Emissions (ton/yr)				Energy Emissions (ton/yr)	
	This study	Elbir T. Et.al.	Agacayak T.	NIR 2010	This study	NIR 2010
Ref.year:	2010	1995	2004	2010	2010	2010
PM	842,488	245,111	169,200		5,451	
SO _x	19,975	41,795			38,638	N.E.
NO _x	10,404	29,300			10,715	20,726
NMVOC	41,291	10,635			3,821	1,116
CO	348,153	565,405			39,463	7,744
CO ₂	19,915,996			17,279,591	6,482,891	6,860,890
CH ₄	468				475	621
NH ₃	28					
N ₂ O					72	75

Table 5.87 : Fuel combustion emissions of integrated iron and steel factories.

Pollutant	Emission Factor (kg/TJ)				Emissions (ton/yr)				Total
	Coal	Brown Coal	Petroleum	Natural Gas	Coal	Brown Coal	Petroleum	Natural Gas	
PM	124.0	124.0	27.5	0.50	4,839	209	391	13	5,451
SO ₂	900.0	900.0	140.0	0.50	35,122	1,515	1,988	13	38,638
CO	931.0	931.0	40.0	38.91	36,332	1,567	568	996	39,463
NO _x	173.0	173.0	100.0	88.01	6,751	291	1,420	2,253	10,715
CO ₂	98,300	101,000	73,300	56,100	3,836,091	169,992	1,040,930	1,435,877	6,482,891
N ₂ O	1.5	1.5	0.6	0.10	59	3	9	3	72
CH ₄	10.0	10.0	3.0	1.00	390	17	43	26	475
NMVOC	88.8	88.8	10.0	2.50	3,465	149	142	64	3,821

Emission factors sources for coal and brown coal: NO_x, CO, NMVOC, SO_x and PM emission factors were taken from EMEP [40]; CO₂, N₂O and CH₄ emission factors were taken from IPCC [123].

Emission factors sources for petroleum combustion: NMVOC and PM emission factors were taken from EMEP [40]; NO_x, CO, SO_x, CO₂ and N₂O emission factors were derived from EPA [50] and CH₄ emission factor was taken from IPCC [123] with the acceptance of fuel oil No: 6 usage in the plants as fuel.

Emission factors sources for natural gas: NO_x emission factor was taken from EPA [39]; CO, PM, SO₂, NMVOC emission factors were derived from EMEP [40]; CO₂, N₂O and CH₄ emission factors were taken from IPCC [123].

SO_x and NO_x emissions are given by EMEP [40] by assuming that NO_x, SO_x and CO emissions are originating mainly from combustion activities. Therefore the values seems lower.

In this study, CO₂ emissions are calculated as 19,915,996 however it is calculated as 17,279,591 in NIR 2010 [26], This would be because of the activity data and/or or emission factor difference CO₂ emissions originated from energy activities are compatible with each other. Table 5.87 shows energy emissions comparison with NIR 2010 [26],

5.6.3. Non-Ferrous Metal Industry

Generally, non-ferrous metals industry covers Copper, Aluminium, Zink, Cadmium, Lead, Precious Metals, Mercury, Refractory Metals, Ferroalloys, Nickel, Cobalt, Carbon and Graphite production. In this study, only Ferroalloys and Aluminium production industries' emissions were calculated since these industries are the main contributors of the non-ferrous metals industry of Turkey.

5.6.3.1. Ferroalloys

Ferroalloys are master alloys containing iron and one or more non-ferrous metals as alloying elements. The ferroalloys are usually classified in two groups: bulk ferroalloys (produced in large quantities in electric arc furnaces), and special ferroalloys (produced in smaller quantities, but with growing importance). Bulk ferroalloys are used in steel making and steel or iron foundries exclusively, while the use of special ferroalloys is far more varied [124].

In 2006, Turkey was the 10th big ferroalloy producer in the world [131]. Ferro-Manganese, Ferro-Silicioum, Ferro-Chromium, Ferro-Molibden and other ferroalloys are produced in Turkey. Ferro-Chromium has big share within these ferroalloy types [62]. In Turkey, there are two types of Ferro-Chromium produced; High Carbon Ferro-Chromium and Low Carbon Ferro-Chromium. Generally high carbon ferroalloy is the most common produced type.

In ferroalloy production, raw ore, carbon materials and slag forming materials are mixed and heated to high temperatures for reduction and smelting. The carbonaceous reductants are usually coal and coke, but bio-carbon (charcoal and wood) is also commonly used as a primary or secondary carbon source. The CO gas produced in

open or semi-closed furnaces is burnt to CO₂ above the charge level. Any CO emitted to the atmosphere is assumed to be converted to CO₂ within days afterwards [133]. Emission factors and calculated emissions are given in Table 5.88. Only Ferro-Chromium production related emissions are calculated within this study, because the contribution of the production of ferroalloys are insignificant, i.e. less than 1 % of the national emissions of any pollutant [9].

Table 5.88 : Ferroalloy production process emissions.

	Uncontrolled		Controlled	
	EF	Emission	EF	Emission
	kg/ton	ton/yr	kg/ton	ton/yr
PM	78	8,983	1.2	138
CO ₂	1300	173,665		

PM emission factor was taken from EPA [152], and controlled emission factor was selected with considering abatement technology as electrostatic precipitator. CO₂ emission factor was taken from IPCC [133].

5.6.3.2. Aluminium

Aluminium production starts with Aluminium ingots production in two ways; ones is primary (from ore) and second one is secondary (from scrap) production. Then Aluminium ingots are used by foundries (Aluminium casting) to produce 4 main type of Aluminium products; flat, conductive, extrusion, architectural products (with sub products).

5.6.3.2.1. Primary aluminium production

Primary aluminium refers to aluminium produced directly from mined ore by converting bauxite ore into aluminium. There is only one producer of primary aluminium in Turkey [131].

The process mainly consists of two stages. First one is alumina (Al₂O₃) production from Bauxite and the second one is Aluminium production from Alumina. Most of CO₂ emission comes from the second stage. The main air pollutants emitted from primary aluminium production are respectively CO₂, SO₂, PM, CO, NO_x, F⁻, PFCs. The emission factors and calculated emissions for primary aluminium production is given in Table 5.89.

Table 5.89 : Process emissions of primary aluminium production.

	Uncontrolled		Controlled	
	EF kg/ton	Emission ton/yr	EF kg/ton	Emission ton/yr
PM	146.5	16,187	7.1	740
CO ₂	1835	115,605	1835	115,605
NO _x	2	126	1	63
SO _x	140	8820	7	441
CO	2440	153,720	122	7686
Fluoride (gaseous and particulate)	1.42	89.46		
PFCs (C2F6+CF4)	0.66	41.58		

PM controlling technologies were accepted as spray tower at bauxite grinding, ESP at Aluminium hydroxide calcining and anode baking furnace, multiple cyclones and ESP at soderberg stud cell.

PM, CO₂, Fluoride and PFC emission factors were taken from EPA; NO_x, SO_x and CO emission factors were taken from EMEP.

5.6.3.2.2. Secondary aluminium production

Secondary aluminium producers recycle aluminium from aluminium-containing scrap, while primary aluminium producers convert bauxite ore into aluminium [13]. Energy for secondary refining consumes only about 5 % of that required for primary aluminium production [141].

In Turkey there are 17 secondary aluminium production plants in 2010 [62]. Emission factors and emissions are given in Table 5.90 and calculated only for processes. Energy emissions of this sector are included in Table 5.92.

Table 5.90 : Process emissions of primary aluminium production.

	Uncontrolled		Controlled	
	EF kg/ton	Emissions ton/yr	EF kg/ton	Emissions ton/yr
TSP	300	27,051	2	180
PM ₁₀	2	189	1.4	126
PM _{2.5}	1	74	0.6	50
CO ₂	20	1803		

There is no emission factor for CO₂ in literature, however scrap metal generally covered with paint which is a source of pyrolysis gases in melting operations. Processed material is accepted as consisted of 60% clean scrap, 20% chips and

turnings, 20% scrap from domestic appliances etc. [44]. The CO₂ emission factor is accepted as 20 kg CO₂/ton of Aluminium produced [44, 128].

Controlled emission factor for TSP is 2 kg / ton Al produced after abatement with considering a conventional plant with ESP, settlers, scrubbers; moderate control of fugitive sources. In this study it is assumed that all pyrolysis gases are sent to an afterburner and converted to CO₂.

Regarding to EMEP [40], SO₂, NO_x and other gases are assumed to be originated from fuel combustion; therefore they are not calculated here. 99.3% abatement efficiency is found for PM after applying controlled and uncontrolled emission factors.

5.6.3.2.3. Aluminium casting

Aluminium melting in foundries generally uses alloyed ingots as a starting material, although in some cases the metal is delivered already as a liquid. The secondary melting of aluminium scrap is usually not performed in foundries [135].

Many different types of melting furnaces are used in aluminium foundries the choice depending on individual requirements. Directly and indirectly heated, fuel and electricity using furnaces are used. The fossil fuels currently used are natural gas, liquid petroleum gas (LPG) and oil. Natural gas is favoured by most foundries on convenience grounds. Electrical heating may be provided by either resistance elements or by induction. The use of a pure starting material and mainly electric and gas-fired heating, results in relatively low emission levels from the melting. Due to the limited concern about off-gas quality, information on the flue-gas composition is limited [135].

The main emissions emitted from foundries are PM, NO_x, CO, VOC and SO₂. Calculated emission factors and used emission factors are given in Table 5.91.

Emission factors were taken from IPPC [135], which gives emission factors which were derived from European industry averages. Therefore emission factors are given for controlled conditions.

Table 5.91 : Process emissions of primary aluminium casting.

	Uncontrolled		Controlled	
	EF	Emissions	EF	Emissions
	kg/ton	ton/yr	kg/ton	ton/yr
PM	24	3072	0.12	15.36
NO _x	3	384	0.18	23.04
SO ₂	0.8	102.4	0.04	5.12
CO	3	384	0.15	19.2
VOC	2.4	307.2	0.12	15.36

There is no information for the control technology of SO₂, CO and VOC emissions; therefore 95% abatement efficiency is accepted for the calculation of controlled conditions' emissions. NO_x emissions are reduced because of the using new production technologies. Bag house was accepted as PM controlling technology with 95% abatement efficiency.

Fuel combustion emissions of aluminium casting industry are included in non-ferrous metal industry fuel combustion emissions, section 5.6.3.3.

5.6.3.3. Fuel combustion emissions of non-ferrous metals industry

Non-ferrous metal industry fuel combustion emissions can not be calculated separately for each of the sub-sector because of the fuel usage data deficit. Overall fuel combustion emissions are given in Table 5.92.

Additionally, calculated emissions are compared with NIR 2010 Turkey [26] in Table 5.93. Regarding to results of this comparison; liquid fuels are also not compatible with this study. However, this problem is same for other sectors because of the inclusion of petroleum coke within liquid fuels in NIR 2010. However final CO₂ emissions seem compatible with each other except other pollutants.

The fuel combustion amounts were taken from MENR 2010 Energy Balance Table [8].

NO_x, CO, NMVOC, SO_x and PM emission factors were taken from EMEP [40]; CO₂, N₂O and CH₄ emission factors were taken from IPCC [123] for brown coal combustion.

Table 5.92 : Non-Ferrous metal industry fuel combustion emissions.

Pollutant	Emission Factor (kg/TJ)				Emissions (ton/yr)				Total
	Petr.coke	Brown Coal	Petroleum	Natural Gas	Coal	Brown Coal	Petroleum	Natural Gas	
PM	27.5	124.0	20.0	0.50	28	315	2	10	354
SO ₂	140.0	900.0	653.4	0.50	140	2,283	81	10	2,514
CO	40.0	931.0	14.3	38.91	40	2,362	2	749	3,153
NO _x	100.0	173.0	193.7	88.01	100	439	24	1,693	2,256
CO ₂	97,500	101,000	73,300	56,100	97,500	256,257	9,078	1,079,330	1,442,165
N ₂ O	1.5	1.5	0.6	0.60	2	4	0.07	2	7
CH ₄	10.0	10.0	3.0	1.00	10	25	0.37	19	55
NMVOC	10.0	88.8	2.3	2.50	10	225	0.28	48	284

Table 5.93 : Non-Ferrous Metal Industry fuel combustion emissions comparison with NIR 2010 Turkey [26].

	LIQUID FUELS (ton/yr)		SOLID FUELS (ton/yr)		GASEOUS FUELS (ton/yr)		TOTAL (ton/yr)	
	This study	NIR 2010	This study	NIR 2010	This study	NIR 2010	This study	NIR 2010
CO ₂	106,578	37,822	256,257	184,333	1,079,330	1,191,656	1,442,165	1,413,811
CH ₄	10.37	3.37	25	19	19	18.586428	55	129
N ₂ O	1.57	0.51	4	2.6	2	2.6	7	5.2
NO _x	124		439		1,693		2,256	3,877
CO	42		2,362		749		3,153	968
NMVOC	10.28		225		48		284	151
SO ₂	221		2,283		10		2,514	NE

Emission factors sources for petroleum combustion are EMEP [40] for NMVOC and PM; EPA [50] for NO_x, CO, SO_x, CO₂ and N₂O; IPCC [123] for CH₄ with the acceptance of fuel oil No: 6 usages in the plants as fuel. Emission factors sources for natural gas: NO_x emission factor was taken from EPA [39]; CO, PM, SO₂, NMVOC emission factors were derived from EMEP [40]; CO₂, N₂O and CH₄ emission factors were taken from IPCC [123].

