Cleen Ltd. MMEA/Deliverable in WP 4.1.2

Future Trends in Atmospheric Emission Measurement and Monitoring





Toni Laurila, Measurepolis Development Ltd, 2011

Report Title: Future Trends in Atmospheric Emission Measurement and Monitoring Key words: Emission Measurement, Emission Monitoring

Abstract

This report has been prepared as a part of the Measurement, Monitoring and Environmental Assessment research programme of the Strategic Centre for Science, Technology and Innovation of the Finnish Energy and Environment Cluster, CLEEN Ltd, in 2010-2011. The report responds to the need to identify emerging requirements and technology trends for the measurement and monitoring of air pollutants. The purpose of the document is to serve as an introductory material for near future trends in atmospheric emission measurement and monitoring. The work is based on a literature survey and interviews amongst the partners of CLEEN Ltd.

Table of Contents

1	Introduction		
•		wieletine Francescultin Frances	•
2		egislative Framework in Europe	
	2.1	,	
		2.1.1 Combustion Plants	
	2.2	2.1.2 Waste Incineration Plants	
	2.2	Public Availablility of Environmental Data	
	_	Best Available Techniques (BAT)	
	2.4	CEN Standards	
	2.5	2.4.1 Accreditation and Audit Scheme	
	2.5	Air Quality and National Emission Ceilings Directives	
		2.5.1 All Quality Directives	
	2.6	Green House Gas Emissions	
	2.0	Creen riouse dus Emissions	
3	М	onitoring Technologies	15
	3.1	Sources of Industrial Emisions and BAT	
	3.2	State of the Art in Monitoring Technology	17
	3.3	Technology Trends	
		3.3.1 Sensor Technology	
		3.3.2 Continuous Emission Monitoring Systems (CEMS)	
		3.3.3 Predictive Emission Monitoring Systems (PEMS)	24
		3.3.4 Measurement of Particulate Matter (PM)	
		3.3.5 Measurement Needs for Carbon Capture and Storage (CCS)	27
4	Fr	om Innovations to Best Available Techniques	20
7	4.1	Emerging Technology for Removal of Nanoparticles	
	→. 1	Emerging reciniology for inemoval or manoparticles	29
_	D	Maranaa	20

Air pollution is bad for our health. It reduces human life expectancy by more than eight months on average and by more than two years in the most polluted cities and regions. Member States must comply with the European Union air quality standards quickly and reduce air pollutant emissions.

Janez Potočnik, EU Commissioner for the Environment

1. Introduction

Clean air is essential to our health and to the environment. However, since the industrial revolution the quality of the air we breathe has deteriorated considerably - mainly as a result of human or anthropogenic activities. Rising industrial and energy production together with the dramatically increased traffic on land, sea and the air all contribute to air pollution which, in turn, can lead to serious health problems.

The public awareness of air pollution monitoring and control rose rapidly in the 1950's and 1960's. In Europe this meant the launch of legislative initiatives that eventually led to the current Directives of European Union (EU), which define today the polluting species and regulate their respective emissions. Pollutants consist of gaseous and particulate contaminants. The most important emissions to air from the combustion of fossil fuels are sulphur dioxide (SO₂), nitrogen oxides (NO_x), carbon monoxide (CO), particulate matter (PM₁₀) and greenhouse gases, such as CO₂ and N₂O. Other substances such as heavy metals, hydrogen fluoride, halide compounds, unburned hydrocarbons, non-methane volatile organic compounds (VOC) and dioxins are typically emitted in smaller quantities yet they may have a significant influence on the environment.

Since the early 70s, the EU has been working to improve air quality by controlling emissions of harmful substances into the atmosphere, improving fuel quality and by introducing environmental protection requirements into the transport and energy sectors (Fig. 1). Similar progress has occurred also in the US (Fig. 2).

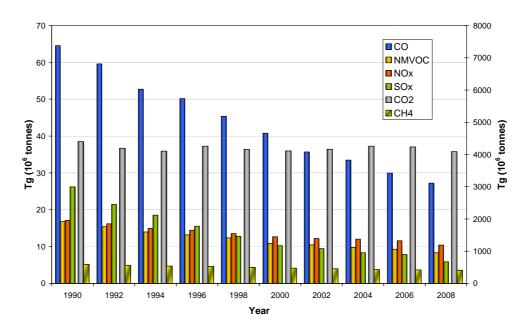


Figure 1. Total Emissions in the EU, 1990-2008. NM = non-mehane. [1].

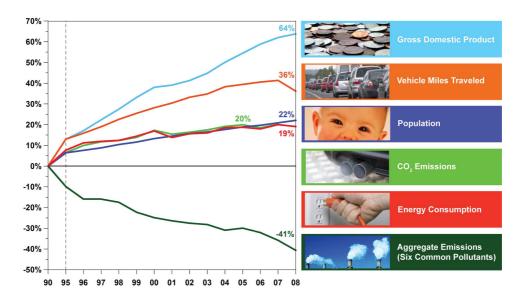


Figure 2. Comparison of growth measures and emissions in the US, 1990-2008. The combined emissions of the six common pollutants ($PM_{2.5}$ and PM_{10} , SO_2 , NO_x , VOCs, CO and lead) dropped 41 percent on average, whereas total CO_2 emissions increased by about 20 percent from 1990 to 2007 [2].

In its broadest sense the measurement and monitoring of atmospheric emissions is a vast topic. The sources of anthropogenic pollutants are many ranging from industrial processes and transportation to households and agriculture (Fig. 3). Although transportation and agriculture are major contributors to atmospheric emissions, these two sectors are not covered. The focus in this report is on industrial gas phase and particle emissions into the air in the EU, where each Member State of is committed to adopt its national legislation to the Directives which set tightening emission limits for selected pollutants. The report sets particular emphasis on the foreseeable needs on novel measurement and monitoring technology associated with industrial combustion processes. The aim has been to identify trends in the legal requirements and associated practical implementation rather than to provide the reader with a full coverage of the existing regulations and best practises. Specific information can be found in the cited legal documents

Industrial monitoring can be divided into three main types: monitoring of industrial emissions at source, monitoring the physical and chemical process parameters in order to confirm that the plant performance is correct and monitoring the impact, i.e., monitoring pollutant levels within the plant's area of influence and the effects on ecosystems. This report focuses on the monitoring of industrial emissions at source.

Emission monitoring means more than just the actual measurement of pollutants using analysers. In addition to the sample extraction and handling, data acquisition and analysis, accurate and reliable long-term monitoring of emissions requires support functions such as competent personnel, regular calibration of the instrumentation using traceable reference techniques and quality control.

The report starts with a summary of the current legislation on industrial emissions into the air in Europe, including an overview on the practical implementation of emission monitoring through Best Available Techniques (BATs) and CEN standards. The state of the art in emission monitoring technology is first summarised in Chapter 3 followed by a discussion on emerging technologies and trends. A couple of example cases on how to get technological innovations into the BAT category will be presented in Chapter 4.

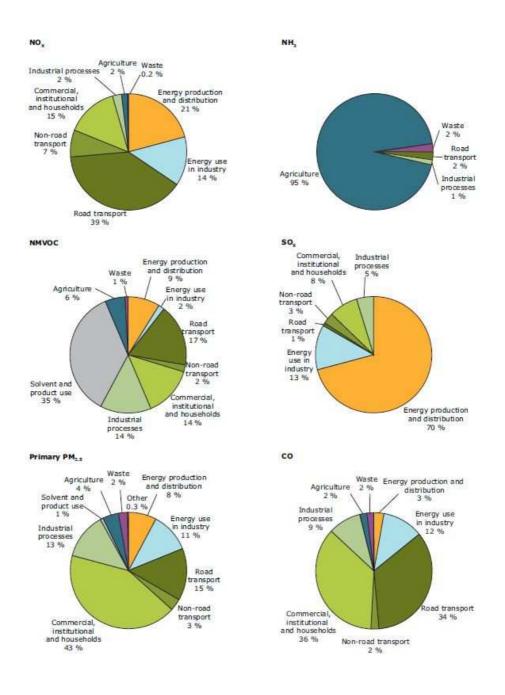


Figure 3. Sources of selected air pollutants in 2008 for EEA-32 and Western Balkan countries [1]. NM = non-methane

2. Legislative Framework in Europe

This chapter introduces the legal framework in Europe governing the industrial emissions into the air. The legislation is one of the major driving forces for novel measurement and monitoring technology. A more detailed discussion on the current status of the European legislation for industrial emissions can be found in a report prepared by the VTT Technical Research Centre of Finland [3].

