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Report

Polycyclic aromatic hydrocarbons (PAH) in industrial emissions

Challenges and strategies to measure, monitor, control and reduce PAH emissions

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SUMMARY

There are hundreds of PAH compounds, and some of them are known to have negative effect on nature and humans if emitted to the environment. On a regulatory level, the long-term goal is to eliminate PAH emissions. It is important to measure PAH correctly to understand where these pollutants come from. Only then will it be possible to reduce or eliminate the sources of PAH
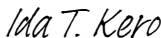
Due to the vast number of PAH compounds, it is not possible to analyze for all. Therefore, a PAH-indicator (called proxy) is necessary. A good proxy represents the PAHs in an acceptable way for the purpose at hand. Since the purposes vary, so does the proxies.

The PAHssion project have come up with a few, new methods for monitoring PAH in industrial emission. The methods are particularly promising with respect to process optimization for emission reduction. This includes two new proxy parameters which may be used when there is little or no dust present.

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Table of contents

Preface

This report was produced in the project IPN PAHssion, in 2022. PAHssion is partly funded by the Norwegian Research Council (Grant No 295744) and partly funded by the industrial partners of the PAHssion consortium, namely: Elkem AS, Eramet Norway AS, Ferroglobe Mangan Norge AS, Wacker Chemicals Norway AS, Finnfjord AS, Tizir Titanium & Iron AS, Fiven Norge AS, Washington Mills AS and Nemko Norlab. The research partners in the PAHssion consortium are SINTEF, NTNU, NORCE and Eyde-cluster.

The PAHssion project was established as a spin-off from the research centre SFI Metal Production. This report is an open publication from the PAHssion project, intended to describe and explain the industrial challenges connected to PAH emissions, sampling and monitoring. The report first gives a brief introduction to the topic of PAH in general and background description of industrial emissions. Then it provides an overview of the key results from the PAHssion project. The idea is that the results from PAHssion may be relevant and valuable also to other parts of industry and society.

Executive summary

The regulatory frameworks for PAH on national and international levels are based on the objective to eliminate emissions. It is important to measure correctly in order to report correct values to authorities but even more important to measure good enough to understand where the PAH comes from. Only then will it be possible to take appropriate actions towards eliminating the sources of PAH. It may not always be optimal to use the same methods for the work carried out towards these two objectives, but the results and experiences from one endeavour may often be useful and complementary for the other.

There are hundreds of PAH compounds, and it is not possible to analyse for all. Therefore, some kind of PAH-indicator is necessary. Such indicators are often called *proxy* parameters. A good proxy must represent the PAH compounds in an acceptable way *for the purpose at hand*. In ambient air regulation the proxy for PAHs is the concentration of one compound, BaP, and for water quality, one normally uses a list of 16 PAHs. Each proxy has its own uses, benefits and drawbacks and comparison between proxies is difficult. The number of compounds in the PAH-category is so vast and their properties and effects are so wide-ranging that the complexity is impossible to describe using limited measurement protocols. To add to the complexity, separate disciplines of science studying PAHs also use various PAH-proxies. These dynamics makes it very challenging to compare measurement data and discuss PAH in a comprehensive manner. Consequently, it is very challenging to discuss PAH as a single topic.

Norwegian air quality (with respect to B(a)P in PM_{10}) complies with the regulatory target value but is sometimes above guideline levels in highly populated areas. For the society as a whole, industry emissions may be less important than other sources in society, like domestic wood burning stoves.

Efforts to lower emissions should target all important sources and to do so, better measurements, standards, and characterization strategies for PAH are necessary. To this end, the PAHssion project has contributed with some new methods which may complement the standard methods used in the industry today.

It is clear that, at least for a large portion of the process industry, process variations significantly influence PAH emissions. Many measurements give a more representative estimate of average PAH emissions over the year. The number of measurements have a bigger influence on the accuracy of the estimated value than the sampling time. The most representative estimate would be based on a continuous signal. Unfortunately, no detector operating in real-time for PAH exists today.

The gas fraction of the PAH can be a useful proxy for PAH, but only when dust concentrations are low. In such cases, the volatile organic compounds (VOC) also represent a possible proxy for PAH. Then, thermal desorption (TD) tubes can be used for sampling and analysis for PAH or VOC. TD tubes constitutes a way to increase the number of measurements without increasing the cost.

A photo ionisation detection (PID) can be used for online monitoring if VOCs can be accepted as a proxy. Real-time methods are able to follow the variations in PAH emissions over time at a relatively high resolution. This gives the industry a possibility to understand how the gases formed relate to operational changes. This, in turn, means that the operations can be optimised to minimise the emissions.