Liquid fuels include petroleum and petroleum coke. Actually petroleum coke is solid fuel derived from refineries but it is evaluated as liquid fuel in NIR 2010 Turkey, therefore petroleum coke is included in liquid fuels title to ease the comparison. Solid fuels include only brown coal and gaseous fuel include natural gas.

The main difference is in CO emissions. In this study, 2362 ton of 3,153 ton CO comes from lignite combustion, a control system like flare would be considered in NIR 2010 for lignite combustion.

5.7. Wood Products Industry

Wood products industry covers pulp and paper production, plywood manufacturing, reconstituted wood products (strand board and fibreboard) manufacturing, charcoal production, wood preserving and engineered wood products. In this study, only pulp and paper production is accepted as key category in wood products industry.

5.7.1. Pulp and Paper

Paper is essentially a sheet of cellulose fibres with a number of added constituents to affect the quality of the sheet and its fitness for intended end use. The pulp for papermaking may be produced from virgin fibre by chemical or mechanical means or by the re-pulping of recovered paper (RCF) [134]. Until 225 g/m² the material is called paper, above that amount it is called cardboard [44].

In the pulping process, the raw cellulose-bearing material is broken down into its individual fibres. Wood is the main raw material but straw, hemp, grass, cotton and other cellulose-bearing materials can be used as well. The precise composition of the wood will vary according to the type and species but the most important constituents are cellulose, hemicelluloses and lignin [134].

Pulp and paper production consists of three major processing steps: pulping, bleaching and paper production. The type of pulping and the amount of bleaching used depends on the nature of the feedstock and the desired qualities of the end product [136].

Only chemical pulping processes are described here. There are 3 chemical pulping techniques; kraft pulping, acid sulphite pulping and neutral sulphite pulping.

Kraft (sulphate) pulping is the most widely used pulping process and is typically used to produce strong paper products. The Kraft pulping process includes wood (or other cellulose bearing materials) digestion in a water solution of sodium sulphite and sodium hydroxide, pulp washing, bleaching, chemical recovery and by-product recovery.

Sulphite pulping (acid sulphite process) involves chemically pulping the wood using sulphur dioxide (SO_2) adsorbed in a base solution. Sulphite pulping produces a weaker paper than some other types of pulping, but the pulp is less coloured making it more suitable for printing, often with little bleaching.

Neutral sulphite semi-chemical pulping (NSSC) is one of the chemical pulping processes that can be used. It involves partial delignification of wood feedstock using a buffered sodium sulphite solution, with completion of the pulping process by mechanical means. NSSC pulps are used in corrugating media and in certain writing and printing papers.

In this study only craft pulping method is described detailed because 80% of worldwide pulping technology is Kraft pulping [136] and it is assumed same for Turkey in the calculations.

The main process steps involved in Kraft pulping are briefly described below and derived from EMEP [134].

Debarking, wood chipping and screening: Wet or dry debarking techniques may be used when wood is debarked.

Digestion: Wood chips are cooked in a digester with white liquor, a mixture of sodium hydroxide (NaOH) and sodium sulphide (Na_2S). There are two types of digester systems: batch and continuous. Once cooking is complete in either a batch or continuous process, the chemical mixture (black liquor) and pulp are discharged

into a blow tank - a low pressure vessel. Vapours from the blow tank may be vented to an accumulator or a vapour sphere for collection. The vapours may be incinerated, stripped, or recovered for resale as turpentine or tall oil.

Washing: The pulp from the blow tank is washed to remove the black liquor from the pulp. There are several types of washers, including counter-current vacuum, diffusion, rotary pressure, horizontal belt filters, chemiwashers, wash press, and dilution/extraction. The black liquor extracted from this process is diluted with wash water, and so is called weak black liquor.

Delignification: In many mills, delignification is done in the digester. However, additional reductions in lignin may be achieved through oxygen delignification and/or ozone bleaching.

Bleaching: The pulp is produced as slurry after removal of spent cooking chemicals and dissolved wood organics. Bleaching is then used to remove further lignin to make the pulp whiter. Bleaching is usually done in different steps using a combination of chlorine dioxide and oxygen-based chemicals. The vast majority of the pulp is bleached.

Turpentine production: The vapours discharged from the digester contain up to about 6 kg turpentine per tonne of pulp, depending upon wood species and cooking conditions. These vapours are normally condensed as part of the odour control system. Turpentine has a different specific gravity than water, and so can be decanted or recovered by other processes based on the density differences. The recovered turpentine is usually purchased by refining companies, or is used as fuel in the mill, most commonly in the lime kiln.

Tall oil recovery: Tall oil precursors can be recovered from black liquor cooling and evaporation. The black liquor can have soap and other tall oil precursors skimmed from the surface of weak, intermediate or strong black liquor storage tanks and from the black liquor oxidation process. The soap can then be sold or processed into tall oil by acidification [137].

5.7.1.1. Process emissions

VOC emissions mainly occur from wood handling. PM emissions occur from pulp drying, bark boiler, lime reburning, recausticizing and recovery boiler. SO₂ is emitted

mainly from oxidation of reduced sulphur compounds in the recovery furnace. The major cause of carbon monoxide emissions from the recovery furnace is furnace operation well above rated capacity, which results in failing to maintain oxidising conditions. NO_x emissions are mainly emitted from recovery and bark boilers.

Emission factors and emissions are given for both of sulphite and kraft pulping method in Table 5.94 and 5.95.

Table 5.94 : Emissions of pulp and paper production with kraft method.

	Uncontrolled		Controlled	
	EF kg/ton	Emission ton/yr	EF kg/ton	Emission ton/yr
NO _x	1.4	2,580	1	1,806
CO	110	198,690	5.5	9,935
NM VOC	40	72,251	2	3,613
SO _x	10	18,063	2	3,613
TSP	200	361,255	1	1,806
PM ₁₀	160	289,004	0.8	1,445
PM _{2.5}	120	216,753	0.6	1,084

Table 5.95 : Emissions of pulp and paper production with sulphite method.

	Uncontrolled		Controlled	
	EF kg/ton	Emission ton/yr	EF kg/ton	Emission ton/yr
NO _x	2.9	1,965	2	1,375
NM VOC	4	2,750	0.2	138
SO _x	20	13,752	4	2,750
TSP	200	137,524	1	688
PM ₁₀	150	103,143	0.75	516
PM _{2.5}	134	92,141	0.67	461

Emission factors are derived from mainly EMEP [136] by comparing with IPCC [134] and Reinders [44]. However these emission factors are given with the assumption that all paper and pulp factories includes kraft pulping method. EMEP [136] assumes this for Tier 1 method and the emission factors are same with Tier 2 kraft pulping method. IPCC [9] did not give emission factors for pulp and paper industry's CO₂ and CH₄ emissions only includes a methodological guidance on CO₂ emissions from use of carbonates from this industry but it is not included in this study.

Abatement efficiency is accepted 95% for CO and NMVOC, 30% for NO_x. SO_x emission factor is given for both of controlled and uncontrolled conditions. Controlling technologies are scrubber and ESP. Additionally 30% abatement efficiency is accepted for NO_x emissions as staged combustion technology.

In this sector, there is only one company in pulp production in Turkey since 2008. Therefore the activity data is confidential due to Law No: 5429. For that reason, the SO₂, NO_x, CO and NMVOC emissions can not be given after 2008 in NIR Turkey in 2010 [26] and there are no specific results in NIR 2010 for this industry to compare this study's calculations.

Pulp and paper industry emissions calculated for the former years in some studies. Agacayak T., calculated SO₂ emissions as 15,200 ton/yr by taking emission factor as 8 kg/ton from IIASA Rains online model. But in this study overall SO₂ emissions are calculated as 6363 ton/yr by taking total emission factor as 2.75 kg/ton for the controlled conditions and 31,815 ton for uncontrolled conditions.

Additionally pulp and paper industry PM, SO_x and NMVOC emissions are calculated by Elbir T. et.al. [52]. PM emission is calculated as 64 ton, SO_x is 905 ton and NMVOC is 77 ton. In this study PM and NO_x emissions are calculated as 2538 ton. The other details are given in Table 5.96.

Table 5.96 : Emissions of pulp and paper production and comparison with other studies.

Emission (ton/year)					
Ref. year:	THIS STUDY			Elbir T.	Agacayak T.
	Process	Process	Energy	Process	
	(Uncontrolled)	(Controlled)	emissions		
	2010	2010	2010	1995	2004
NO _x	4,545	3,182	1,396		
CO	198,690	9,935			
NMVOC	75,001	3,750		77	
SO _x	31,815	6,363	1,903	905	15,200
CO ₂			2,150,085		
TSP	498,779	2,494		64	

The results of the calculations seem incompatible with each other even without calculations are made for different reference years. The main reason can be the quality of activity data and selected emission factor.

5.7.1.2. Energy emissions

In integrated pulp and paper mills the excess heat produced by the pulp mill is not quite enough to cover the energy consumption of the paper production. The additional demand for heat has to be produced in auxiliary steam boilers. Fossil fuel is used as support fuel in bark and sludge boilers and as the main fuel in auxiliary boilers as well. The fuels used in the boilers are coal, fuel oil, natural gas, peat, wood waste and fibrous sludge from effluent treatment. The emissions from power production are dependent on the fuel, the fuel mixture and the impurities content. For instance oil and coal contain sulphur but natural gas does not. NO_x emissions are relatively low due to the low combustion temperature (800°C -950°C) [134]. SO_x emissions come from boilers and depend on the fuel type.

Table 5.97 : Energy emissions of pulp and paper production.

	EF kg/ton	Emission ton/yr
NO _x	0.55	1,396
SO _x	0.75	1,903
CO ₂	0.0015	2,150,085
Total	1.3	3,299

Boilers can not be separated because emission factors are given totally in IPPC and EMEP, therefore only auxiliary boilers are separated and included in energy emissions section.

In this section fuel type is not considered because of the data deficit, emission factors are derived from the facility average emissions given by IPPC [134]. CO₂ emission factor is calculated by Alp K. [29].

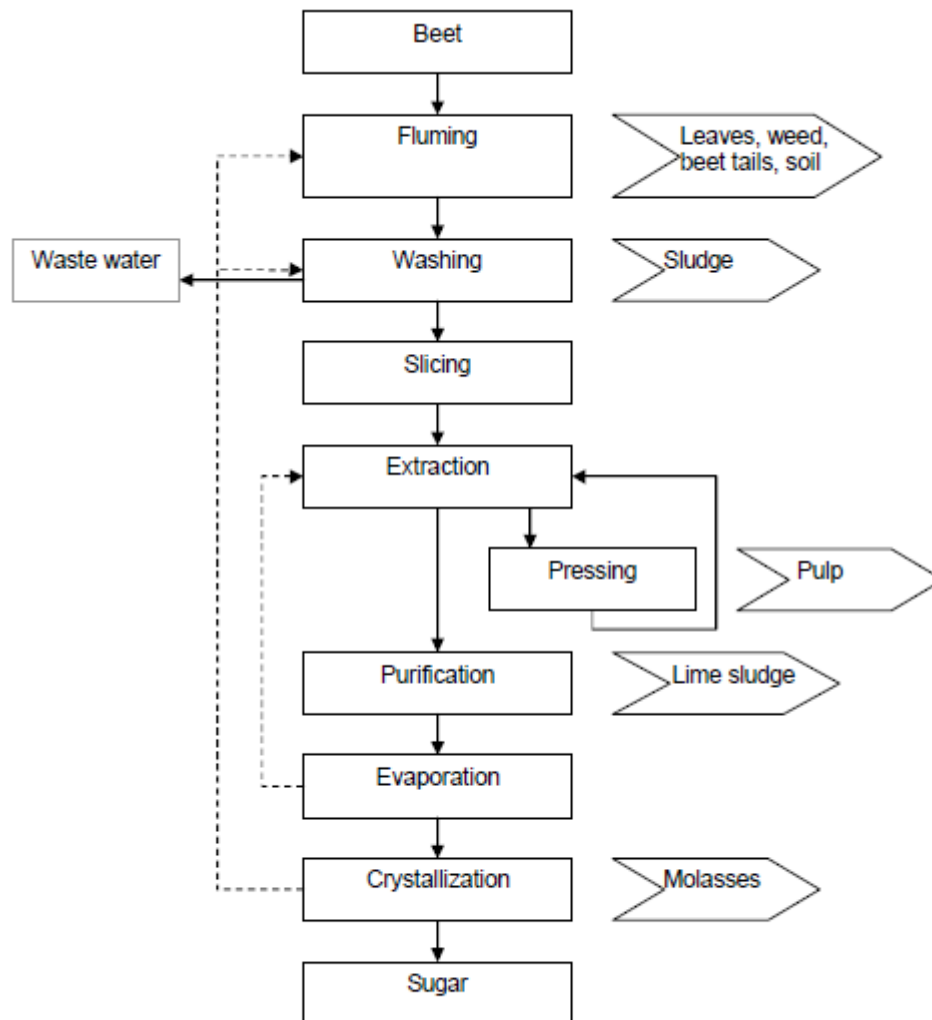
5.8. Food and Beverages Industry

Only sugar production sector is investigated under this category.

5.8.1. Sugar Production

There are two main raw materials for the production of the sugar; sugar beet and sugar cane. The ecology of Turkey is not available for sugar cane therefore all of the sugar is produced from sugar beet [138]. Only sugar beet originated sugar production is described in this study.