Industrial activities in Europe have a significant impact on the environment. The largest industrial installations account for a considerable share of total emissions of key atmospheric pollutants, 83% for sulphur dioxide, 34% for oxides of nitrogen, 43% for dust and 55% for volatile organic compounds (VOCs) [4]. Largest facilities also have other important environmental impacts, such as emissions to water and soil, generation of waste and the use of energy. Emissions from large industrial installations have therefore been subject to Union-wide legislation for some time. Since the 1970's various Directives have been drawn up which ultimately led to the adoption of the Integrated Pollution Prevention and Control (IPPC) Directive in 1996 (revised 2008) [5]. IPPC set out the main principles for the permitting and control of installations and the application of Best Available Techniques (BAT) which are the most effective techniques available to achieve a high level of environmental protection, taking into account the costs and benefits. Socalled sectoral Directives lay down specific minimum requirements, including emission limit values for most industrial activities. Sectoral Directives cover large combustion plants, incineration and co-combustion of waste, activities using organic solvents and the production of titanium dioxide. This set of legislation seeks to prevent and control air, water and soil pollution by industrial installations in the EU [6].

2.1 Industrial Emissions Directive (IED)

At the end of 2005 the European Commission undertook a review to examine how the legislation on industrial emissions can be improved to offer a high level of protection for the environment and human health while simplifying the existing legislative framework. It was seen appropriate to alleviate the administrative burden and to protect the environment as a whole by introducing a more integrated approach. In 2007 a Directive on industrial emissions was proposed and the new Industrial Emissions Directive (IED; 2010/75/EU) [7] entered into force on January 6 2011. The IED recasts the following Directives into a single entity:

- IPPC Directive (2008/1/EC) concerning integrated pollution prevention and control
- **LCP Directive** (2001/80/EC) on the limitation of emissions of certain pollutants into the air from large combustion plants
- Directive 200/76/EC on the incineration of waste
- Directive 1999/13/EC on the limitation of **volatile organic compounds** due to the use of organic solvents in certain activities and installations)
- Three different Directives relating to the production of titanium dioxide: (i)
 Council Directive 78/176/EEC; (ii) Council Directive 82/883/EEC; and (iii) Council Directive 92/112/EEC

The IED has to be transposed into national legislation by the Member States by January 7 2013. According to the IED, new plants must apply the cleanest available technology from 2016, though a transition period is foreseen until 30 June 2020. The IED forms the main piece of legislation in the EU for setting emission limits for polluting substances released from large industrial installations into air, water and soil. Currently 52 000 installations are covered by the IED. The IED introduces tightened emission limits for NO_x, SO₂ and dust from power plants and large combustion installations with total rated thermal input power greater than 50 MW_{th}. In addition, installations below 50 MW_{th} contribute significantly to the atmospheric emissions as well. Such small and medium scale facilities are currently regulated by the national legislation but the Commission is likely to review the need to establish the most suitable controls also for installations below the 50 MW_{th} level. It is worth noticing, that EU allows each Member State to set stricter emission limit values in their national laws than what is laid down in Directives, but not the opposite.

2.1.1 Combustion Plants

The IED regulates the emission of the following polluting substances from combustion plants:

- NO_x
- SO₂
- CO
- · dust including fine particulate matter
- mercury

The IED requires that for combustion plants having rated thermal input power equal or greater than 100 MW $_{th}$ the concentrations of NO $_{x}$, SO $_{2}$, CO and the amount of dust in waste gases must be monitored *continuously*. Such continuous monitoring shall also include continuous measurement of the so called peripheral parameters, i.e., oxygen concentration, temperature, pressure and water vapour content* of the waste gases. For combustion plants firing coal or lignite, the emissions of total mercury shall be measured at least once per year.

2.1.2 Waste Incineration Plants and Co-Incineration of Waste

For the incineration of waste the IED requires monitoring of the following polluting substances:

- NO₂ and NO
- SO₂
- CO
- HCI
- HF
- total dust
- total organic carbon (TOC) of gaseous and vaporous organic substances
- dioxins and furans
- the following heavy metals and their compounds: Cd, Ti, Hg, Sb, As, Pb, Cr, Co, Cu, Mn, Ni and V

The IED lists the following substances as polluting substances for air:

^{*} The continuous water vapour measurement is not necessary if the sampled waste gas is dried before the analysis of the emissions.

- SO₂ and other sulphur compounds
- NO_x and other nitrogen compounds
- CC
- volatile organic compounds
- metals and their compounds
- dust including fine particulate matter
- chlorine and its compounds
- fluorine and its compounds
- arsenic and its compounds
- polychlorinated dibenzodioxins and polychlorinated dibenzofurans
- asbestos*
- cyanides*
- substances and mixtures possessing carcinogenic or mutagenic properties or properties which may affect reproduction via the air*

2.2 Public Availability of Environmental Data

The European Pollutant Release and Transfer Register (E-PRTR; regulation EC 166/2006) provides freely accessible environmental data on the internet from industrial facilities in Europe. E-PRTR contains data reported annually by some 28 000 industrial facilities covering 65 economic activities. Data is provided for 91 polluting substances from facilities exceeding specific capacity thresholds set in EC 166/2006 [8]. The respective authorities in the countries compile and check the quality of the reported data.

2.3 Best Available Techniques

Best Available Techniques (BAT; also referred as Best Available Technology) is an important concept which was introduced in 1984 with the Air Framework Directive. The IPPC (96/61/EC) Directive defines BAT in the following fashion:

"Best Available Techniques shall mean the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole:

- *techniques* shall include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned,
- available techniques shall mean those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator,
- best shall mean most effective in achieving a high general level of protection of the environment as a whole."

The national legislation and derived permits for operators are set on the basis of BAT (Fig. 4). The permits contain all the measurands necessary to achieve a high level of protection of the environment, including emission limit values for polluting substances. From the

^{*}neither emission limit value nor monitoring liability has been defined yet for these substances

emission monitoring point of view, BAT closely follows the performance that be obtained in the monitoring of polluting substances using commercially available state of the art analytical technology.

The Commission is required to organise 'an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring and developments in them' and to publish the results of the exchange. The development and exchange of information about BAT redresses technological imbalances and promotes the worldwide dissemination of limit values. In order to realise such exchange of information, the Commission has established an information exchange forum and 33 technical working groups for different industrial sectors. The *Best Available Techniques Reference Documents* (BREF) of each sector reflect this information exchange carried out between the Member States, industry and environmental non-governmental organisations. *BAT conclusions* are documents which summarise the essential outcomes of BREF documents. An important change introduced with the IED is the fact that in the future the emission limit values defined in BAT conclusions are legally binding.

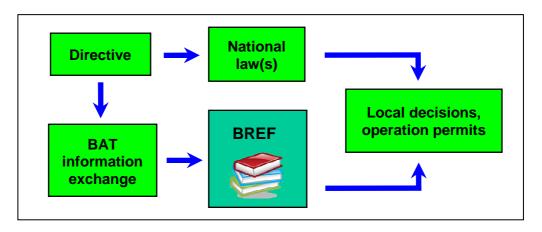


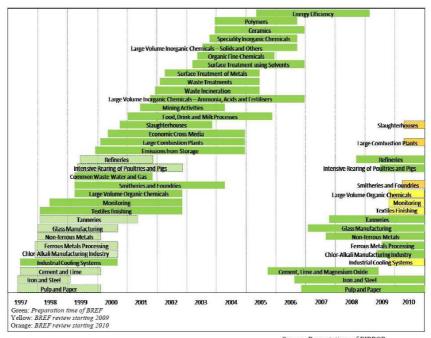
Figure 4. Interplay between EU legislation and BAT.