1 Introduction and background

Polycyclic aromatic hydrocarbons (PAHs) originate from incomplete combustion and are of concern for human health because some PAH-substances have been linked to cancer. Exposure to PAHs is commonly caused by breathing air containing smoke from cigarettes, wood fires, vehicle exhausts and asphalt road fumes. PAH intake may occur by eating grilled or charred meats, or other contaminated foods or liquids. More accidental exposure can happen if one comes into contact with contaminated air, water, or soil near a hazardous waste site. In a workplace environment, several industrial processes can discharge PAH into air, for example the production of creosote oils (fungicide wood impregnation), oil mists, asphalt, coke, coal, tar, and the pitches formed from the distillation of coal tars. Work-place exposure is also known to occur at smokehouses and municipal trash incineration facilities.[1]

1.1 PAH definition and terminology

PAHs are a group of organic compounds whose molecules contain two or more fused benzene rings, see figure 1.1. The benzene molecule consists of six carbon atoms forming a ring. The bonds between the carbon atoms alternate between single and double bonds. Each carbon is also bound to a hydrogen atom.

PAHs are also known as polynuclear aromatic hydrocarbons, polyaromatics and polycyclic aromatic carbons (PAC)[2]. Theoretically, there is no upper limit for how many benzene rings a PAH compound can contain. Hence the number of compounds included in the PAH family is almost unlimited.

The PAH compounds can exist as gases, liquids or solids and the compounds will shift between these forms depending on the temperature. Naphthalene is the lightest among the PAHs and is typically a gas in industrial off-gases. As a PAH molecule grows in size, the temperature for when it becomes a gas (boiling temperature) increase. Therefore, the larger PAH molecules are most often liquids or solids.
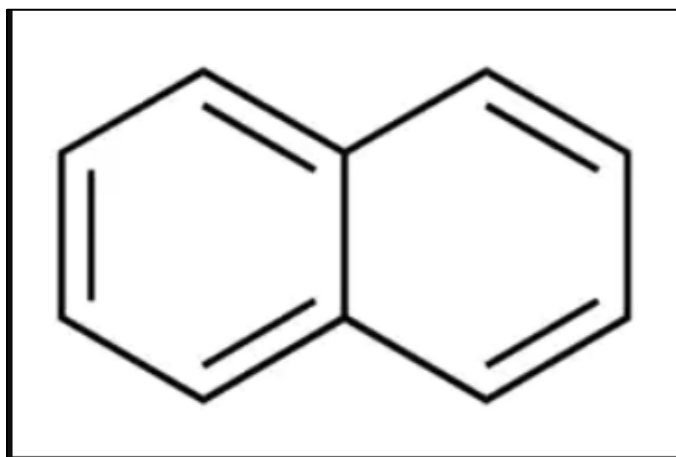

Figure 1.1: Naphthalene consists of two fused benzene rings.

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[1] Agency for Toxic Substances and Disease Registry, Division of Toxicology and Human Health Sciences, Public Health Statement for Polycyclic Aromatic Hydrocarbons (PAHs), 2014, https://wwwn.cdc.gov/TSP/PHS/PHS.aspx?phsid=120&toxid=25

[2] Finlayson-Pitts, B. J. "Airborne polycyclic aromatic hydrocarbons and their derivatives: atmospheric chemistry and toxicological implications." Chemistry of the upper and lower atmosphere: Theory, experiments, and applications (2000).

In industrial off-gases (for example from ferroalloy furnaces), the PAH compounds containing 2-3 benzene rings are typically gaseous and often referred to as the *light* PAH compounds. The PAH compounds which contain more benzene rings tend to be semi-volatile, meaning they change dynamically between being gases and liquids. Therefore, they can be adsorbed on dust particles in an off-gas. The large molecules, known as the *heavy* PAH, are solid. Solid PAHs are strongly linked to *soot* and liquid PAHs are often referred to as *tar*.