Sugar beet processing is the production of sugar (sucrose) from sugar beets. By-products of sugar beet processing include pulp and molasses. Most of the molasses produced is processed further to remove the remaining sucrose. The pulp and most of the remaining molasses are mixed together, dried, and sold as livestock feed [139].



Source : Adapted from the [Comité Européen des Fabricants de Sucre \(CEFS\)](#), 2003.

Figure 5.29 : Sugar production process from beet [155].

The beets are cut into thin slices called cossettes. They are passed into a water-based counter current extraction apparatus called a diffuser and emerge as impure sugar juice and beet pulp. The fresh water used in the extraction process is actually condensed water from the subsequent evaporation steps together with recirculated water from the pulp pressing. The temperature inside the diffuser is 68 to 72 °C [140].

Fresh cossettes fall from a conveyor belt into the lower end. The cossettes are transported upwards by the two screws to a paddle wheel, which lifts the exhausted cossettes out of the extractor. Fresh water is introduced at the upper end and the sugar juice leaves the extractor through a screen at the lower end.

The crystallisation process takes place in vacuum pans in which the juice is boiled under vacuum to minimise the temperatures involved. The growth of the sucrose crystal only involves sucrose and water. The non-sugars contained in the sugar juice are not incorporated into the crystal structure; instead most of them remain in the liquid phase while some are released to the vapour phase. The sugar crystals are removed from the liquid phase by centrifugation.

Sugar to be stored in silos must be deducted and cooled to the storage temperature. This is carried out in a sugar cooler, which is a device in which warm and dried sugar is intensively aerated by cold filtered external air to cool the sugar to the storage temperature, approximately 20 to 30 °C. The most common systems in use are typically drum or fluidised bed coolers with chilling systems that have a counter current or cross-current phase flow.

Raw sugar is typically a minimum of 96 % sucrose. The impure crystals, with adhering molasses, are blended in a saturated sugar solution to soften the surface molasses film which can then be removed by centrifugation. The partly processed sugar is dissolved in reclaimed liquors, i.e. light waters from the refining process. Carbonation, which is treatment with milk of lime and carbon dioxide, then follows. This produces a precipitate which contains impurities such as pectin and proteins and removes suspended impurities such as waxes, gums and starches. The sugar syrup is filtered and decolourised using ion exchange resins and activated carbon to produce a fine liquor, which may be sold as a finished product or passed on for crystallisation. The fine liquor is concentrated by evaporation to produce a syrup of around 60 – 70 % solids, known as thick juice. The juice is filtered and transferred to vacuum pans. When the liquor is slightly supersaturated, the pan is seeded with fine icing sugar to initiate crystallisation. The mixture is centrifugally separated to extract crystalline sugar, which is dried, conditioned for packaging or bulk loaded. Each pan boiling yields around 50 % of the available sugar.

The liquor separated during centrifugation, also called jet, is re-boiled for further extraction. Three boiling yield white sugar. A fourth boiling yields off white industrial sugar. Jet four, together with liquor from blending, goes to a recovery house for three further boiling to produce brown sugars which go back to the start of the refining process and are treated as raw sugar. Various intermediary products from jets one to four and the corresponding syrups from recovery and boiling are sold as the starting materials for syrups such as molasses and treacle.

Molasses are sometimes used in animal feed, alcoholic fermentation and a number of non-food products.

The process description is adapted from IPPC [140].

5.8.1.1. Process emissions

Process emissions are mainly PM from processes, storage and handling etc and NMVOC emissions from the chemicals and fugitive sources.

Table 5.98 : Sugar industry process emissions.

	Uncontrolled		Controlled	
	EF	Emission	EF kg/ton	Emission ton/yr
NMVOC	10	24,386	0.5	1,219
PM	0.097	340	0.00485	17

It is accepted that, PM emission and NMVOC emission reduction efficiency is 95%.

Process emissions of sugar production industry are not calculated in NIR 2010 Turkey [26], except NMVOC. NMVOC emissions are calculated in ‘other’ category and emission factor is selected as 10 kg/ton.

5.8.1.2. Energy emissions

Significant thermal energy is consumed for the evaporation and beet pulp drying. Electrical energy is needed for the pumps and for driving the centrifuges.

The overall emissions and comparisons with NIR are given in Table 5.99. Only energy emissions of sugar production are compared, because process emissions, except NMVOC, are not calculated by NIR 2010 Turkey [26]. The fuel combustion amounts were taken from MENR 2010 Energy Balance Table [8].

Energy related emission factor are taken from EPA [139], the emission factor unit is lb/ton of pressed wet pulp to the dryer, therefore emissions are calculated by considering process flow. Also this emission seems lower than NIR 2010. It can be because of the less developed technologically processes are not considered in this source.

Table 5.99 : Sugar industry energy emissions comparison with NIR.

	LIQUID FUELS (ton/yr)		SOLID FUELS (ton/yr)		GASEOUS FUELS		TOTAL	
	This study	NIR 2010	This study	NIR 2010	This study	NIR 2010	This study	NIR 2010
CO ₂	27,234	27,545	377,904	234,090	108,514	119,279	513,652	380,914
CH ₄	1	0.7	38	24.7	2	10.6	41	36
N ₂ O	0.2	0.2	6	0.21	0.19	0.2	6	1
NO _x	37		529		170		736	
CO	15		2,847		75		2,937	
NMVOC	4		272		5		280	
SO ₂	52		1,096		0.97		1,149	
PM	10		379		0.97		390	

5.9. Other Combustion Emissions

This category is added to include fuel combustion emissions that can not be categorized under one of the sectors included in this study. Because energy balance table does not separate some of the industries, therefore they have a total fuel consumption amount. These sectors are; glass manufacturing, pulp and paper, food and beverages and Tobacco. The small scaled sector names are not mentioned here but covered under this category as fuel combustion emissions.

The fuel combustion amounts were taken from MENR 2010 Energy Balance Table [8].

Emission factors sources for coal and brown coal: NO_x, CO, NMVOC, SO_x and PM emission factors were taken from EMEP [40]; CO₂, N₂O and CH₄ emission factors were taken from IPCC [123].

Table 5.100 : Other sectors' fuel combustion emissions

Pollutant	Emission Factor (kg/TJ)							Emissions (ton/yr)							Total
	Hard Coal	Brown Coal	Petr. Coke	Coke	Asphaltite	Petroleum	Natural Gas	Coal	Brown Coal	Petr.Coke	Coke	Asphaltite	Petroleum	Natural Gas	
PM	124.0	124.0	124.0	124.0	124.0	27.5	0.50	1,188	8,141	2,411	59.8	218.8	1,065	108	13,190
SO ₂	23.4	900.0	23.4	900.0	900.0	140.0	0.50	8,775	59,088	454.9	434.1	1587.9	5,421	108	75,868
CO	931.0	931.0	931.0	931.0	931.0	40.0	38.91	8,916	61,123	18,100	449.0	1642.6	1,549	8,368	100,148
NO _x	173.0	173.0	173.0	173.0	173.0	100.0	88.01	1,657	11,358	3,363	83.4	305.2	3,872	18,927	39,566
CO ₂	98,300	101,000	97,500	94,600	94,600	73,300	56,100	941,449	6,630,974	1,895,578	45,627	166,904	2,838,350	12,064,467	24,583,350
N ₂ O	1.5	1.5	0.6	2	1.5	0.6	0.10	14	98	12	0.7	2.6	23	22	173
CH ₄	10.0	10.0	3.0	10	10	3.0	1.00	96	657	58	4.8	17.6	116	215	1,164
NMVOC	88.8	88.8	88.8	88.8	88.8	10.0	2.50	850	5,830	1,726	42.8	156.7	387	538	9,531

Emission factors sources for petroleum combustion: NMVOC and PM emission factors were taken from EMEP [40]; NO_x, CO, SO_x, CO₂ and N₂O emission factors were derived from EPA [50] and CH₄ emission factor was taken from IPCC [123] with the acceptance of fuel oil No: 6 usage in the plants as fuel.

Emission factors sources for natural gas: NO_x emission factor was taken from EPA [39]; CO, PM, SO₂, NMVOC emission factors were derived from EMEP [40]; CO₂, N₂O and CH₄ emission factors were taken from IPCC [123].

This category cannot be compared with a study, because the category was not included in other studies.

6. EVALUATION OF THE RESULTS

In this thesis, it is aimed to calculate controlled and uncontrolled industrial emissions emitted from industrial processes and fuel combustion activities for energy purposes in 2010 for Turkey. Emissions were calculated in Section 5 for controlled and uncontrolled conditions. Specific comparisons with other studies were submitted for each of the pollutant at the end of the related chapter.

Uncontrolled process emissions were calculated to show the effectiveness of the controlling technology. Process emissions do not include emissions of public electricity and heat production.

In this section the emissions which were calculated in Section 5 are summarized totally to see the place of each industry and compared with other studies to see the place of this study within other studies.

Emissions were listed under two topics; process emissions and fuel combustions emissions (public electricity and heat production and industrial energy use emissions were evaluated as sub-topics).

6.1. Process Emissions

Process emissions were calculated for twelve pollutants PM, PM₁₀, PM_{2.5}, SO_x, NO_x, CO₂, CO, CH₄, VOC, NMVOC, N₂O, and NH₃, if it exists.

Despite of being given only VOC emission factors for some of the sectors, the NMVOC + CH₄ emission factors were given for other industries, therefore NMVOC / CH₄ / VOC emissions were evaluated separately. VOC emissions include NMVOC and CH₄ emissions; therefore if VOC emission exists it was accepted to be inclusive for other two. Furthermore PM emissions include both PM₁₀ and PM 2.5 emissions. Therefore NMVOC, CH₄, PM₁₀, PM_{2.5} emissions were not given in Figure 6.1.

Controlled process emissions distribution was not given because CO₂ emissions account 99% of the controlled emissions.

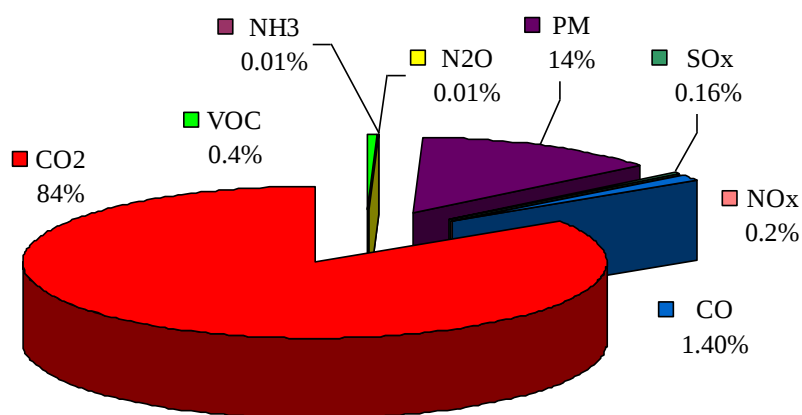


Figure 6.1: Uncontrolled process emission distribution.

CO₂ emissions accounts 84% with 55,124,262 ton, PM is 14% with 8,998,982 ton and 7,186,267 ton of PM emissions comes from cement industry, CO is 1.4% with 920,889 ton which is emitted mainly from iron and steel industry, VOC emissions accounts 0.4% with 289,166 ton mainly emitted from petroleum refining and pulp and paper industry, SO_x is 0.16% with 106,271 ton which is mainly comes from respectively petroleum refining, pulp and paper and iron and steel industry, NO_x is 0.2% with 123,906 ton mainly comes from cement industry (fuel combustion emissions were included in process emissions), inorganic chemicals and iron and steel industry, NH₃ is 0.01% with 8,920 ton and mainly comes from fertilizer production and finally N₂O emission accounts 0.01% with 6,921 ton which of all comes from nitric acid production.

Process emissions regarding to the sectors are given in Figure 6.2 for uncontrolled conditions and in Figure 6.3 for controlled conditions. PM emissions account 12% of uncontrolled emissions. However, mineral industry accounts 80% of all industries' PM emissions under uncontrolled conditions where reduces its share up to 33% between all industries under controlled conditions because of the usage of effective PM control technologies in the cement factories such as ESPs and fabric filters which have nearly 99% abatement efficiencies. Iron and steel industry accounts 9% of PM emissions under uncontrolled conditions and 49% under controlled conditions despite of reducing PM emissions from 842,488 ton to 20,020 ton, the sector share is affected from high reduction amounts in mineral industry.