BREF documentation can be divided into vertical (sectoral) and horizontal BREFs [9]. Vertical BREFs are industry-specific referring to a particular industrial sector, such as Large Combustion Plants BREF, Pulp and Paper Industry BREF, Waste Incineration BREF etc. Horizontal BREFs, on the other hand, address more generic issues covering several sectors, e.g., Energy Efficiency BREF and BREF on General Principles of Monitoring [10], the latter being very relevant in the context of this report.

The term BAT constitutes a moving target on practices, since developing societal values and advancing technology change from what is currently regarded as *reasonably achievable* and *best available*. The Commission aims to update BAT reference documents not later than eight years after the publication of the previous version (Fig. 5).

2.4 CEN Standards

Directive 98/34/EC sets the legal foundation for European standards and technical specifications. European Committee for Standardisation (CEN) is a major provider of European standards. CEN standards are also national standards in each of the EU Member States. CEN standards help build a European internal market for goods and services. International Organization for Standardization (ISO) is CEN's international counterpart.



Source: Presentations of EIPPCB

Figure 5. Planned review process for BREFs.

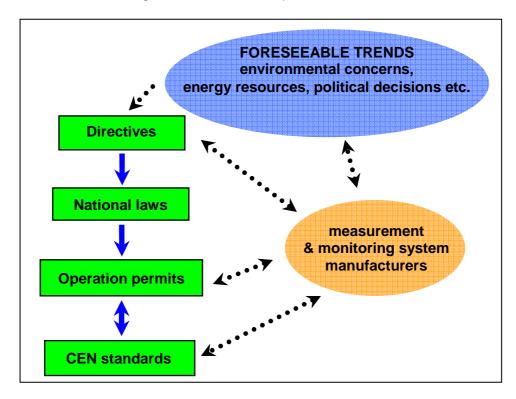


Figure 6. Relations between the Directive level setting the general principles and the standards level with technical details.

Standards set the most detailed technical guidelines for measurement and monitoring. As far as the amount of technical details in the guidelines is concerned, the interplay between Directives, national laws, operation permits and standards is depicted in Figure 6. CEN standards define, for example, reference measurement methods for each of the polluting substances discussed in Chapter 2.1. Full list of CEN standards relevant to atmospheric emission measurements can be found in [3,11].

For operators running their own continuous emission monitoring systems (CEMS; see Chapter 3.3.1) or automated measuring systems (AMS) CEN-14181 standard *Stationary* source emissions – Quality assurance of automated measuring systems is an important standard ensuring that the accuracy and reliability of data is acceptable. The quality assurance scheme of CEN-14181 is split into four sections (see Fig. 7):

- QAL-1: pre-sale product verification for any specific application; in order to calculate
 the measurement uncertainty it is necessary to know certain information about the
 application and detailed performance specifications of the CEMS product. Practically
 this means that the CEMS/AMS needs to pass independent performance testing, e.g.,
 by TÜV or MCERTS.
- QAL-2: in-depth commissioning and validation by an accredited (e.g. ISO 17025) organisation. Must be accomplished every 5 years (3 years for waste incineration) or within 6 months after a major changes or modification to the process or CEMS itself.
- QAL-3: ongoing quality assurance programme of the operator; on site zero and span tests, maintenance activities
- AST (Annual Surveillance Test): between QAL-2 tests to ensure correct operation

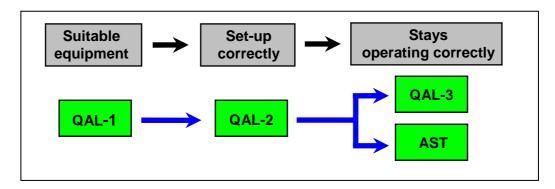


Figure 7. Quality assurance chain for CEMS/AMS according to CEN-14181.

The QAL-1 phase calls for determination of the uncertainty budget of the monitoring. In principle, the manufacturer itself can specify the performance parameters, In practise however, it is usual that the testing performed by an independent and established third party, such as TÜV or MCSERS. Operators routinely require TÜV or MCSERS approval of the instrumentation. CEN is introducing standards on certification of continuous emission monitoring systems, e.g., CEN-15267 *Air Quality – Certification of automated measuring systems*, which any accredited European body (see below) can grant for new monitoring instruments, yet it seems likely that established parties like TÜV and MCSERS will be favoured for some time.

2.4.1 Accreditation and Environmental Audit Scheme

Directives, regulations and standards refer in many cases to reference measurement techniques which are maintained by accredited non-commercial laboratories and commercial calibration service providers. Such independent third parties are essential in securing the accuracy, reliability and international traceability of measurements. Although accreditation is voluntary, it is a de facto requirement for credible reference measurements. The accreditation is realised through national accreditation bodies whose mandate stems from international co-operation organisations, such as the European co-operation for Accreditation and International Accreditation Forum.

The Eco-Management and Audit Scheme (EMAS) of the EU is a voluntary management tool for companies and other organisations to evaluate, report and improve their environmental performance [12]. By carrying out annual updates of environmental policy targets and actions to implement and evaluate them, registered organisations continually improve their environmental performance and provide evidence that they comply with all environmental legislation that is applicable to them. Third-party verification from independent auditors significantly adds credibility to registered organisations by guaranteeing the value of both the actions taken and the disclosed environmental information. Transparency is generated by the environmental statement, which an organisation is required to provide as part of their EMAS registration.

2.5 Air Quality and National Emission Ceilings Directives

Legislation for ambient air quality does not directly set limiting values for industrial emissions into the air, yet it contributes indirectly to the monitoring and control of emission sources. Therefore the air quality legislation and caps for green house gas emissions will be next summarised.

2.5.1 Air Quality Directives

Air Quality 'Framework' Directive (96/62/EC) on ambient air quality assessment and management sets in place a framework to establish air quality objectives with which Member States must comply, to assess and improve air quality and to improve information provision to the public. Under the Framework Directive, four subsequent 'Daughter Directives' set limit and target values for a range of ambient air pollutants with effects harmful to human health and to ecosystems at the local level. They also lay down requirements for assessing local air quality and, where this does not meet the required limit values, to put in place programmes and plans with measures to bring about sufficient reductions in pollutant concentrations such that the limit values are met. They also set out arrangements for providing information to the public about air quality. The Daughter Directives are:

- 1999/30/EC for sulphur dioxide, oxides of nitrogen, particulate matter (PM₁₀) and lead
- 2000/69/EC for carbon monoxide and benzene
- 2002/3/EC for ozone
- 2004/107/EC for arsenic, nickel, cadmium, mercury and PAHs

2.5.2 National Emission Ceiling Directive

Directive on the national emission ceilings (NECD; 2001/81/EC) covers emissions of four pollutants which arise as a result of human activities:

- sulphur dioxide (SO₂),
- nitrogen oxides (NO_x),
- volatile organic compounds (VOC)
- ammonia (NH₃)

These pollutants are responsible for the phenomena of acidification, eutrophication and tropospheric ozone formation ("bad ozone" present at low altitude, as opposed to

stratospheric ozone), irrespective of the sources of pollution. The purpose of the NECD is to reduce the areas with critical loads of acid depositions, reduce ground-level ozone loads above the critical level for human health and crops.

NECD sets national emission ceilings and requires the progressive reduction of their annual national emissions. As an example, the national emission ceilings for SO_2 , NO_x , VOC and NH_3 in Finland are 110, 170, 130 and 31 kilotonnes, respectively. Member States must prepare and annually update national emission inventories and emission projections. The Commission will also report on the extent to which emissions from international maritime traffic and aircraft contribute to atmospheric chemistry. The Commission has recognised a need for joint efforts in the revision process of the Air Quality and National Emission Ceiling Directives [13]. The Commission aims to reduce emissions of the four polluting gaseous species by setting more stringent ceilings under a revision of the NECD [14]. It also wants to set limit values on $PM_{2.5}$ (see Chapter 3.3.4) under the revision of the first daughter Directive 1999/30/EC [15].

2.6 Greenhouse Gas Emissions

Atmospheric greenhouse gases absorb thermal radiation from planetary surface and reradiate it in all directions. Since part of this re-radiation is back towards the surface, energy is transferred to the surface and the lower atmosphere, resulting into a higher temperature than would be if direct heating by solar radiation were the only warming mechanism. The primary greenhouse gases in the atmosphere are water vapour, carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and ozone. Taking into account just the impact of different *anthropogenic gases*, CO₂, CH₄ and N₂O contribute 72%, 18% and 9% to the global warming, respectively. The only important greenhouse gases from the combustion of fossil fuels in large combustion plants are CO₂ and N₂O. CO₂ released by large combustion plants is responsible for approximately one third of the world's global CO₂ emissions.

Annual Greenhouse Gas Emissions by Sector

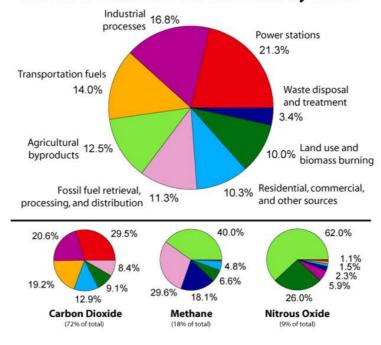


Figure 7. Global anthropogenic greenhouse gas emissions from 8 different sectors in 2000 [16].

Industrial CO_2 emissions are not regulated by the IED. Under the European Union Emissions Trading Scheme (EU ETS) large emitters of CO_2 must monitor and annually report their CO_2 emissions. In 2008 the Commission proposed a number of changes to the current ETS, including centralized allocation by an EU authority instead of national allocation plans, increased auctioning of permits and inclusion of other greenhouse gases, such as N_2O and perfluorocarbons. These changes are still in a draft stage and are only likely to become effective from January 2013 onwards (3rd Trading Period under the EU ETS). The proposed caps for the 3rd Trading Period foresee an overall reduction of greenhouse gases by 21% in 2020 compared to 2005 emissions.

3. Monitoring Technologies

3.1 Sources of Industrial Emissions and BAT

NO_x Emissions

The principal oxides of nitrogen emitted during the combustion are nitric oxide (NO) and nitrogen dioxide (NO₂), referred as NO_x. The formation of NO_x is governed by three essential mechanisms [17]:

- thermal NO_x results from the reaction between O₂ and N₂ from the air
- fuel NO_x is formed from the nitrogen contained in the fuel
- prompt NO_x is formed by the conversion of molecular nitrogen in the flame front in the presence of intermediate hydrocarbon compounds

For pulverised coal combustion plants, the reduction of NO_x emissions by primary and secondary measures, such as selective catalytic reduction (SCR), is BAT, where the reduction rate of the SCR system ranges between 80 and 95 %. The use of SCR or non-catalytic SCR has the disadvantage of a possible emission of unreacted ammonia. For pulverised lignite and peat-fired combustion plants, the use of advanced low NO_x burners in combination with other primary measures such as flue-gas recirculation, staged combustion, reburning, etc. is considered BAT. The use of primary measures tends to cause incomplete combustion, resulting in a higher level of unburned carbon in the fly ash and some CO emissions. For new gas turbines, dry low- NO_x (DLN) premix burners are BAT. For existing gas turbines, water and steam injection or conversion to the DLN technique is BAT. For gas-fired stationary engine plants, the lean-burn approach is BAT analogous to the dry low- NO_x technique used in gas turbines. For most gas turbines and gas engines, SCR is also considered to be BAT.

SO₂ Emissions

Emissions of sulphur oxides mainly result from the presence of sulphur in the fuel. Natural gas is generally considered free from sulphur. However, certain industrial fuels may require the use of flue gas desulphurisation (FGD) techniques. FGD methods include wet scrubbing using a slurry of alkaline sorbent, spray-dry scrubbing using similar sorbent slurries, dry sorbent injection systems, wet sulfuric acid process recovering sulfur in the form of commercial quality sulfuric acid and SNOX flue gas desulphurisation removing SO_2 , NO_x and particulates.

CO Emissions

Carbon monoxide (CO) always appears as an intermediate product of the combustion process BAT for the minimisation of CO emissions is complete combustion, which goes along with good furnace design, the use of high performance monitoring and process control techniques, and maintenance of the combustion system.

Heavy Metals

The emission of heavy metals results from their presence as a natural component in fossil fuels. Most of the heavy metals considered (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, Zn) are normally released as compounds, e.g., oxides, chlorides in association with particulates. Therefore, BAT to reduce the emissions of heavy metals is generally the application of high performance dedusting devices such as electrostatic precipitators (ESPs) or fabric filters (FFs).

Only Hg and Se are at least partly present in the vapour phase. Mercury has a high vapour pressure at the typical process temperatures and its collection by particulate matter control devices is highly variable. For ESPs or FFs operated in combination with flue gas desulphurisation (FGD) techniques, such as wet limestone scrubbers, spray dryer scrubbers or dry sorbent injection, an average removal rate of Hg is 75 % (50 % in ESP and 50 % in FGD) and 90 % in the additional presence of a high dust SCR can be obtained.

Particulate Matter (Dust) Emissions

Particulate matter (dust) emitted during the combustion of solid or liquid fuels arises almost entirely from their mineral fraction. By combustion of liquid fuels, poor combustion conditions lead to the formation of soot. Combustion of natural gas is not a significant source of dust emissions. The emission levels of dust, in this case, are normally well below 5 mg/Nm³ without any additional technical measures being applied. For the dedusting of off-gases from new and existing combustion plants, use of an ESP or an FF is considered BAT. Cyclones and mechanical collectors alone are not BAT, but they can be used as a pre-cleaning stage in the flue-gas path.

Co-combustion of Waste and Recovered Fuel

Large combustion plants, designed and operated according to BAT, use effective measures for the removal of dust, SO₂, NO_x, HCI, HF and other pollutants as well as techniques to prevent water and soil contamination. In general, these techniques can be seen as sufficient and are, therefore, also considered as BAT for the co-combustion of secondary fuel. A higher input of pollutants into the firing system can be balanced within certain limits by adaptation of the flue-gas cleaning system or by limitation of the percentage of secondary fuel that can be co-combusted. Regarding the impact of co-combustion to the quality of the residues, the main BAT issue is maintaining the quality of gypsum, ashes, slag and other residues and by-products at the same level as those occurring without the co-combustion of secondary fuel for the purpose of recycling. If co-combustion leads to significant (extra) disposal volumes of by-products or residues or extra contamination by metals, e.g., Cd, Cr, Pb or dioxins, additional measures need to be taken to avoid this.

Volatile Organic Compounds, persistent Organic Compounds, Dioxins and Furans

The emission sources of volatile organic compounds (VOC) due to industrial activities are numerous, with the combustion of fossil fuel being one of the most significant.

Waste and Residues

Attention has been paid to the utilisation of combustion residues and by-products, instead of just depositing them in landfills. Utilisation and re-use is the best available option and, therefore, has priority. There are many different utilisation possibilities for different by-products such as ashes. The quality criteria are usually connected to the structural properties of the residue and the content of harmful substances, such as the amount of unburned fuel or the solubility of heavy metals. For example, the end-product of the wet scrubbing technique is gypsum, which is a commercial product for the plant in most EU countries. Most gypsum produced in power plants is utilised in the plasterboard industry. The purity of gypsum limits the amount of limestone that can be fed into the process.

3.2 State of the Art in Monitoring Technology

The following tables summarise the reference methods and prevailing industrial techniques used for monitoring of pollutants. More comprehensive list of CEN standards relevant to atmospheric emission measurements can be found in [3,11].