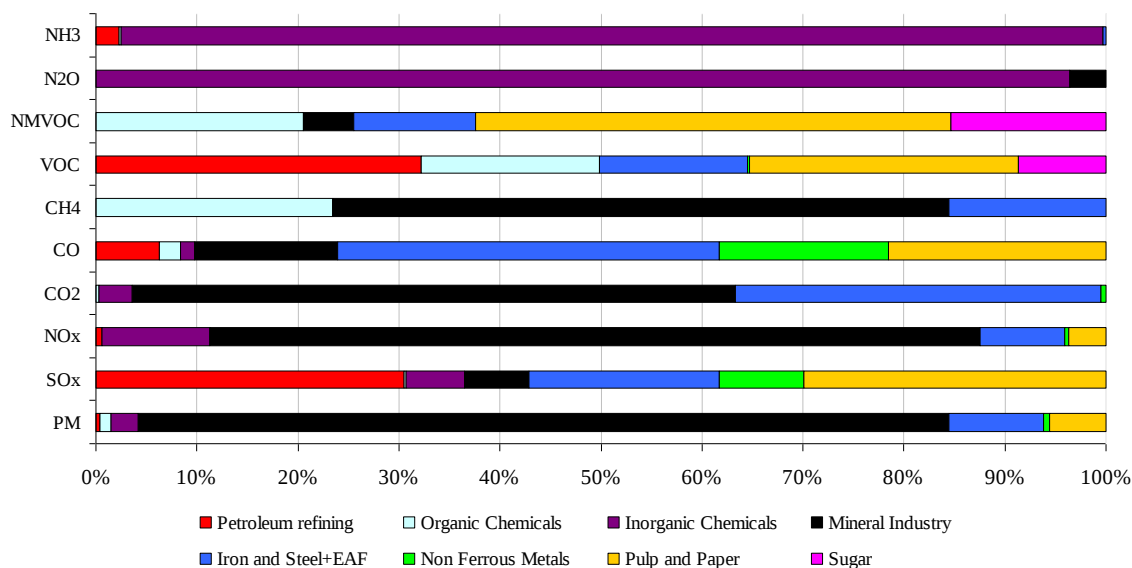


Figure 6.2: Uncontrolled process emission distribution regarding to the sectors.

SO_x process emissions are mainly emitted by petroleum refining industry catalytic cracking systems, iron and steel industry furnaces, pulp and paper production by sulphite method. These three industries cover 79% of SO_x emissions emitted by all industry processes under uncontrolled conditions. SO_x abatement methods such as flue gas desulphurisation, scrubbing, feedstock hydrodesulphurization are used to calculate controlled SO_x emissions; finally 75-80% SO_x reduction is achieved. Thus the SO_x amount is reduced to 24,721 ton from 106,271 ton.

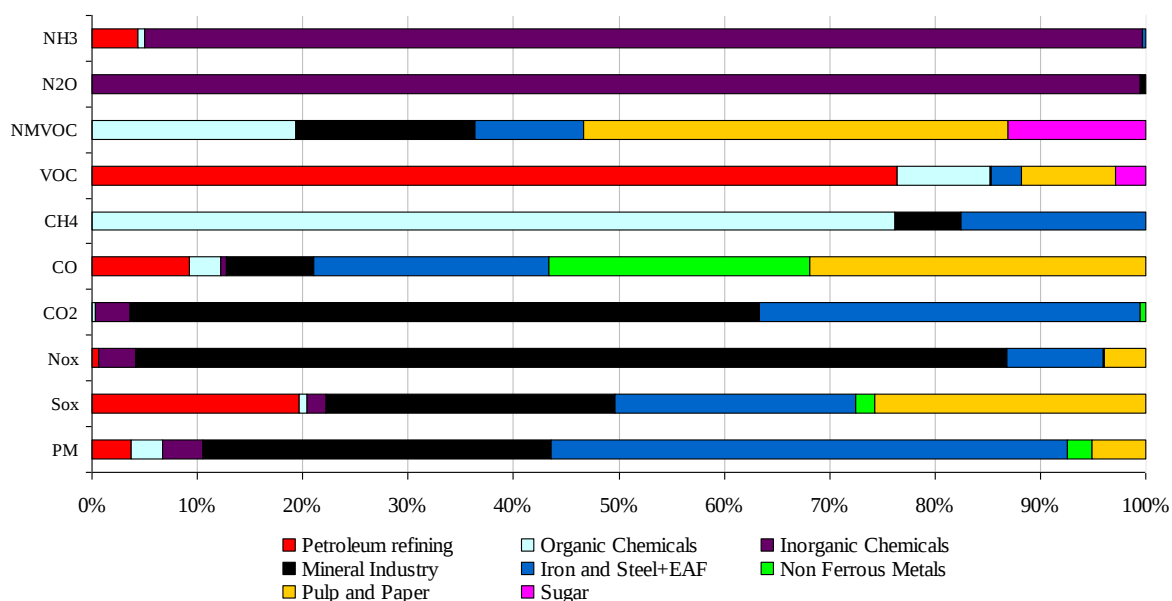


Figure 6.3 : Controlled process emission distribution regarding to the sectors.

Process related NO_x emissions account 0.2% of all emissions and is mainly emitted by mineral industry (76%), inorganic chemicals (11%), iron and steel industry (8%) and pulp and paper industry (4%) under uncontrolled conditions. Total NO_x emission for uncontrolled condition is 123,906 ton and 79,944 ton for controlled conditions. 10,762 ton of the uncontrolled NO_x process emissions come only from nitric acid production in the inorganic chemicals industry. Nitric acid production related NO_x emission is also calculated for LRTAP convention [159] as 7,080 ton for 2002, and Petroleum and glass industry process related NO_x emissions are calculated in NIR 2010 Turkey [26].

NO_x control technologies were considered for each of the industries, if it is available. Generally staged combustion (20-30% abatement efficiency), catalytic reduction (approximately 50% abatement efficiency), low excess air combustion (15-20 % abatement efficiency) [158] techniques were accepted to be used by industries for the control of the NO_x emissions; finally emissions were reduced by 35%. In controlled conditions, iron and steel industry NO_x emission share increased to 9% from 8%, because average NO_x abatement efficiency is selected as 30% which is below the average and increased the share of the industry under controlled conditions. Only nitric acid manufacturing industry is accepted as using new technologies for NO_x reduction, therefore AE% is high.

CO₂ emissions for industrial process emissions were calculated as 55,124,262 ton in this study and 49,019,701 ton in NIR 2010 Turkey [26]. Only cement, lime and iron and steel (only integrated plants) industry process related CO₂ emissions were calculated in NIR. Emissions are given in Table 6.1. Generally results seem compatible with NIR.

Table 6.1 : Comparison of the calculated CO₂ emissions with NIR 2010 Turkey.

	CO ₂ emissions (ton)	
	This study	NIR 2010
Cement	29,807,076	28,923,120
Lime	2,743,421	2,816,991
Iron and Steel	18,243,604	17,279.59

60% of the process originated CO₂ emissions are emitted from mineral industry (cement, lime, glass, carbide). The other sources are 36% of from iron and steel industry, 3% from inorganic chemicals industry, 1% from non-ferrous metals and

0.3% from organic chemicals industry. No controlling technology is assumed for CO₂ emissions, therefore there is no difference between controlled and uncontrolled CO₂ emissions. CO₂ emissions account 99.5% of all controlled emissions emitted from industrial processes because controlling technologies are applied to other pollutants except CO₂.

Uncontrolled CO emissions are mainly emitted from iron and steel industry (38%), pulp and paper industry (22%), non-ferrous metals (17%), mineral industry (14%), catalytic cracking units of petroleum refining processes (6%), and others. CO emissions are generally sent to flare. Thermal cracking or oxidative oxidation techniques are used to control CO emissions. In this study thermal cracking method is used with the assumption of approximately 95% abatement efficiency. Finally industrial processes originated, controlled CO emission is found 31,166 ton which is reduced from 920,889 ton.

Totally 3000 ton CH₄ emissions were emitted under uncontrolled conditions with the help of aromatics, ethylene oxide and acrylonitrile production plants in organic chemicals industry (46%), coke production in integrated iron and steel plants (40%), and carbide production in mineral industry (14%). Under controlled condition CH₄ emission is calculated 133 ton per year.

VOC and NMVOC emissions are explained together because the emission factor is given either for VOC or NMVOC and depends on the source. Petroleum refining, pulp and paper industry is one of the emitting sources of (NM)VOC. Especially it is emitted from fugitive sources such as storage tanks, valves etc. approximately 95% abatement technology is applied in the calculation of controlled (NM)VOC emissions.

The almost entire amount of N₂O emissions (6,921 ton for uncontrolled conditions) is emitted from nitric acid production in inorganic chemicals industry. Controlled conditions' emission is calculated by considering catalytic reduction technology for some of the industries, but not at all, because one of the plants is outdated and the other one started to use the abatement technology after 2010. Therefore controlled N₂O emission is calculated as 2,264 ton.

NH₃ emissions are mainly emitted from soda ash, fertilizer and ammonia production in the inorganic chemicals industry. 85-95% abatement efficiency is accepted for

scrubbers when calculating controlled NH_3 emissions and the emission is reduced to 457 ton from 8,920 ton.

Some of the pollutants are calculated in other studies such as NIR 2010 Turkey [26] and European Environment Agency LRTAP Convention [159]. Comparison of the results is given in Figure 6.4. Only current emission inventories were considered in the chart for comparison. LRTAP emissions were calculated for 2009, NIR was calculated for 2010.

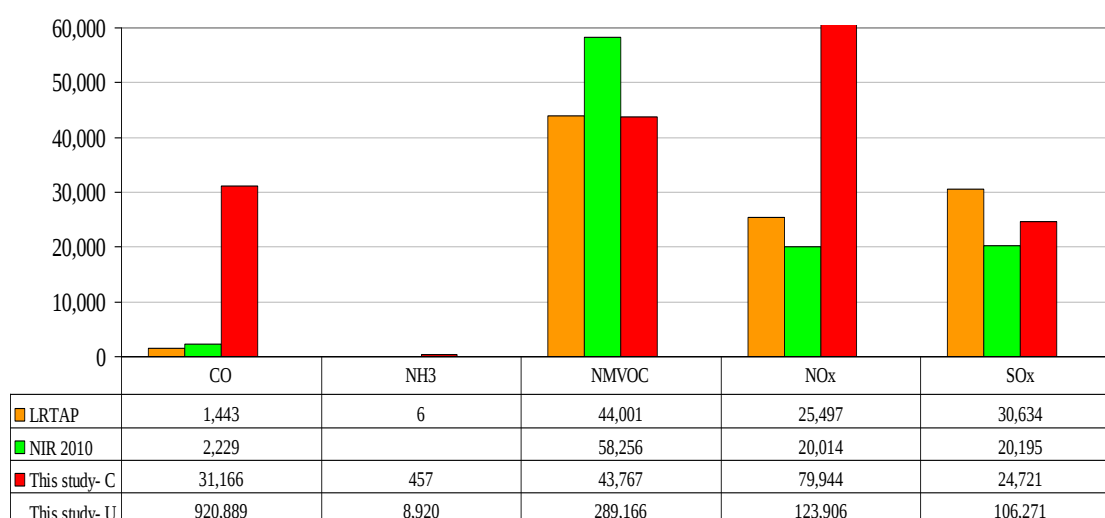


Figure 6.4 : Process emissions comparison with other studies.

CO emissions are very high when compared to other studies, despite of controlled emissions are evaluated in this chart. Because CO emissions were calculated only for mineral and petroleum refining industries in NIR 2010, but 45% of CO emissions comes from metallurgical industry even though under controlled conditions.

NH_3 emissions were not calculated for the industrial processes in NIR, but it was calculated in LRTAP as very low as 6 ton for only nitric acid production. This value seems not realistic for the Turkish industry which has large fertilizer production plants.

NMVOC emissions were not calculated totally in this study; therefore VOC emissions were given in Figure 6.4 under NMVOC emissions title. It should be noted that, CH_4 emissions account 1% of all VOC emissions, in this context, it can be accepted that most of the VOC emissions are NMVOCs.

In this study VOC emissions are calculated as 43,767 ton for controlled conditions and 289,166 ton for uncontrolled conditions. Also in NIR, it is calculated as 58,236 ton. 44,001 ton is calculated by LRTAP for Turkey for 2009 and the total NMVOC emissions of 27 European countries' industrial process emissions (1,348,696 ton). Uncontrolled process emissions should be considered for comparisons.

NO_x emissions were calculated by all of the studies. The result of this study (79,944 ton) which represents controlled conditions seems higher when compared with NIR (20,014 ton by including only petroleum refining and glass industry) and LRTAP (25,497 ton by excluding cement, non ferrous metals, pulp and paper industries). But these emissions include cement industry fuel combustion emissions. The same thing with NO_x emissions is valid when comparing SO_x emissions; 24,721 ton is the controlled process emission of this study.

6.2. Fuel combustion emissions

Fuel combustion emissions were evaluated within 2 titles, one is public electricity and heat production and the second one is energy use in the industry.

Total emissions distribution of these two energy industries is summarized as percentages in Figure 6.5. PM₁₀ and PM_{2.5} emissions are not calculated for cement industry whose PM emissions are 3.67% of all fuel combustion industry.

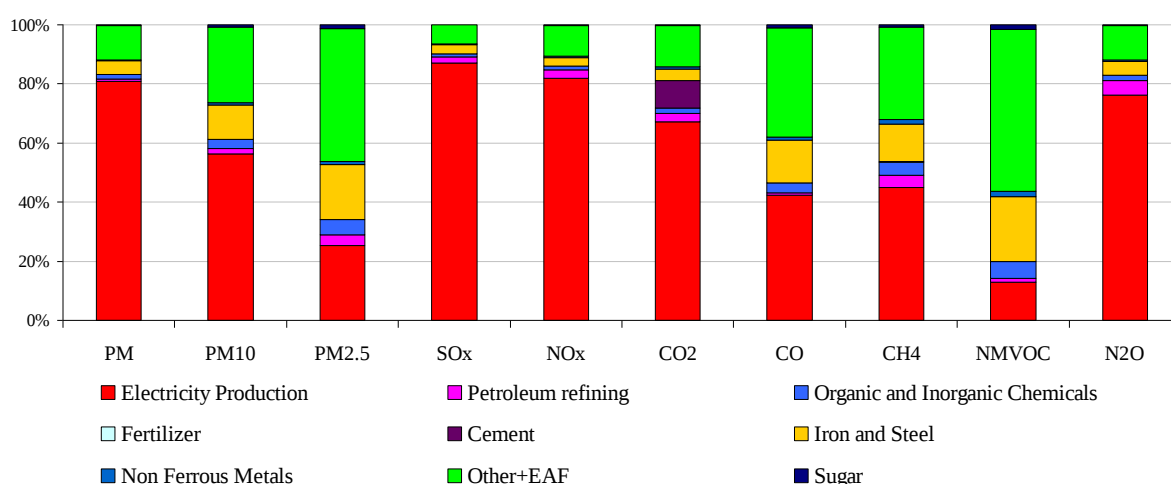


Figure 6.5 : Fuel combustion emissions distribution regarding to the sectors.

Electricity production industry consumes different type of fuels in the large power plants. For example 80% of the lignite in Turkey market is consumed by electricity production industry, 11% is by industries and 9% is by residential reasons. The

quality of the lignite is very changeable; therefore emission distribution is different between the sectors and pollutants. This situation is valid for other fuels.

Cement industry contributes to mainly NMVOC, CO, CH₄ and NO_x emissions. Cement industry PM₁₀ and PM_{2.5} emissions are not considered in Figure 6.5.

Other sector includes energy consumption of electrical arc furnaces' fuel combustion emissions in the MENR table. The sector contributes to mainly PM, NMVOC emissions.

6.2.1. Public electricity and heat production

Public electricity and heat is mainly produced by thermal power plants (65%) in Turkey. The fuel percentages used in thermal power plants were 27.5% lignite, 58.2% natural gas, 10.6% hard coal and 3.7% was others such as biomass, asphaltite, diesel oil, naphtha and fuel oil in 2010.

Emissions of public electricity and heat production industry are summarized in Figure 6.6 and compared with other studies and two European countries.

The countries were decided with comparing their population with Turkey (74,724,269). Selected countries are Germany (81.702.329) and France (64,876,618), because their population is close to Turkey. However, they use more clean technologies such as nuclear and wind for public electricity production, therefore emissions can be low when compared to Turkey.

CO emissions are mainly emitted from solid fuels such as lignite, hard coal and asphaltite. In Turkey, 27.5% of the electricity is supplied from only lignite combustion; therefore CO emissions should be high. In this study, CO emissions are calculated as 115,428 ton which is compatible with NIR 2010 (115,826 ton), but incompatible with LRTAP (29,062 ton). According to LRTAP [159], CO emission of this industry at EU is 506,075 ton, then Turkey accounts as 23% of CO emissions of 27 EU countries.

NH₃ emissions were not calculated in this study and NIR 2010. CO₂ emissions of this study were found compatible with NIR 2010 Turkey [26]. CH₄ emissions found 3,728 ton but it was 4,137 ton in NIR. In this study, default emission factors were selected by considering fuel type from IPCC [65].

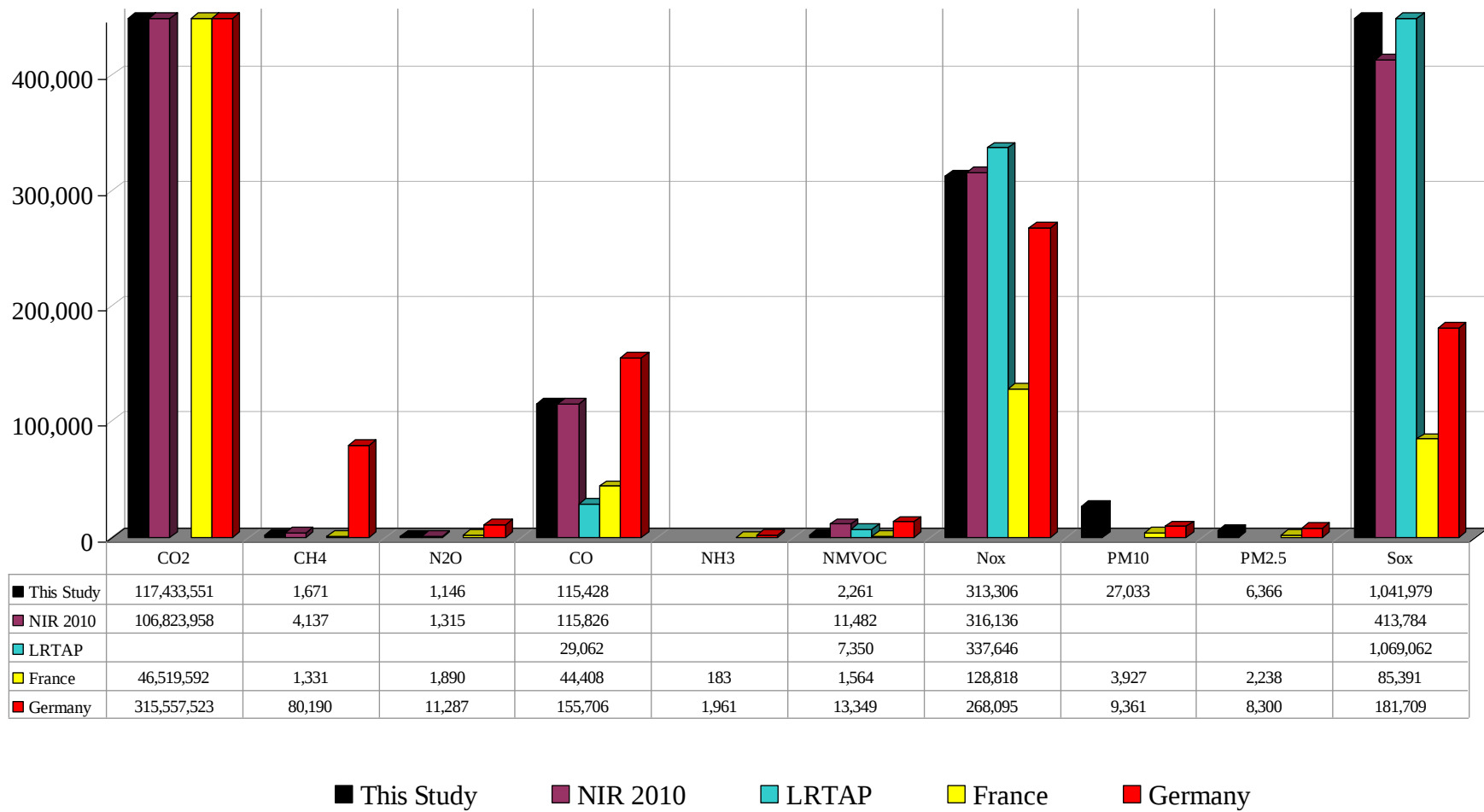


Figure 6.6: *Electricity production emissions comparison with other studies and countries.*

NMVOC emissions which were calculated in this study seem low. The emission factors recommended by EMEP [15] were used in this study.

NO_x emissions were calculated as 313,306 ton for this sector and compatible with LRTAP and EMEP [15].

PM₁₀ and PM_{2.5} emissions were not calculated by NIR and LRTAP.

SO_x emission was calculated 1,041,979 ton in this study and 1,069,062 ton by LRTAP but it is calculated very low in NIR as 413,784. This is because of using default emission factor of EMEP [15] which is given as 820 kg/TJ and is approximately equal to 6.8 kg SO₂/ton of lignite, based on 1 % mass sulphur content and without SO₂ abatement. In this study, fuel specific emission factors were generated for lignite combustion with considering abatement technology and actual sulphur content in the fuel. Finally emission factor was found 3 times higher than EMEP [15].

According to LRTAP, Turkey was the highest NO_x and SO_x emission emitting country from electricity production sector in the Europe in 2009. Total emissions (for the pollutants CO, NMVOC, NO_x and SO_x) of electricity production sector and comparisons with EU countries are given in Figure 6.7 according to LRTAP.

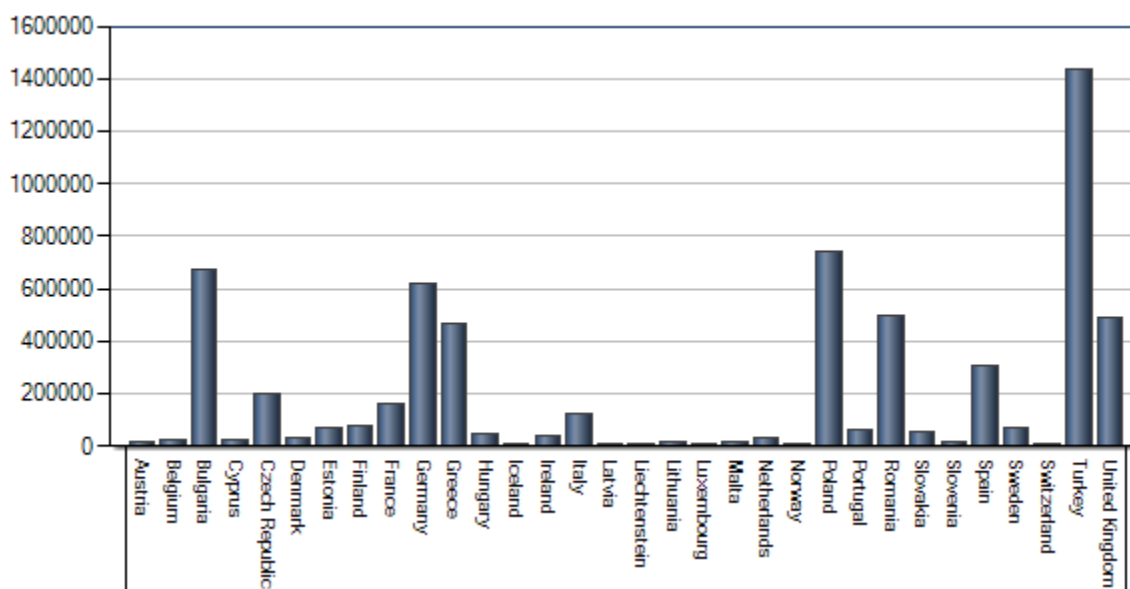


Figure 6.7 : Public electricity and heat production sector comparison with EU by LRTAP for the total of CO, NMVOC, NO_x and SO_x [159].

According to LRTAP, Turkey was the biggest emission emitting country in the Europe for the total of pollutants CO, NMVOC, NO_x and SO_x for public electricity and heat production sector with 1,443,120 ton total emissions in 2009. It was found 1,472,974 ton in this study. Also the calculations of LRTAP are generally compatible with this study, except NMVOC and CO.

In this graph, the countries such as Germany and France which has close population with Turkey has less emissions despite of higher per capita energy usages (Germany is the 5th in the world [160]). However Bulgaria has higher emissions from these 2 countries with 7.543.325 population. The main reason is the usage of clean technologies such as nuclear and wind by developed countries.

6.2.2. Energy use in the industry

Industries need energy and supply it either purchasing from state or produce by itself; therefore they burn fuels and cause emissions. Also fuels are used in the processes by some of the industries such as coke consumption as a reducing agent in iron and steel production process.

Industrial energy usage related emissions are given in Figure 6.8 and compared with NIR 2010, LRTAP 2009, Germany and France.

CO₂ emission was calculated as 57,663,913 ton in this study, also it is 62,429,656 ton in NIR 2010. The main reason is the 'other' sector which is calculated CO₂ emissions are 4,000,000 ton lower than NIR 2010 despite of using higher emission factor for natural gas in this study. In detailed, emission calculated from petroleum is 2,000,000 and natural gas is 1,000,000 ton lower than NIR 2010. The other emissions seem compatible. Petroleum type is accepted No:6 fuel oil, if TurkStat used another liquid fuel in calculations, then the lower value could be understandable, but this is not valid for natural gas.

CH₄ emissions were calculated as lower than NIR. Default emission factors were selected from IPCC [65] by considering fuel type. N₂O emissions seem compatible with NIR.

NMVOC emissions are calculated 15,120 ton (by excluding 5,422 ton from cement industry) in 2010.