Ambient Air Quality

Pollutant	Common/emerging techniques	Reference technique [18] (CEN standard)
NO _x		chemiluminescence (EN 14211)
CO		non-dispersive infrared (EN 14626)
SO ₂		UV fluorescence (EN 14212)
Benzene		gas chromatography (EN 14662)
Particulate matter (PM ₁₀ , PM _{2.5} is coming: EN 14907)	quartz mass balance, attenuation of beta radiation, absorption and scattering of light, tapered element oscillation microbalance, electrostatic impactor	gravimetric method (EN 12341)
Pb, Cd, As and Ni contained in PM ₁₀		graphite furnace atomic absorption spectroscopy or inductively coupled plasma mass spectrometry (EN 14902, see also EN 15841),
O_3	UV, FTIR	UV absorption (EN 14625)
Hg	cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry, see Chapter 3.3.2	cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry, see Chapter 3.3.2 (EN 15852 and 15853)

Industrial Emissions into the Air

Pollutant	Common/emerging techniques	Reference technique	
NO _x	chemiluminescence, IR spectroscopy (FTIR, non- dispersive IR etc.), electrochemical sensor	chemiluminescence (EN 14792)	
SO ₂	IR, electrochemical sensor	ion chromatography or Thorin titration method (EN 14791)	
СО	IR, electrochemical sensor	non-dispersive infrared (EN 15058)	
CO ₂	IR		
HF	IR, diode laser spectroscopy	ion selective electrode or titration	
HCI	IR	ion-exchange chromatography, photometry and potentiometry (EN 1911)	
VOCs		activated carbon and solvent desorption (EN 13649)	
NH ₃	UV, IR, chemiluminescence	ion chromatography	
Total organic carbon	FTIR	flame ionisation detection (EN 12619, 13526)	
Total dust	quartz mass balance, attenuation of beta radiation, absorption and scattering of light, tapered element oscillation microbalance, electrostatic impactor	gravimetric (EN 13284)	
PM ₁₀ /PM _{2.5}	quartz mass balance, attenuation of beta radiation, absorption and scattering of light, tapered element oscillation microbalance, electrostatic impactor	impactor (EN ISO 23210)	
Heavy metals (As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Ti, V)	high-performance liquid chromatography	high-performance liquid chromatography (EN 14385)	
Hg	UV fluorescence/ absorption (see Chapter 3.3.2)	(EN 13211 for manual measurement, EN 14884 for automated moniotoring)	
Dioxins		gas chromatography & mass spectrometry (EN 1948)	
Furans		gas chromatography & mass spectrometry	

^{*}IR spectroscopy includes techniques such as FTIR (Fourier transform infrared spectroscopy), NDIR (Non-dispersive Infrared Spectroscopy) and GFC-IR (gas filter correlation infrared spectroscopy)

Peripheral measurements

Measurand	Common techniques	Candidate techniques
Oxygen	paramagnetic (EN 14789), zirconium oxide sensor,	IR diode laser spectroscopy
	electrochemical sensor	,
Water vapour	condensation/adsorption (EN 14790), measurement of	IR diode laser spectroscopy
	thermodynamic parameters, IR spectroscopy	1, 1,
Temperature	thermocouple, IR thermometry, resistance thermometers	IR diode laser spectroscopy
Pressure	piezoelectric, resistive strain gauges, capacitive	micro- electromechanical (MEMS) sensors, fibre optic
Gas flow (ISO 16911 is under development)	pitot tube, ultrasound, hot wire anemometer, transit time measurement of labelling species	optical techniques (Doppler shift, particle scattering)

3.3. Technology Trends

From the progression point of view, the current monitoring technology can be seen as a three level structure. The production of raw measurement data (physical measurement) forms the first level. Smart sensors and instrumentation can be considered as the second layer. At the third level smart sensors are followed by computer assisted processing, analysis and presentation of the measurement data. Publicly available real-time data, e.g., weather services, and spatially resolved monitoring, e.g., emission maps, are relatively recent trends falling both into the highest third level. The objective of the first Work Package of the MMEA research programme is to develop novel solutions and approaches for automated data handling and processing at the third level. This report is focuses on the foreseeable technology trends at the first and second level.

Large and relatively complex analysers are common for the measurement and monitoring of atmospheric emissions and ambient air quality. Many environmental measurements take place at very low analyte concentrations, and thus, necessitate the use of sophisticated measurement techniques and analysis in the laboratory to fulfil the required accuracy and reliability. Ever improving sensitivity of the state of the art laboratory analysers means that attention must be paid to correct sample extraction, handling and conditioning (e.g. ISO 10396) before the actual measurement.

In contrast to the centralised laboratory level and stationary measurements, large volume sensor markets show clear trends towards smaller, faster and more affordable mass-producible sensors. Continuous monitoring of CO and CO₂ using non-dispersive IR spectroscopy is an example of low-cost and compact sensor technology. Continuous emission monitoring (CEMS) will be discussed in Chapter 3.3.2. Smart (wireless) sensor networks can produce complementary and multi-disciplinary data which can be used, for

example, to derive or simulate the wanted output parameter without direct measurement of it. Predictive emission monitoring systems (PEMS) are emerging and the measurement needs therein are discussed in Chapter 3.3.3. Completely new measurement strategies and instrumentation are required for emerging applications such as carbon capture and strorage (CCS), which will be discussed in Chapter 3.3.5.

3.3.1 Sensor Technology

Revenues for the global sensor market in 2009 were estimated to be 44.1 billion USD, reaching 69.2 billion USD by 2013 [19]. The 2008 global revenues by sensor types and end users are shown in Figures 8 and 9, respectively. The measurement of very basic quantities, such as pressure, flow, position & displacement and temperature, still contributes to more than third of the global sensor revenue (Fig. 8). Biosensors (13.9%) and image sensors (7.3%) represent newer sensor types that have already gained substantial shares of the total. Although going strong, many traditional contact sensors have reached their market maturity. Largest development potential is predicted for noncontact sensors, such as IR temperature and gas sensors and magnetostrictive (position) sensors [19]. Wireless sensors and integrated silicon based sensors are also likely to continue to exhibit strong growth at the instrument and system levels (cf. Fig. 10).

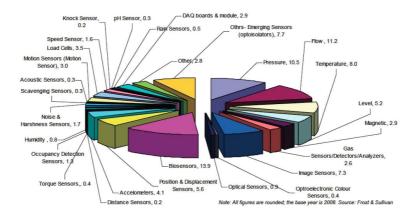


Figure 8. Global Revenue (%) by major sensor types in 2008 [19].

Large end user segments for sensors include chemical & petrochemical industry (12%), oil & gas (6.5%), medical (11%) and automotive industry (12%). The environmental sector shows a somewhat smaller (2%) share of the global revenue but is expected to grow like most end user applications. Disaster management is also arriving to the scene.

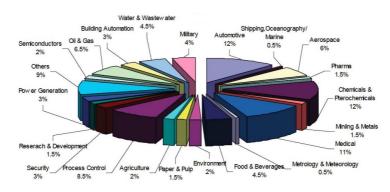


Figure 9. Global Sensors Revenue (%) by end users in 2008 [19].

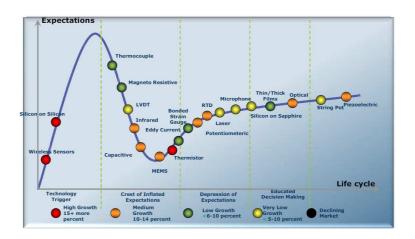


Figure 10. Sensors technology perspective and life cycle expectation trends [20]. LVDT = linear variable differential transformer, MEMS = micro-electromechanical system, RTD = resistance temperature detector

End users seek sensors that offer faster/real-time and more reliable information. Sensor technology is evolving from being mechanical, bulky and expensive to being small and affordable. Wireless sensor networks become smarter by incorporating, in addition to the actual measurement, features such as self-check, automated sensor calibration and autonomous operation through energy harvesting. Wireless sensors can be interfaced with local data networks or with a large centralised control system. The probability of success for wireless sensor networks by application sector is estimated in Figure 11.

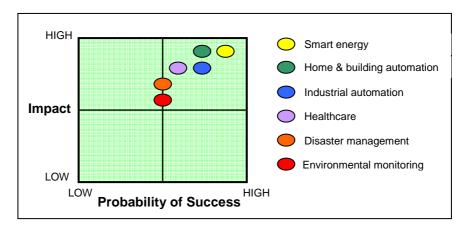


Figure 11. Opportunity analysis of wireless sensor network applications [19].

3.3.2 Continuous Emission Monitoring Systems (CEMS)

In general, direct measurements are the most accurate and preferred methods for emission monitoring. Continuous emission monitoring of a number of components in gases or in waste water is possible and in several cases, accurate concentrations (mg/Nm³, ppm or mg/l) can be reported continuously or as mean values over agreed time periods (half hourly, daily, etc.). FTIR technology presents the state of the art CEMS for simultaneous multi-species monitoring of gaseous species like NO_x, SO₂, CO, CO₂, HF and HCI. FTIR is indeed a viable CEMS for cases where 5 or more gases needs to be monitored simultaneously, as is the case with waste incineration. However, for certain large combustion plants where the monitoring of only NO_x, SO2 and CO is required, discrete sensors for each gas may present the most economically viable solution.

CEMS means more than just the actual measurement of pollutants. In addition, sample extraction and handling, data acquisition and analysis, accurate and reliable long-term monitoring of emissions requires support functions such as competent personnel, regular calibration of the instrumentation using traceable reference techniques and quality control. CEMS allows for analysis of the averages and the use of percentiles provides a flexible method for demonstrating compliance with permit conditions. In other cases where over/under pressures in the flue-gas, fluctuations in flue-gas pressure and temperature can exist, for example, discontinuous measurements, e.g. annual/six monthly measurements may be the preferred method.

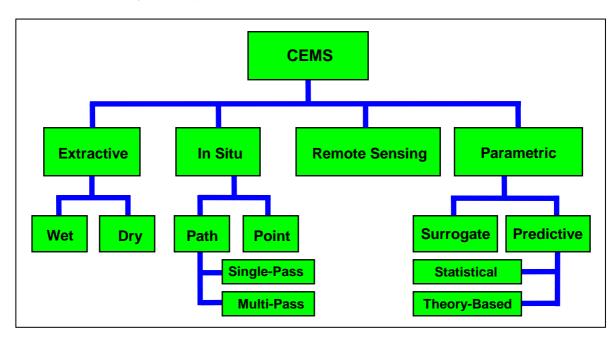


Figure 12. Types of CEMS.

CEMS for Heavy Metals

Both the European and American legislation is driving CEMS for heavy metals. The Industrial Emission Directive [ref. 7, page 18] expresses the following: 'The commission should be empowered to adopt delegated acts...in respect of the setting of the date from which continuous measurements of emissions into the air of heavy metals and dioxins and furans are to be carried out...'. Mercury is easier to measure than most other heavy metals because of its high vapour pressure, which means that a substantial part of total mercy is in atomic vapour phase even at room temperature. This is not the case for many

heavy metals that are bound to various molecular complexes. Another complication is the fact that heavy metals and their compounds tend to stick to particulates. Therefore, continuous measurement of the total concentration of a specific heavy metal species is challenging [21]. Mass-spectrometry based methods are one option but such instruments are fairly expensive and require skilled personnel for operation. Another option is to thermally atomise all the molecular complexes and the smallest particles using a high temperature plasma source with subsequent analysis using e.g. atomic absorption spectroscopy in the ultraviolet spectral range [22]. However, the long-term stability and repeatability of such measurements need to be studied further.

The national legislation in Germany requires CEMS for mercury in the incineration of waste. In the USA the Environmental Protection Agency (EPA) has prepared Clean Air Mercury Rule (CAMR) [23] which sets caps for Hg emissions from coal-fired power plants. However, the US Supreme Court declined the CAMR which would have not taken full effect until after 2020. Five US States have already introduced legal requirements for CEMS of mercury. The other States are still waiting for how the CAMR process will continue. The EPA performance specification (PS-12A) was promulgated for evaluating the acceptability of CEMS for total vapor phase Hg installed on exit gases from fossil fuel fired boilers. According to PS-12A the CEMS for mercury must be capable of measuring the total concentration of vapor phase mercury on a dry basis, corrected to 20°C and 7 percent CO₂. Particle-bound mercury is not included.

Most mercury CEMS are extractive monitors, which remove a continuous or semi-continuous gas sample from a stack and subsequently transfer it to an analyser. Difficulties arise from the fact that current Hg CEMS only measure elemental mercury directly, while mercury emissions in the flue gas can consist of elemental, oxidized or particle-bound mercury. Consequently, the measurement of total mercury as well as mercury speciation can only be achieved indirectly. For this purpose, all oxidized mercury is reduced to its elemental form by a conversion system. Although, in principle, it is possible to recover particle-bound mercury as well, difficulties in transfer and the potential interference of the particulate matter (PM) with the measurement process have made this approach impractical. Therefore, most commercially available CEMS filter out particulate matter, including particle-bound mercury.

As a result, mercury CEMS usually consists of two components, a pretreatment/conversion unit and an analytical unit. The pre-treatment unit is a subject of continuing research and development. The analytical part of the detection system has matured providing more accurate and sensitive detection of elemental mercury. The following detection methods are most commonly used in current mercury CEMS:

- Cold Vapor Atomic Absorption Spectroscopy (CVAAS)
- Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS)
- Atomic Emission Spectroscopy (AES)
- Ultraviolet Differential Optical Absorption Spectroscopy (DOAS)
- Zeeman-Modulated Atomic Absorption Spectroscopy (ZAAS)

In one form or another, all these methods exploit the characteristic absorption lines of mercury in the ultraviolet spectral range, typically the 253.65 nm resonance line. CVAAS and CVAFS are the most common detection methods. In the case of CVAAS, the concentration of elemental mercury in a gas sample is retrieved by directly measuring the light that is absorbed by mercury atoms at their characteristic wavelengths. Interferences with CVAA detection can occur because components of the sample gas, such as SO_2 , NO_x and some VOCs, possess strong absorption bands near the mercury absorption line. CVAFS avoids most of such interferences because there the re-radiated energy (fluorescence) from excited Hg atoms is detected rather than the excitation light [24].

3.3.3 Predictive Emission Monitoring Systems (PEMS)

The PEMS† concept takes the already existing sensors and available process data to calculate and monitor the amount of emissions. It is clear that PEMS has financial benefits over CEMS because there is no need to purchase and install new sensors and analysers.

PEMS was developed in the early 70's for gas turbines. Standardisation and implementation of PEMS has been pioneered in the US. Currently there are no Federal rules in the USA requiring the use of PEMS, however, some operators have obtained administrator approval to use PEMS as alternatives to CEMS. In the US PEMS is currently regulated by the performance specification 16 (PS-16) of the EPA. PS-16 defines PEMS to mean all of the equipment required to predict an emission concentration or emission rate. PEMS may consist of any of the following sub-systems: sensors and sensor interfaces, emission model, algorithm or equation that uses process data to generate an output that is proportional to the emissions, diluent emission model, data recorder and sensor evaluation system. According to PS-16, systems that use fewer than 3 variables are not qualified as PEMS unless specifically approved.

In Europe the legislative framework for PEMS is not ready yet. However, PEMS and related concepts have been briefly addressed in some BREF documents. BREF for LCP discusses PEMS in the context of combustions installations operated on off-shore platforms [25]. LCP BREF describes a complete PEMS to consist of a mathematical module, a quality assurance module and a report module. In general, the mathematical module can be realised in three different ways: first principles, statistical regression or artificial intelligence. In the first principles approach, the mathematical module is based on a physico-chemical model of the combustion process, e.g. [26]. The statistical regression and artificial intelligence approaches both require a set of historical operational data together with simultaneous data in order to predict the emissions.

BREF for Monitoring Techniques [10] cites a few references on predictive emission monitoring studies and endorses the use of other than direct monitoring approaches, such as surrogate parameters, mass balances, calculations and emission factors, if direct measurement is complex, costly and/or impractical. According to the Monitoring BREF, the competent authority can decide whether to approve the use of an approach after considering the following aspects:

- fitness for purpose (Is the method suited to the original reason for monitoring as shown by the limits and performance criteria for an installation?)
- legal requirements (Is the method in line with EU or national laws?)
- facilities and expertise (Are the facilities and expertise available adequate for the proposed method, e.g., staff experience and technical equipment?)

Whenever direct measurements are not used, the relationship between the method used and the parameter of interest should be demonstrated and well documented. It is worth noticing that the use of surrogate parameters, mass balances or calculations (emission factors) transfers the burden of uncertainty and traceability (to a specified reference) to the measurement of several other parameters and to the validation of the numerical model. After installation of PEMS, testing is necessary to compare the measured (actual) emissions with those predicted by PEMS. According to the US PS-16, owners and operators of PEMS are required to conduct quarterly relative accuracy audits (RAA) and

-

[†] LCP BREF uses PEMS as an acronym for Parametric Emission Modelling System

yearly relative accuracy test audits (RATA). The same 10% relative accuracy limit (with respect to a reference method) is required for PEMS as for CEMS.