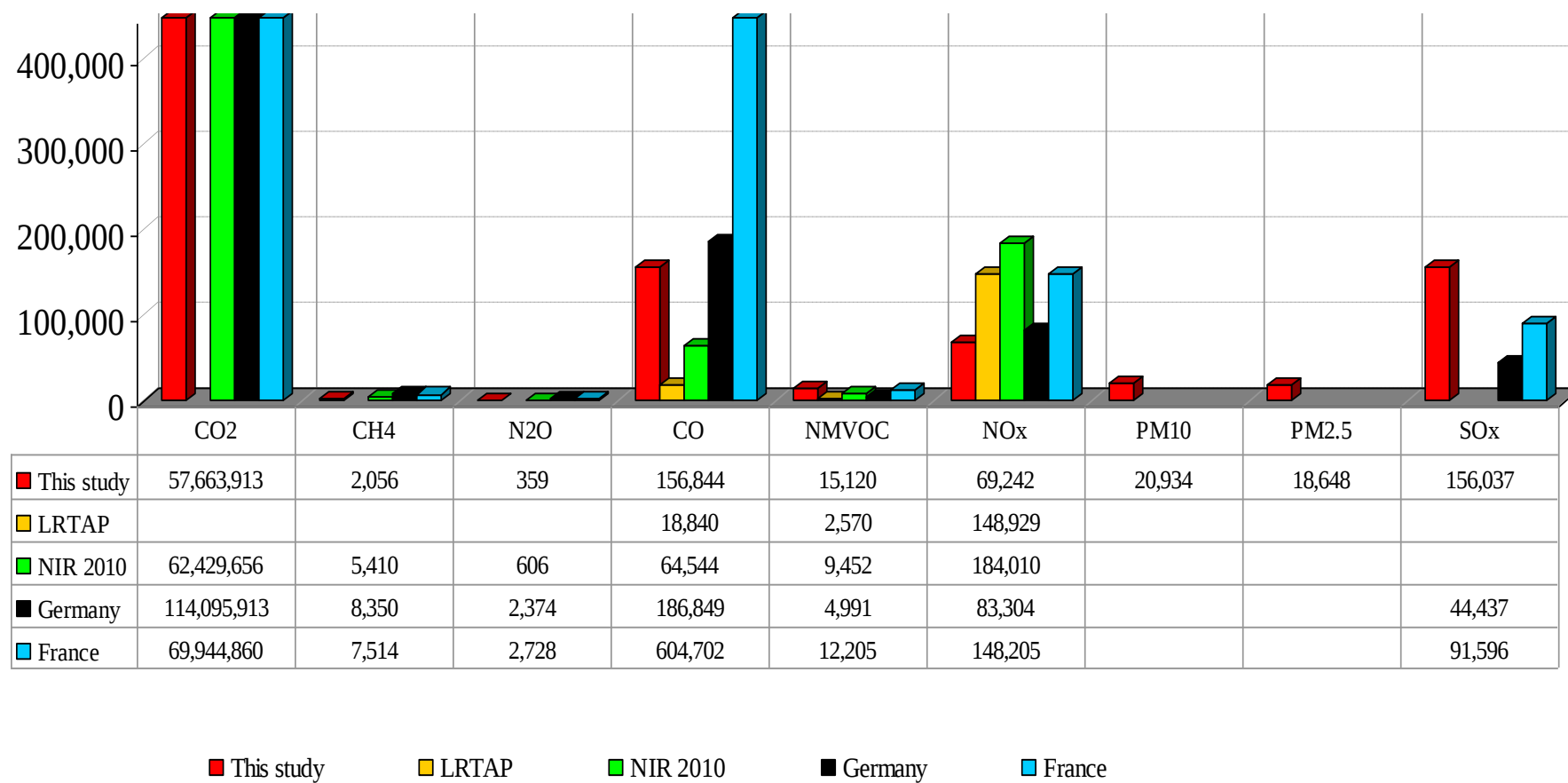


Figure 6.8: Emissions emitted from energy use in the industries and comparison with other studies and countries.

TSP emissions are calculated as 26,360 ton in this study and not given in Figure 6.8. 13,190 ton is comes from other category. Furthermore PM₁₀ (20,934 ton) and PM_{2.5} (18,648 ton) are given in the figure, but not compared.

SO_x emissions were calculated neither in NIR 2010 nor by LRTAP. However it was calculated higher than Germany and France as other electricity production emissions.

6.3. Pollutant Based Summary of All Industries

In this section the emissions calculated in Section 5 are summarized totally and compared with other studies.

Table 6.2: Comparison of the overall results with other studies.

	ref. year:	Uncontrolled 2010	Controlled 2010	NIR 2010 2010	LRTAP 2009	Elbir T. et.al. 1995
PM	Energy	5,345,080	115,010			597,581
	Process	8,998,982	49,034			324,265
SO _x	Energy		1,198,016	413,784	1,069,062	450,926
	Process	106,271	24,721	413,784	30,634	143,430
NO _x	Energy		382,548	500,146	486,574	58,592
	Process	123,906	79,944	20,014	25,497	55,421
CO ₂	Energy	175,097,464	175,097,464	169,253,615		
	Process	55,124,262	55,124,262	49,019,701		
CO	Energy		272,272	180,370	47,902	24,963
	Process	920,889	31,166	2,229	1,443	632,955
CH ₄	Energy		3,728	9,547		
	Process	3,000	133			
NMVOC	Energy		17,381	20,935	9,920	6,594
	Process	289,166	9,310	58,256	44,001	239,423
N ₂ O	Energy		1,505	1,922		
	Process	6,921	2,264			

Unlike Section 5, this section gives a brief summary of all industries as pollutant and condition (controlled/uncontrolled) based for each of the process and energy related emissions. For example pulp and paper industry emissions are calculated in Section 5.7.1 and compared with other studies for all of the pollutants emitted from this industry, but in this section, a specific pollutant (for example PM) is evaluated for all

industries by including PM emission comes from pulp and paper industry and also other industries' PM emissions. Also comparisons with other studies are placed in this section.

The share of the pollutants generated from industrial processes in the 'process + energy' emissions is summarized like that; process related PM emissions account 28% of all PM (energy + process) emissions, SO_x is 1%, NO_x and CO₂ are 3%, CO is 9%, N₂O is 56%, NMVOC is 23%.

7. CONCLUSIONS AND RECOMMENDATIONS

The objective of this study is to calculate uncontrolled and controlled air pollutant emissions, especially CO₂, PM, SO₂, CO, NO_x, NMVOC, VOC, CH₄, and N₂O parameters of industries in Turkey for 2010 by separating source of emissions into two sub-categories as ‘processes’ and ‘fuel combustion’.

Calculations are separated into two parts; energy industries and industrial processes. Also energy industries are evaluated as ‘public electricity and heat production sector’ and ‘industrial energy consumption sector’.

Regarding to results of the study, public electricity production emissions consist 67% of all fuel combustion emissions in the energy sector, remaining part of the emissions are emitted from combustion activities in industrial sectors.

Public electricity and heat production industries’ total CO₂ emissions were calculated as 117,433,551 ton in this study by generating power plant specific emission factors for only lignite-fired power plants. Also it is calculated in NIR as 106,823,958 ton, which is official national inventory report of Turkey and submitted in 2010 to UNFCCC. These values show that two studies need to be compared detailed in terms of calculation details by considering resource for activity data and details for the emission factors.

SO₂ emission factors were generated for lignite-fired power plants by using plant specific fuel characteristics. Total SO₂ emission of public electricity and heat production industry was calculated as 1,041,979 ton. Also it is calculated as 413,784 ton in NIR by taking emission factor from EMEP (European Monitoring and Evaluation Programme) and 1,069,062 ton by LRTAP (UNECE Convention on Long-range Transboundary Air Pollution). The huge difference between NIR and other two results is mainly related with the selected emission factor, because SO₂ emission factor for lignite-fired power plants is found approximately 3 times higher than EMEP and lignite accounts 27.5% of the fuels used in public electricity and heat

production sector. The result of this study and LRTAP are compatible with each other.

NO_x emission of the public electricity and heat production sector is calculated as 313,306 ton in this study and it is given as 316,136 ton in NIR. CO emissions are calculated as 115,428 ton in this study; however a very close emission value is given in NIR as 115,428 ton for public electricity production sector. CO and NO_x emissions are severely compatible in both studies.

CH₄ emissions of public electricity and heat production are calculated lower than NIR. 1,671 ton is calculated in this study and it is given as 4,137 ton in NIR. The value calculated in this study seems more realistic when consumed wood and plant and animal tissue amount is considered.

NMVOC emissions of public electricity and heat production are calculated as 2,261 ton in this study; however it is 20,905 ton in NIR. The difference between these two studies on NMVOC emissions can not be interpreted.

Additionally PM emissions are calculated for public electricity and heat production sector as 5,345,080 ton for uncontrolled conditions and 93,043 ton for controlled conditions with approximately 98% abatement efficiency which can be supplied by the usage of ESPs and/or fabric filters. PM parameter was calculated neither in NIR nor by LRTAP.

The second energy sector is 'industrial energy consumption sector'. CO₂ emissions are calculated as 57,663,913 ton in this study; however it is given as 62,429,656 in NIR as the sectorial fuel consumption emissions. This difference is mainly because of the calculations for 'other' sector.

SO_x emission of industrial energy consumption sector is calculated as 156,037 ton in this study. There is no information for SO_x emissions of the industrial fuel combustion sector in NIR; therefore comparisons can not be given.

NO_x emissions are calculated higher than other studies as 69,242 ton for industrial energy consumption. In this study, cement industry fuel combustion emissions are not considered in industrial energy consumption sector, except CO₂. Therefore other studies' NO_x emissions are high when compared to this study. It is calculated as 184,010 ton in NIR (10% from cement industry) and 148,929 ton by LRTAP by including cement industry fuel combustion emissions in industrial energy

consumption sector. Before excluding SO_x , NO_x , CO, NMVOC, CH_4 and N_2O emissions of cement industry, the emission values are calculated as; 48,073 ton SO_x , 94,452 ton NO_x , 130,029 ton CO, 1665 ton CH_4 , 7904 ton NMVOC and 250 ton N_2O . Finally all of these fuel combustion related emissions of cement industry are included in process emissions of the cement industry.

CO emission of industrial energy consumption was calculated high when compared to other studies. It was calculated as 156,844 ton in this study. However it is calculated as 64,544 ton in NIR and 18,840 ton by LRTAP. The difference may be because of the applied controlling technology in NIR and by LRTAP.

Additionally PM emissions were calculated for energy emissions sector as 21,967 ton. PM parameter is calculated neither in NIR nor by LRTAP.

Industrial process emissions are investigated separately and do not include fuel combustion emissions except cement industry. Emissions are calculated for controlled and uncontrolled conditions.

PM emissions are calculated as 8,966,190 ton for uncontrolled and 45,736 ton for controlled conditions. 81% of the controlled PM emissions come from cement industry and 9% is come from iron and steel industry.

CO_2 emissions are calculated as 55,124,262 ton for industrial processes. 60% of this emission comes from mineral industry mainly from cement industry and 35% is emitted from iron and steel industry. It is also given in NIR as 49,019,701. In this study, CO_2 emissions are calculated approximately 6,000,000 ton higher than NIR. However approximately 2,000,000 ton of this excess CO_2 emission is generated from iron and steel industry, 2,000,000 ton comes from chemistry sector and the last 2,000,000 ton CO_2 comes from mineral industry.

NO_x emissions were calculated by all of the studies. Controlled NO_x emissions of the industrial processes are calculated as 79,944 ton for controlled conditions (13,827 ton controlled NO_x by excluding cement) in this study. However it is calculated as 15,245 ton by LRTAP and 20,014 ton in NIR by excluding cement industry process emissions. The difference should be mainly related with the selected controlling technologies, because uncontrolled NO_x emission is calculated as 29,454 ton for industrial processes by excluding cement industry.

Controlled SO_x emission is calculated in this study as 25,721 ton and 106,271 ton for uncontrolled conditions (by including cement industry as 7,211 ton for controlled conditions). Also it was calculated as 20,195 ton in NIR and 30,903 ton by LRTAP (by excluding cement industry). Results seem compatible with each study.

VOC emissions were calculated as 43,767 ton for industrial processes for controlled conditions and 289,166 ton for uncontrolled conditions. 77% of these emissions come from petroleum refining industry. NMVOC emissions are given in NIR as 58,236 ton for industrial processes but includes only mineral, sugar and petroleum refining industries. Additionally emissions can not be compared with NIR because they are calculated in different ways, but VOC emissions calculated in this study include NMVOCs.

N₂O emissions were calculated as 2,264 ton for controlled conditions and 6,921 ton for uncontrolled conditions. Nearly total N₂O emission comes from inorganic chemical industry. N₂O emission is not calculated in NIR.

Finally total CO₂ emissions from both energy industries and industrial processes were calculated as 230,221,726 ton and include controlled emission factors. Also this is calculated as 218,273,316 ton in NIR. Total PM emissions are calculated 160,745 ton under controlled conditions. PM emissions are not calculated by other studies. SO_x emissions are calculated as 1,222,737 ton in this study for controlled conditions and given as 433,979 ton in NIR and 1,099,965 ton by LRTAP. NO_x emissions are calculated as 462,491 ton in this study for controlled conditions and 520,160 ton in NIR and 513,814 ton by LRTAP.

Turkey should determine a ceiling for the emissions originated from energy industries and industrial processes. This is an obligation because of the harmonisation of Turkey's legislation with NEC directive which is applied for 15 years in European countries and Turkey is under preparation for the harmonisation of this directive. Development potential, resources, technologies, the quality of natural resources and economic power should be considered for determining ceilings for the parameters of the NEC Directive.

5-8 % average annual development rate is predicted for Turkey. This development requires 6-8% additional capacity increase in energy sector. Currently in Turkey, energy supply is mainly dependent on fossil fuels to meet energy need. Especially

domestic lignite have some environmental risks by having low calorific values and high moisture, sulphur and ash content. Natural gas as the most important fossil fuel is an outside dependent energy source and this dependence should be reduced for a strategically independent country. On the other hand, the important amount of current power plants has old technologies or completed their economical life.

Wind and solar energy has an important role in renewable energy potential of Turkey. Increasing the rate of these energy types up to 30% will be advantage for the application of NEC directive. However there should be 10-15 years adaptation period for the harmonisation.

50% reduction in the fossil fuel originated energy amount requires not only increasing the share of renewable energy but also increasing the yields and number of emission controls, updating the technologies of current and planned thermal power plants.

The share of the pollutants generated from industrial processes in the ‘process + energy’ emissions is summarized like that; process related PM emissions account 28% of all PM (energy + process) emissions, SO_x is 2%, NO_x 17%, CO₂ are 25%, CO is 10%, N₂O is 60%, NMVOC is 34%.