Netherlands, Sweden, France and Denmark are leading the legal acceptance of PEMS and they have already adapted their national legislation on emissions monitoring to allow the use of PEMS as an alternative to CEMS. In the Netherlands PEMS is already included in the implementation of the EN 14181 standard on quality assurance of CEMS [27].

It can be surmised that PEMS is more prone to operate properly under stable operating conditions without large changes in the quality (composition) of the fuel. Gas turbines, fuel cells and in some cases IC engines can fulfil such criteria. However, application of PEMS to combustion systems running on variable quality biofuels and co-combustion processes can be challenging, unless (real-time) information about the fuel composition is at hand.

As an example, a commercial PEMS manufacturer claims that at any normal operation points the predicted emissions (NO_x) from a typical gas turbine are within 1-2% of those measured and in very atypical operation points of gas turbines, e.g., 50% load or less, the accuracy is still claimed to be high with a maximum deviation of about 10% [28]. On the other hand, in a study using 16 identical marine diesel engines it was found out that PEMS may require engine/rig specific function parameters [29], i.e., PEMS parameters for each particular process may need tailoring and fine tuning despite the fact that the physical rig design is identical.

3.3.4 Measurement of Particulate Matter (PM)

Several studies have demonstrated consistent associations between concentrations of particulate matter (PM) and adverse effects on human health (respiratory symptoms, morbidity and mortality) at concentrations commonly encountered in Europe and USA. Particulate matter in the atmosphere is a complex mixture of different chemical species and origins. Primary PM is emitted directly to the atmosphere by anthropogenic activities and natural processes. Secondary PM mostly originates from anthropogenic sources, and they are formed from precursor gases of SO₂, NO_x, NH₃ and non-methane volatile organic compounds (NMVOCs). The majority of the particle pollution can be grouped into five categories: sulfate, nitrate, elemental (black) carbon, organic carbon and crustal material. Carbonaceous particles have received much attention lately because of the possible health and climatic effects.

Particulate matter is characterized according to the size - mainly because of the different health effects associated with particles of different diameters. PM is the general term used for a mixture of solid particles and liquid droplets in the air. It includes aerosols, smoke, fumes, dust, ash and pollen. The composition of particulate matter varies with place, season and weather conditions. PM can be categorised according to its size. PM_{10} is a notation used to describe particulate matter of 10 micrometer aerodynamic diameter or less. Fine particulate matter is particulate matter that is 2.5 microns in aerodynamic diameter or less ($PM_{2.5}$). $PM_{2.5}$ particles penetrate the respiratory system further than larger particles. Fine particulate matter is also responsible for environmental effects such as corrosion, soiling, damage to vegetation and reduced visibility. Particles below 0.1 micrometers are classified as ultra-fine particles ($PM_{0.1}$) (see Fig. 13).

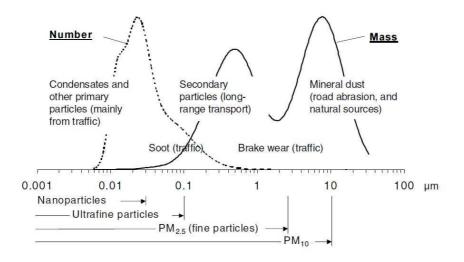


Figure 13. Mass and number distributions of PM in a busy street [15].

PM emission monitoring typically takes place by surrogate means using, for example, light absorption or scattering methods. Proper correlation of the calibration line with the actual PM emissions as measured using the reference methods can be challenging. The real changes in the PM emissions may not necessarily match the meter readings, since the change can be caused by different size fractions leading to different optical properties of particulates, and hence to erroneous meter readings.

Directive 1999/30/EC sets limits for PM_{10} level in the ambient air. The Directive also necessitates the installation of measurement stations supplying representative $PM_{2.5}$, although no emission limit values for $PM_{2.5}$ has been defined yet. However, EU wants to introduce limit values on $PM_{2.5}$ [15]. The need to measure ever smaller particulates drives the development of novel PM analyser technology capable of measuring number distribution instead of mass distribution (cf. Fig. 13) because the smallest particles cannot be reliably measured using methods based on weighing the collected samples.

Monitoring of PM in ambient air is typically realised using stationary measurement stations. Emerging PM measurement approaches include satellite-based remote sensing and continuous PM sensors attached directly to the source of PM emission. Satellite-based PM observations are based on the correlation between a factor known as aerosol optical depth and PM₁₀. European automotive industry is paving the way for *on-board* particulate number density measurement as a part of the Euro 6 emission standard, which is expected to enter into force in September 2014. The standard and the associated on-board measurement technology for PM number concentration are to be defined as soon as possible. Enabled by such novel measurement technology for particle number density, PM research is likely to experience a surge in studies investigating correlations between the chemical composition, health effects and aerodynamic size of PM. It should be noted that several sources of particles and precursors to particles are not controlled at the moment or have only limited or national controls. Such sources include shipping, domestic heating (solid fuel), aviation, off-road machinery, farming, forestry and constructions [15].

3.3.5 Measurement Needs for Carbon Capture and Storage (CCS)

CCS is a novel technology that brings with it many new measurement challenges and needs for novel measurement technology [30]. According to the EU Carbon Capture and Storage Directive (CCSD; 2009/31/EC) the ambition of the EU is to have 12 fully developed CCS demonstration plants in operation by 2015 in order to allow the subsequent commercialisation of CCS by 2020. Measurement is crucial in order to control the CCS processes, for verification under emissions trading schemes and for environmental purposes to detect CO₂ leakage. Besides, the public require assurance that the perceived environmental, health and safety risks associated with CCS, e.g., the release of concentrated CO₂, are being properly mitigated and controlled. The need for flow measurements, sampling and leak detection in CCS systems is clearly called up in the CCSD.

Carbon capture prefers a relatively pure stream of CO₂, so that CO₂ can be economically transported and sequestered. Pathways for CCS come from three potential sources. First, several industrial processes produce highly concentrated streams of CO₂ as a byproduct. Second, power plants emit more than one third of the CO₂ emissions worldwide, making them a prime candidate for CCS. Although the quantity is large, the cost of capture is significant because the CO₂ concentrations are low, typically 3–5% in gas plants and 13–15% in coal plants. Third, future opportunities exist for CO₂ sequestration from producing hydrogen fuels from carbon-rich feedstock, such as natural gas, coal, and biomass. Some options for geological storage of CO₂ are shown in Fig. 14.

To date, chemical absorption is the only technique that has been used commercially to capture CO_2 from flue gas [31]. The general method involves exposing a gas stream to an aqueous amine solution which reacts with the CO_2 in the gas by an acid-base neutralization reaction to form a soluble carbonate salt. This reaction is reversible, allowing the CO_2 gas to be liberated by heating in a separate stripping column. Therefore, the major advantage to this technique is that, in the ideal situation, the amine is not consumed and may be continuously recycled through the process. However, in practise the alkanolamines, such as monoethanolamine, can degrare during the recycling process [31] which is likely to introduce control and monitoring requirements for CCS processes employing chemical absorption.

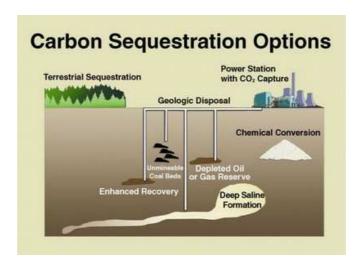


Figure 14. Geological storage options for CO₂ [32].

Furthermore, accurate monitoring of CCS will be imperative due to fiscal reasons, custody transfer and trading purposes. To put the importance of accurate CO_2 measurement into perspective, consider a large-scale power station emitting over 22 million tonnes of CO_2 per annum, for example. Under the EU ETS every 1% uncertainty in measurement could result in a 6.6 M \in financial exposure in the trading scheme (based on a carbon trading price of 30 \in /tonne). Financial interests also involve CO_2 composition control for storage capacity which is directly dependent on fluid density and pressure, and therefore dependent on content of less compressible gases such as N_2 and O_2 .