Despite of accounting 1% of all emissions (process+energy) under controlled condition, 106,271 ton SO_x emission is emitted from uncontrolled industrial processes contributes to acidification, with potentially significant impacts including adverse effects on aquatic ecosystems in rivers and lakes, and damage to forests. Also 17% NO_x emissions emitted from only industrial processes, which is a greenhouse gas, have same symptoms with SO_x emissions.

Further studies can include future projections with scenario analyzing by considering development rate and planned measurements of the country up to 2050. Same studies should be maintained for transportation, residential heating, waste management, agriculture sectors. Sound databases should be reached easily for public usage and to be used in emissions calculations and specific emission factors should be generated for Turkey.

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APPENDICES

APPENDIX A: Uncontrolled Process Emissions.

APPENDIX B: Controlled Process Emissions.

APPENDIX C: Process Emissions Calculated in NIR 2010 Turkey.

APPENDIX D: Energy Emissions.

APPENDIX E: Energy Emissions Calculated in NIR 2010 Turkey.

APPENDIX F: Uncontrolled Process Emissions of Sub-Sectors.

APPENDIX G: Controlled Process Emissions of Sub-Sectors.

APPENDIX H: Summary and Comparison of the Sectors Calculated in This Study.

APPENDIX A

Table A.1: Uncontrolled process emissions calculated in this study.

	TOTAL	Electricity Production	Petroleum refining	Chemical Industry		Mineral Industry	Metallurgical Industry		Pulp and Paper	Sugar
				Organic Chemicals	Inorganic Chemicals		Iron and Steel+EAF	Non Ferrous Metals		
PM	8,998,982		36,827	94,271	244,131	7,226,854	842,488	55,293	498,779	
PM ₁₀	5,845,476		N.E.	N.E.	N.E.	5,440,190	N.E.	13,139	392,147	
PM _{2.5}	3,305,501		N.E.	N.E.	N.E.	2,990,867	N.E.	5,740	308,894	
SO _x	106,271		32,403	187	6,192	6,778	19,975	8,922	31,815	
NO _x	123,906		729		13,266	94,452	10,404	510	4,545	
CO ₂	55,124,262			164,374	1,825,078	32,927,740	19,915,996	291,073		
CO	920,889		57,805	19,591	12,516	130,029	348,153	154,104	198,690	
CH ₄	3,000			702		1,831	468			
VOC	289,166		90,584	49,541	150		41,291	307	75,001	24,386
NMVOC	159,283			32,758		7,904	19,233		75,001	24,386
N ₂ O	6,921				6,671	250				
NH ₃	8,920		201	19	8,672		28			

Table A.2: Controlled process emissions calculated in this study.

	TOTAL	Electricity Production	Petroleum refining	Chemical Industry		Mineral Industry	Metallurgical Industry		Pulp and Paper	Sugar
				Organic Chemicals	Inorganic Chemicals		Iron and Steel+EAF	Non Ferrous Metals		
PM	49,034		1,841	1,424	1,904	16,219	24,020	1,115	2,494	17
PM ₁₀	13,170		N.E.	N.E.	N.E.	11,209	N.E.	N.E.	1,961	
PM _{2.5}	8,543		N.E.	N.E.	N.E.	6,998	N.E.	N.E.	1,544	
SO _x	24,721		4,860	187	438		5,648	446	6,363	
NO _x	79,944		510		2,766	66,117	7,283	86	3,182	
CO ₂	55,124,262			164,374	1,825,078	32,927,740	19,915,996	291,073		
CO	31,166		2,890	927	146		6,963	7,705	9,935	
CH ₄	133			101		8	23			
VOC	43,767		32,254	3,711	22		1,214	15	3,750	1,219
NMVOC	9,310			1,798			962		3,750	1,219
N ₂ O	2,264				2,252					
NH ₃	457		20	3	433		1			

Table A.3: Process Emissions Calculated in NIR 2010 Turkey.

	TOTAL	Electricity Production	Petroleum Refining	Chemical Industry		Mineral Industry	Metallurgical Industry		Pulp and Paper	Sugar
				Organic Chemicals	Inorganic Chemicals		Iron and Steel	Non Ferrous Metals		
PM										
PM ₁₀										
PM _{2.5}										
SO _x	20,195					20,195				
NO _x	20,014		1,303			18,711				
CO ₂	49,019,701					31,740,111	17,279,591			
CO	2,229		2,084			144				
CH ₄	0					NA				
VOC	0					N.E.				
NMVOC	5,536		5,536			N.E.				41,480
N ₂ O	0					NA				
NH ₃	0					N.E.				

APPENDIX B

Table B.1: Energy emissions calculated in this study.

	TOTAL	Electricity Production	Petroleum refining	Organic and Inorganic Chemicals	Fertilizer	Cement	Metallurgical Industry		Other+EAF	Sugar
							Iron and Steel	Non Ferrous Metals		
PM	119,403	93,043	855	1,715	12	4,393	5,451	354	13,190	390
PM ₁₀	47,967	27,033	855	1,507	11	*	5,608	307	12,280	367
PM _{2.5}	25,015	6,366	855	1,308	9	*	4,644	281	11,214	337
SO _x	1,198,016	1,041,979	26,822	10,976	71	*	38,638	2,514	75,868	1,149
NO _x	382,548	313,306	11,300	4,430	238	*	10,715	2,256	39,566	736
CO ₂	175,097,464	117,433,551	5,144,874	2,979,309	152,768	16,439,049	6,482,891	1,442,165	24,583,350	439,507
CO	272,272	115,428	2,071	8,924	148	*	39,463	3,153	100,148	2,937
CH ₄	3,728	1,671	161	163	3	*	475	55	1,164	34
NMVOC	17,381	2,261	193	998	12	*	3,821	284	9,531	280
N ₂ O	1,505	1,146	74	28	0	*	72	7	173	5

* added to process emissions of cement industry

Table B.2: Energy emissions calculated in NIR 2010, Turkey.

	TOTAL	Electricity Production	Petroleum refining	Organic and Inorganic Chemicals	Fertilizer	Cement	Metallurgical Industry		Other+EAF	Sugar
							Iron and Steel	Non Ferrous Metals		
PM										
PM ₁₀										
PM _{2.5}										
SO _x	413,784	413,784								
NO _x	500,146	316,136	15,218	8,839	456	52,187	20,726	3,877	81,574	1,133
CO ₂	169,253,615	106,823,958	5,581,854	3,094,087	168,997	16,355,867	6,860,890	1,413,811	28,573,236	380,914
CO	180,370	115,826	1,511	1,749	90	25,967	7,744	968	26,078	438
CH ₄	9,547	4,137	175	171	14	1,734	621	129	2,529	36
NMVOC	20,935	11,482	433	337	15	3,467	1,116	151	3,872	62
N ₂ O	1,922	1,315	31	29	0.45	243	75	5	220	4

APPENDIX C

Table C.1: Detailed- Uncontrolled process emissions calculated in this study.

		Uncontrolled Process Emissions (ton/yr)												
		CO ₂	TSP	PM	PM ₁₀	PM _{2.5}	SOx	NOx	CO	CH ₄	VOC	NMVOC	NH ₃	N ₂ O
ORGANIC CHEMICAL		164,374	1,145	93,126	165	8	187	0	19,591	702	16,783	32,758	19	0
1	Synthetic Rubber										171			
2	Ethylene-Propylene											2,246		
3	Aromatics									0	2,995			
4	EDC/VCM	2,452									3,719	914		
5	Ethylene Oxide/Glycol	67,878								141	1,612			
6	Acrylonitrile	94,045							11,756	339	4,702		19	
7	Phthalic Anhydride			4,784			187		6,000			48		
8	LDPE		59								3,032			
9	LLDPE		47								3,032			
10	HDPE		53									1,259		
11	Poly Propylene		535									201		
12	Poly Styrene			2								385		
13	Poly Vinyl Chloride		433		165	8						341		
14	Synthetic Fiber and Yarn			23,952								4,814		
15	Formaldehyde		18						436			255		
16	Crude Teraphtalic Acid								1,400			1,459		
17	Detergents			62,226										
18	Paint			2,114								9,059		
19	Varnish			0								8,987		
20	Ink			48								2,791		

Table C-1 cont.

		CO ₂	TSP	PM	PM ₁₀	PM _{2.5}	SO _x	NO _x	CO	CH ₄	VOC	NMVOC	NH ₃	N ₂ O
	INORGANIC CHEMICAL	1,825,078	11,368	232,763	1,439	550	6,192	13,266	12,516	0	150	0	8,672	6,671
1	Boron			2,559	1,439	550								
2	Soda Ash	598,768		148,916					12,000				1,000	
3	Chromium Oxides			22,690										
4	Magnesium Oxide	360,000	11,368					1,872						
5	Fertilizer													
1	Ammonium Sulphate			4,648							150			
2	Ammonium Nitrate			5,503									1,548	
3	Urea			823				116					1,074	
4	TSP			15,494										
5	DAP			3,372			1,983						694	
6	NPK			1,309									3,272	
6	Inorganic Phosphate													
1	DCP			3,545										
2	STPP			21,420										
7	Sulphuric Acid	4,345					4,162							
8	Phosphoric Acid			2,485										
9	Chlor Alkali	555												
10	HCl													
11	Ammonia	861,410					46	516	516				1,084	
12	Nitric Acid							10,762						6,671
	MINERAL INDUSTRY	32,927,740	40,562	7,186,292	5,440,190	2,990,867	6,778	94,452	130,029	1,831		7,904		250
1	Cement	29,807,076		7,186,267	5,422,294	2,982,262	6,778	94,452	130,029	1,665		7,904		250
2	Lime	2,743,421	32,921		12,803	2,561								
3	Carbide	37,419		25						166				
4	Glass	339,824	7,641		5,093	6,045								

Table C-1 cont.

		CO ₂	TSP	PM	PM ₁₀	PM _{2.5}	SO _x	NO _x	CO	CH ₄	VOC	NMVOC	NH ₃	N ₂ O
	METALLURGICAL	20,207,070	30,123	867,658	13,139	5,740	28,897	10,914	502,257	468	22,366	19,233	28	
1	Integrated Plants	18,243,604		319,866			11,613	6,522	264,534	468	22,059		28	
1	Coke production	2,045,989		37,291			1,869	3,886	8,811	468	22,059		28	
2	Steel Production	16,197,615		282,574			9,744	2,636	255,723					
2	EAF	1,672,393		522,623			8,362	3,882	83,620			19,233		
3	Ferroalloys	173,665		8,983										
4	Aluminium	117,408	27,051	16,187	13,139	5,740	8,820	126	153,720					
1	Primary	115,605		16,187	12,949	5,665	8,820	126	153,720					
2	Secondary	1,803	27,051		189	74								
5	Al. Casting		3,072				102	384	384		307			
	WOOD PRODUCTS		498,779		392,147	308,894	31,815	4,545	198,690			75,001		
1	Pulp and Paper		498,779		392,147	308,894	31,815	4,545	198,690			75,001		
	PETROLEUM REFINING			36,827			32,403	729	57,805		90,584		201	
1	Process			36,827			32,403	729	57,805		43,762		201	
2	Fugitive										19,920			
3	Storage										26,903			
	FOOD and DRINK			340								24,386		
1	Sugar			340								24,386		

Table C.2: Detailed- Controlled process emissions calculated in this study.

		Controlled Process Emissions (ton/yr)												
		CO ₂	TSP	PM	PM ₁₀	PM _{2.5}	SO _x	NO _x	CO	CH ₄	VOC	NMVOC	NH ₃	N ₂ O
ORGANIC CHEMICAL		164,374	1,145	93,126	165	8	187	0	19,591	702	16,783	32,758	19	0
1	Synthetic Rubber										119			
2	Ethylene-Propylene											300		
3	Aromatics									22	51			
4	EDC/VCM	2,452									860	224		
5	Ethylene Oxide/Glycol	67,878								62	2			
6	Acrylonitrile	94,045							588	17	94		3	
7	Phthalic Anhydride			254			187		318			4		
8	LDPE		4								455			
9	LLDPE		3								332			
10	HDPE		8									189		
11	Poly Propylene		20									80		
12	Poly Styrene			0								5		
13	Poly Vinyl Chloride		39		15	1						51		
14	Synthetic Fiber and Yarn			132								722		
15	Formaldehyde		0						7			0		
16	Crude Teraphtalic Acid								14			15		
17	Detergents			747										
18	Paint			211								91		
19	Varnish			0								90		
20	Ink			5								28		

Table C-2 cont.