Unlike other transported fluids including oil, gas and water, the chemistry involved in CO_2 and combined pipeline contaminants, coupled with the CCS process and plant conditions, make measurement and monitoring extremely difficult [30]. CO_2 will be transported through the CCS chain (capture/transportation/storage) in liquid, gaseous and supercritical‡ phases. There is lack of knowledge on the ability of flow measurement technologies and secondary sensors to accurately measure CO_2 under such extreme and multi-phase conditions. There is also uncertainty on the integrity and suitability of the materials for use in CCS schemes, particularly the long-term degradation of seals in supercritical CO_2 .

To date, very little research has been carried out on CO_2 rich flow metering, composition measurement and fugitive emissions measurement from pipelines and geological storage strata. Ultrasonic meters using time of flight technology represent state of the art in single phase flow, including gas, water and oils. The measurement uncertainty limit of 1.5% as proposed by the EU is readily achievable for single phase, steady, predictable and controllable flow conditions, however, it is not known if any one flow metering technology would meet the proposed uncertainty limit for CO_2 and CO_2 mixtures under varying phase conditions. Furthermore, monitoring technologies are required to accurately measure the CO_2 capture efficiency.

[‡] temperature above 31.1 deg C and pressure above 72.9 atm

4. From Innovations to Best Available Techniques

The Member States of the EU are requested to promote the development and application of new technology. Attaining BAT recognition can create improved business opportunities for manufacturers of industrial process and monitoring systems. Formal instructions do not currently exist how to take technical innovations forward from the proof-of-principle and prototype phase up to the point where the technique can be listed in the BAT category. The Commission may prepare instructions how to do this in the future. The promotion of new techniques into the BAT category takes currently place through participation in the technical working group of a particular BREF. In the following a couple of case studies will be presented to provide examples of how novel techniques can be introduced to the BAT level.

4.1 Emerging Technology for Removal of Nanoparticles

Tassu ESP Oy, Finland is a technology supplier which commercialises the electrostatic precipitator (ESP) innovation from the Tampere University of Technology to eliminate small and dangerous particles from the process gas flows. Tassu ESP Oy was established in 2008. Their ESP technology is now available for various industries including glass and glass wool manufacturing, large diesel engines, the metal industry and domestic wood combustion, e.g., fireplaces and other furnaces.

In collaboration with the Finland's Environmental Administration (SYKE), Tassu ESP has introduced their NASU ESP technology to the chapter 6. "Emerging Techniques" of the draft version (24 June 2011) of the forthcoming BREF for the Manufacture of Glass. In contrast to conventional ESP employing electrostatic particle charging, the Tassu ESP charges the particles using supersonic air flow ionisation (diffusion ionisation). Advantages of the TASSU ESP include: better charging of smaller (below 2 μm) particles which results in more efficient removal of fine PM, separate ionisation and PM collector units prevent the fouling of the ionisation electrodes. The system can also be very cost effective with respect to the existing ESP systems. In order for an emerging technique to enter the full BAT category, more experimental evidence on the effective operation of the proposed technique will be required as well as proven information on the installation and operational costs.

REFERENCES

- 1. European Environment Agency: *The European Environment State and Outlook 2010, Air Pollution* (2010), http://www.eea.europa.eu/soer
- 2. http://www.epa.gov/airtrends/2010/report/airpollution.pdf (retrieved February 10 2011)
- 3. A. Wemberg, *A Review of the EU Environmental Legislation and Emission Monitoring*, VTT Technical Research Centre of Finland (2011)
- Communication from the Commission to the Council, the European Parliament, the Economic and Social Committee and the Committee of Regions, *Towards an* improved policy on industrial emissions, December 21 2007, http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2007:0843:FIN:EN:PDF
- Directive (IPPC) 2008/1/EC of the European Parliament and of the Council of 15 January 2008 concerning integrated pollution prevention and control, http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1996:257:0026:0040:EN:PDF
- European Commission homepage on Industrial Emissions, http://ec.europa.eu/environment/air/pollutants/stationary/index.htm (retrieved December 27 2010)
- 7. Directive (IED) 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (IED), http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2010:334:0017:0119:EN:PDF (retrieved June 10 2011)
- 8. European Pollutant Release and Transfer Register, http://prtr.ec.europa.eu/
- 9. BREF documentation, http://eippcb.irc.es/reference/
- 10. BREF on the general principles of monitoring, ftp://ftp.jrc.es/pub/eippcb/doc/mon-bref-0703.pdf
- 11. European Committee for Standardisation, http://www.cen.eu
- 12. Eco-Management and Audit Scheme, http://ec.europa.eu/environment/emas/
- 13. http://ec.europa.eu/environment/air/review_air_policy.htm (retrieved February 10 2011)
- 14. http://europa.eu/legislation_summaries/environment/air_pollution/l28095_en.htm (retrieved February 9 2011)
- 15. Milieu Ltd., the Danish National Environmental Research Institute and the Center for Clean Air Policy: Assessment of the Effectiveness of European Air Quality Policies and Measures, Case Study 4: Comparison of the EU and US Approaches Towards Control of Particulate Matter (2004), http://ec.europa.eu/environment/archives/cafe/activities/pdf/case_study4.pdf (retrieved January 5 2011)

- the Emission Database for Global Atmospheric Research version 3.2, fast track 2000 project, http://themasites.pbl.nl/en/themasites/edgar/emission_data/edgar_32ft2000/
- 17. Directive (LCP) 2001/80/EC of the European Parliament and of the Council of 23 October 2001 on the limitation of emissions of certain pollutants into the air from large combustion plants, http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2001:309:0001:0021:EN:PDF
- 18. R. Kartastenpää, V. Pohjola, J. Walden, T. Salmi, H. Saari, *Ilmanlaadun mittausohje versio 1.0*, Ilmatieteen laitos (2004) Helsinki
- 19. Frost & Sullivan Ltd.: Global Sensors Outlook 2009: A Review of Key Market Revenue Trends, Technology Snapshots and Growth Perspectives, (2009) USA
- 20. Frost & Sullivan Ltd.: Sensors and Instrumentation Markets, (2010) USA
- 21. P. Monkhouse, *On-line diagnostic methods for metal species in industrial process gas*, Progress in Energy and Combustion Science 28 (2002) 331-381.
- 22. R. Oikari, *Direct current plasma-excited atomic absorption spectroscopy a method for real-time monitoring of toxic metals in industrial gas flows*, PhD thesis, (2002), Tampere University of Technology, Finland
- 23. Clean Air Mercury Rule of the US Environmental Protection Agency, http://www.epa.gov/CAMR/
- 24. Gasmet Oy: Continuous Mercury Monitor, http://www.gasmet.fi/products/continuous-emissions-monitoring-systems/gasmet_cmm/ (retrieved 12 April 2011)
- 25. BREF for LCP, pp. 453-454, ftp://ftp.jrc.es/pub/eippcb/doc/lcp_bref_0706.pdf
- 26. V. Fichet, M. Kanniche, P. Plion, O. Gicquuel, *A reactor network model for predicting Nox emissions in gas turbines*, Fuel 89 (2010), 2202-2210.
- 27. M. Lövholm, *Predikterande emissionsmätsystem i stora fyrtaktsmotorer*, M.Sc. thesis, (2010) Åbo Akademi, Finland
- 28. Weel & Sandvig: WS.GT-PEMS predictive emission monitoring of gas turbines, http://www.weel-sandvig.dk/docs/pems.uk.htm (retrieved January 11 2011)
- 29. D.A. Cooper, M. Ekström, Applicability of the PEMS technique for simplified NOx monitoring on board ships, Atmospheric Environment 39 (2005) 127-137.
- 30. TUV NEL report 2009/54: A Study of Measurement Issues for Carbon Capture and Storage (2009)

- 31. B.R. Strazisar, R.R. Anderson, C.M. White: Degradation of Monoethanolamine Used in Carbon Dioxide Capture from Flue Gas of a Coal-fired Electric Power Generating Station, National Energy Technology Laboratory, USA, http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/4b3.pdf (retrieved June 10 2011)
- 32. image from www.whitehouse.gov/omb