		CO ₂	TSP	PM	PM ₁₀	PM _{2.5}	SO _x	NO _x	CO	CH ₄	VOC	NMVOC	NH ₃	N ₂ O
	INORGANIC CHEMICAL	1,825,078	11,368	232,763	1,439	550	6,192	13,266	12,516	0	150	0	8,672	6,671
1	Boron			2,559	1,439	550								
2	Soda Ash	598,768		148,916					12,000				1,000	
3	Chromium Oxides			22,690										
4	Magnesium Oxide	360,000	11,368					1,872						
5	Fertilizer													
1	Ammonium Sulphate			4,648							150			
2	Ammonium Nitrate			5,503									1,548	
3	Urea			823				116					1,074	
4	TSP			15,494										
5	DAP			3,372			1,983						694	
6	NPK			1,309									3,272	
6	Inorganic Phosphate													
1	DCP			3,545										
2	STPP			21,420										
7	Sulphuric Acid	4,345					4,162							
8	Phosphoric Acid			2,485										
9	Chlor Alkali	555												
10	HCl													
11	Ammonia	861,410					46	516	516				1,084	
12	Nitric Acid							10,762						6,671

Table C-2 cont.		CO ₂	TSP	PM	PM ₁₀	PM _{2.5}	SO _x	NO _x	CO	CH ₄	VOC	NMVOC	NH ₃	N ₂ O
MINERAL INDUSTRY		32,927,740	40,562	7,186,292	5,440,190	2,990,867	6,778	94,452	130,029	###	0	7,904	0	250
1	Cement	29,807,076		7,186,267	5,422,294	2,982,262	6,778	94,452	130,029	###		7,904		250
2	Lime	2,743,421	32,921		12,803	2,561								
3	Carbide	37,419		25						166				
4	Glass	339,824	7,641		5,093	6,045								
METALLURGICAL		20,207,070	30,123	867,658	13,139	5,740	28,897	10,914	502,257	468	22,366	19,233	28	
1	Integrated Plants	18,243,604		319,866			11,613	6,522	264,534	468	22,059		28	
1	Coke production	2,045,989		37,291			1,869	3,886	8,811	468	22,059		28	
2	Steel Production	16,197,615		282,574			9,744	2,636	255,723					
2	EAF	1,672,393		522,623			8,362	3,882	83,620			19,233		
3	Ferroalloys	173,665		8,983										
4	Aluminium	117,408	27,051	16,187	13,139	5,740	8,820	126	153,720					
1	Primary	115,605		16,187	12,949	5,665	8,820	126	153,720					
2	Secondary	1,803	27,051		189	74								
5	Al. Casting		3,072				102	384	384		307			
WOOD PRODUCTS			498,779		392,147	308,894	31,815	4,545	198,690			75,001		
1	Pulp and Paper		498,779		392,147	308,894	31,815	4,545	198,690			75,001		
PETROLEUM REFINING				36,827			32,403	729	57,805		90,584		201	
1	Process			36,827			32,403	729	57,805		43,762		201	
2	Fugitive										19,920			
3	Storage										26,903			
FOOD and DRINK				340								24,386		
1	Sugar			340								24,386		

APPENDIX D

Table D.1: Detailed- Energy emissions of sub-sectors calculated in this study.

ton/yr	CO ₂	TSP	PM ₁₀	PM _{2.5}	SO _x	NO _x	CO	CH ₄	NMVOC	N ₂ O
ELECTRICITY PRODUCTION	117,433,551	93,043	27,033	6,366	1,041,979	313,306	115,428	1,671	2,261	1,146
Lignite	45,580,186	83,154	20,789	3,118	802,067	150,695	47,302	419	712	628
Hard Coal	19,034,845	5,809	3,873	1,743	158,785	60,029	29,046	194	232	290
Other coals (imported coal)	6,599,471	2,031	1,354	609	55,503	24,367	7,649	68	115	102
Asphaltite	819,733	252	117	53	6,894	3,027	950	8	14	13
Fuel-oil	2,689,830	917	73	37	17,798	7,890	183	110	29	22
Motorin	64,410	3	2	1	400	156	13	3	1	1
Naphta	41,939	2	1	1	263	103	9	2	0	0
Natural Gas	42,210,936	677	677	677	226	66,222	29,277	752	1,129	75
Wood	43,610	20	15	13	4	82	100	12	3	2
Biowaste	348,593	178	132	115	38	736	899	105	25	14
PETROLEUM REFINING	5,144,874	855	855	855	26,822	11,300	2,071	161	193	74
Petroleum	3,007,530	821	821	821	26,810	7,947	589	123	94	62
Natural Gas	2,137,345	34	34	34	11	3,353	1,482	38	99	11
CHEMICAL INDUSTRY	2,979,309	1,715	1,507	1,308	10,976	4,430	8,924	163	998	28
Hard Coal	210,885	266	251	232	1,966	371	1,997	21	191	3
Brown Coal	619,077	760	717	662	5,517	1,060	5,707	61	544	9
Petroleum	1,827,680	686	536	411	3,491	2,493	997	75	249	15
Natural Gas	321,667	3	3	3	3	505	223	6	14	1
FERTILIZER	152,768	12.08	10.74	9.45	71.1	238.1	148.2	3.4	12.2	0.4
Hard Coal	5,021.1	6.3	6.0	5.5	46.8	8.8	47.6	0.5	4.5	0.1
Petroleum	12,103.8	4.5	3.6	2.7	23.1	16.5	6.6	0.5	1.7	0.1
Natural Gas	135,642.9	1	1	1	1.2	212.8	94.1	2.4	6.0	0.2

Table D-1 cont.

	CO ₂	TSP	PM ₁₀	PM _{2.5}	SO _x	NO _x	CO	CH ₄	NMVOC	N ₂ O
CEMENT	16,439,049	4,393								
Hard Coal	7,599,377	N.E.	N.E.	N.E.	20,279	84,046	108,446	773	5,422	116
Brown Coal	2,041,178	2,506	N.E.	N.E.	18,189	3,496	18,815	202	1,795	30
Petroleum Coke	6,688,815	1,887	N.E.	N.E.	9,604	6,860	2,744	686	686	103
Petroleum	78,675	0	N.E.	N.E.	0	2	2	3	0	1
Natural Gas	31,004	0.3	N.E.	N.E.	0	49	22	1	1	0
IRON and STEEL	6,482,891	5,451	5,608	4,644	38,638	10,715	39,463	475	3,821	72
Hard Coal	3,836,091	4,839	4,566	4,215	35,122	6,751	36,332	390	3,465	59
Brown Coal	169,992	209	197	182	1,515	291	1,567	17	149	3
Petroleum	1,040,930	391	833	234	1,988	1,420	568	43	142	9
Natural Gas	1,435,877	13	13	13	13	2,253	996	26	64	3
NON FERROUS METALS	1,442,165	354	307	281	2,514	2,256	3,153	55	284	7
Petroleum	9,078	2	3	2	81	24	2	0	0.28	0
Lignite	256,257	315	297	274	2,283	439	2,362	25	225	4
Petrocoke	97,500	28	7.79582	5	140	100	40	10	10	2
Natural Gas	1,079,330	10	N.E.	N.E.	10	1,693	749	19	48	2
OTHER	24,583,350	13,190	12,280	11,214	75,868	39,566	100,148	1,164	9,531	173
Petroleum	2,838,350	1,065	833	639	5,421	3,872	1,549	116	387	23
Coal	941,449	1,188	1,121	1,034	8,775	1,657	8,916	96	850	14
Lignite	6,630,974	8,141	7,681	7,091	59,088	11,358	61,123	657	5,830	98
Coke	45,627	60	56	52	434	83	449	5	43	1
Petrocoke	1,895,578	2,411	2,275	2,100	455	3,363	18,100	58	1,726	12
Asphaltit	166,904	219	206	191	1,588	305	1,643	18	157	3
Natural Gas	12,064,467	107.5264	107.526	108	108	18,927	8,368	215	537.6322	22

Table D-1 cont.

	CO₂	TSP	PM₁₀	PM_{2.5}	SO_x	NO_x	CO	CH₄	NMVOC	N₂O
SUGAR	439,507	390	367	337	1,149	736	2,937	34	280	5
Hard Coal	185,779	234	221	204	44	327	1,760	19	168	3
Brown Coal	117,980	145	137	126	1,051	202	1,088	12	104	2
Coke										
Petroleum	27,234	10	8	6.130354	52	37	15	1	4	0.2
Natural Gas	108,514	0.967151	0.96715	0.967151	0.9671508	170	75	1.934302	4.835754	0.19343

APPENDIX E

Table E.1: Parameters calculated in this study for each sub-sector and comparison with other studies.

	THIS STUDY												NIR 2010												LRTAP											
	PM	PM10	PM2.5	SOx	NOx	CO2	CO	CH4	VOC	NM VOC	N2O	NH3	PM	PM10	PM2.5	SOx	NOx	CO2	CO	CH4	VOC	NM VOC	N2O	NH3	PM	PM10	PM2.5	SOx	NOx	CO2	CO	CH4	VOC	NM VOC	N2O	NH3
Electricity and Heat Production	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓					✓	✓	✓	✓	✓		✓	✓					✓	✓		✓			✓		✓
Lignite-Fired	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓					✓	✓	✓	✓	✓		✓	✓					✓	✓		✓			✓		✓
Hard coal-fired	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓					✓	✓	✓	✓	✓		✓	✓					✓	✓		✓			✓		✓
imported lignite-fired	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓					✓	✓	✓	✓	✓		✓	✓					✓	✓		✓			✓		✓
Asphaltite	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓					✓	✓	✓	✓	✓		✓	✓					✓	✓		✓			✓		✓
Natural Gas	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓					✓	✓	✓	✓	✓		✓	✓					✓	✓		✓			✓		✓
Fuel-Oil	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓					✓	✓	✓	✓	✓		✓	✓					✓	✓		✓			✓		✓
Diesel	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓					✓	✓	✓	✓	✓		✓	✓					✓	✓		✓			✓		✓
Oil Refineries																						✓														
Process	✓			✓	✓		✓		✓								✓		✓										✓		✓					
Fugitive									✓																											
Storage									✓																											

Table E.1: cont.

		THIS STUDY												NIR 2010												LRTAP													
		PM	PM10	PM2.5	SOx	NOx	CO2	CO	CH4	VOC	NMVOC	N2O	NH3	PM	PM10	PM2.5	SOx	NOx	CO2	CO	CH4	VOC	NMVOC	N2O	NH3	PM	PM10	PM2.5	SOx	NOx	CO2	CO	CH4	VOC	NMVOC	N2O	NH3		
Organic Chemical Industry																																							
Synthetic Rubber									✓																														
Ethylene-Propylene										✓																													
Aromatics								✓																															
Vinyl Chloride Monomer						✓		✓	✓	✓																													
EO/EG						✓		✓	✓																														
Acrylonitrile						✓	✓	✓	✓			✓																											
Phthalic Anhydride		✓			✓		✓			✓																													
Poly Ethylene		✓																																					
LDPE		✓							✓																														
LLDPE		✓							✓																														
HDPE		✓																																					
Polypropylene		✓								✓																													
Polystyrene		✓								✓																													
PVC		✓	✓	✓						✓																													
Synthetic Rfibre and Yarn		✓					✓			✓																													
Formaldehyde		✓					✓			✓																													
Isopropyl Alcohol																																							
Methanol																																							
Ethanol																																							
Crude Teraphtalic Acid							✓			✓																													
Soap																																							
Detergents		✓																																					
Paint/Varnish/Ink		✓								✓																													

Table E.1: cont.

		THIS STUDY											NIR 2010											LRTAP														
		PM	PM10	PM2.5	SOx	NOx	CO2	CO	CH4	VOC	NMVOC	N2O	NH3	PM	PM10	PM2.5	SOx	NOx	CO2	CO	CH4	VOC	NMVOC	N2O	NH3	PM	PM10	PM2.5	SOx	NOx	CO2	CO	CH4	VOC	NMVOC	N2O	NH3	
Inorganic Chemical Industry																																						
Boron Compounds		✓	✓	✓																																		
Soda Ash		✓					✓	✓					✓																									
Chromium Oxides		✓																																				
Magnesia (MgO)		✓				✓	✓																															
Fertilizer																																						
Ammonium Sulphate		✓								✓																												
Ammonium Nitrate		✓									✓		✓																									
Urea		✓				✓							✓																									
TSP		✓																																				
DAP		✓			✓								✓																									
Compose Fertilizer		✓											✓																									
Inorganic Phosphate		✓																																				
STPP		✓																																				
DCP		✓																																				
Sulphuric Acid					✓		✓																															
Phosphoric Acid		✓																																				
Chlor Alkali							✓																															
Hydrochloric Acid																																						
Ammonia					✓	✓	✓	✓																														
Nitric Acid						✓						✓																									✓	
													</																									

Table E.1: cont.

			THIS STUDY												NIR 2010												LRTAP												
			PM	PM10	PM2.5	SOx	NOx	CO2	CO	CH4	VOC	NMVOC	N2O	NH3	PM	PM10	PM2.5	SOx	NOx	CO2	CO	CH4	VOC	NMVOC	N2O	NH3	PM	PM10	PM2.5	SOx	NOx	CO2	CO	CH4	VOC	NMVOC	N2O	NH3	
Mineral Products Industry																																							
	Cement		✓	✓	✓	✓	✓	✓			✓						✓		✓											✓	Other								
	Lime		✓	✓	✓		✓											✓																					
	Carbide		✓	✓	✓		✓		✓			✓																											
	Glass		✓				✓										✓						✓																
Metallurgical Industry																																							
	Iron and Steel		✓			✓	✓	✓											✓										✓		✓			✓					
	Integrated Steelworks		✓			✓	✓	✓	✓										✓																				
	Coke		✓			✓	✓	✓	✓	✓									✓																				
	EAFs		✓			✓	✓	✓	✓			✓																							✓				
Non-Ferrous Metal Industry																																							
	Ferroalloys						✓																																
	Aluminium						✓	✓																															
	Primary Al.		✓	✓	✓	✓	✓	✓																															
	Secondary Al.		✓	✓	✓		✓																																
	Casting		✓			✓	✓		✓		✓	✓																											
Wood Products Industry																																							
	Pulp and Paper		✓			✓	✓		✓		✓	✓																											
Food and Beverages Industry																																							
	Sugar		✓								✓												✓												✓				

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