The solid and liquid PAHs tend to be attached to dust particles, as illustrated in figure 1.2. These compounds are called the *particle-bound* PAH fraction. Solid PAH may form soot particles themselves or be deposited as layers on other dust particles and/or on the inside surfaces of the off-gas system. Hence, PAH compounds often play a role in clogging of industrial off-gas systems and may also condense onto the surfaces of heat exchangers which, in turn, reduces the efficiency of the energy recovery system.
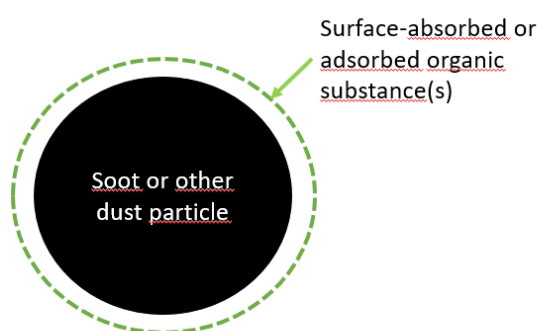

Figure 1.2: Schematic illustration of a particle covered by adsorbed substances.

Since PAHs are such a large category of compounds, it is not possible to measure them all. Whenever measurements are to be made, a group of PAHs must be selected so that one knows what to measure. Such groups of compounds are often called PAH-indicators or *proxy* parameters. A good proxy is one that can represent the PAH in an acceptable way *for the purpose at hand*. Measurement for different purposes uses different proxy parameters, for example B(a)P for cancer risk assessments and EPA16 for water quality assessment. The number of compounds in the PAH-category is vast and their properties and effects are so varied that the inherent complexity is almost impossible to describe, using only one proxy.

1.2 PAH sources in society

The main known health risks of PAH exposure to humans are cancer (mainly lung cancer), heart and lung disorders, birth defects and damage to the genetic material. The effect of being exposed to any toxic substances always depend on dosage, the length of the exposure, and a person's underlying traits and habits. PAHs can be toxic to people even at small concentrations, especially when a person is exposed to over a long period of time. It also matters how a person is exposed, for example if it is through skin contact or inhalation. One of the main pathways for exposure is through inhalation of polluted air containing soot particles that penetrate deep into the lungs.[3]

PAHs enter water through discharges from industrial and wastewater treatment plants. Airborne PAHs can also be transferred to soil and water by so-called deposition from air. Most PAHs do not dissolve easily in water, but they are soluble in fat which makes them available for uptake and accumulation by many organisms. Hence, the PAH contents of plants and animals may be higher than the PAH content of the soil

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[3] https://www.fhi.no/nettpub/luftkvalitet/temakapitler/pah/

or water in which they live. Microorganisms on the other hand, can break down PAHs in soil or water within a period of weeks or months. In water and soil systems (as well as air), the PAHs tends to stick to solid particles. Therefore, they typically follow the water streams and settle with sediment on the bottom of lakes or rivers. Especially the heavy PAH compounds accumulate in sediments because they degrade slowly. [4]

PAHs can form through incomplete combustion processes. All thermal processes with carbon and hydrogen are thus possible sources of PAH and the exact conditions required for PAH formation are still not well-known.[5] Man-made PAHs are typically formed by the burning of organic materials like oil, wood, or waste. In nature, PAHs can be released in large amounts during forest fires and volcano eruptions. From an air pollution perspective however, it is the man-made PAHs which are the main concern and ought to be reduced.

PAHs generally occur as complex mixtures of organic substances, for example as part of combustion products such as soot and tar. They never naturally occur as single compounds, but they can be manufactured as individual compounds. As pure chemicals, PAHs generally exist as colourless, white, or pale yellow-green solids. They can have a faint odour. A few PAHs are used in medicines and to make dyes, plastics, and pesticides. PAHs can also be found in substances such as crude oil, coal, coal tar pitch, roofing tar, and creosote (a fungicide use for wood impregnation). PAHs are also contained in the asphalt used in road construction.

Figure 1.3 shows the sources of PAH emissions in Norway in 2011 as reported by the Norwegian institute of national health (NIPH). Wood burning stoves in private homes was the largest source of PAH emissions while industrial sources were the second largest. The contributions from different sources to the local air varies greatly. The wood burning stoves, for example, are mainly used in the winter and in rural areas. In the urban societies on the other hand, road traffic tends to be a very important source.

Emissions to air are important because inhaling air that contain PAH is thought to be the most common way for PAH exposure. In 2019 the Norwegian Environment Agency estimated that 86 % of PAH emission was to air, and about 12 % and 2 % were emitted to water and soil, respectively[6].

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[4] Fadum, E. OSPAR Commission Background document on Polycyclic Aromatic Hydrocarbons (PAHs). Update 2009.
[5] Arbeidstilsynet (NLIA), Grunnlag for fastsettelse av grenseverdi Polysykliske aromatiske hydrokarboner (PAH), 2021
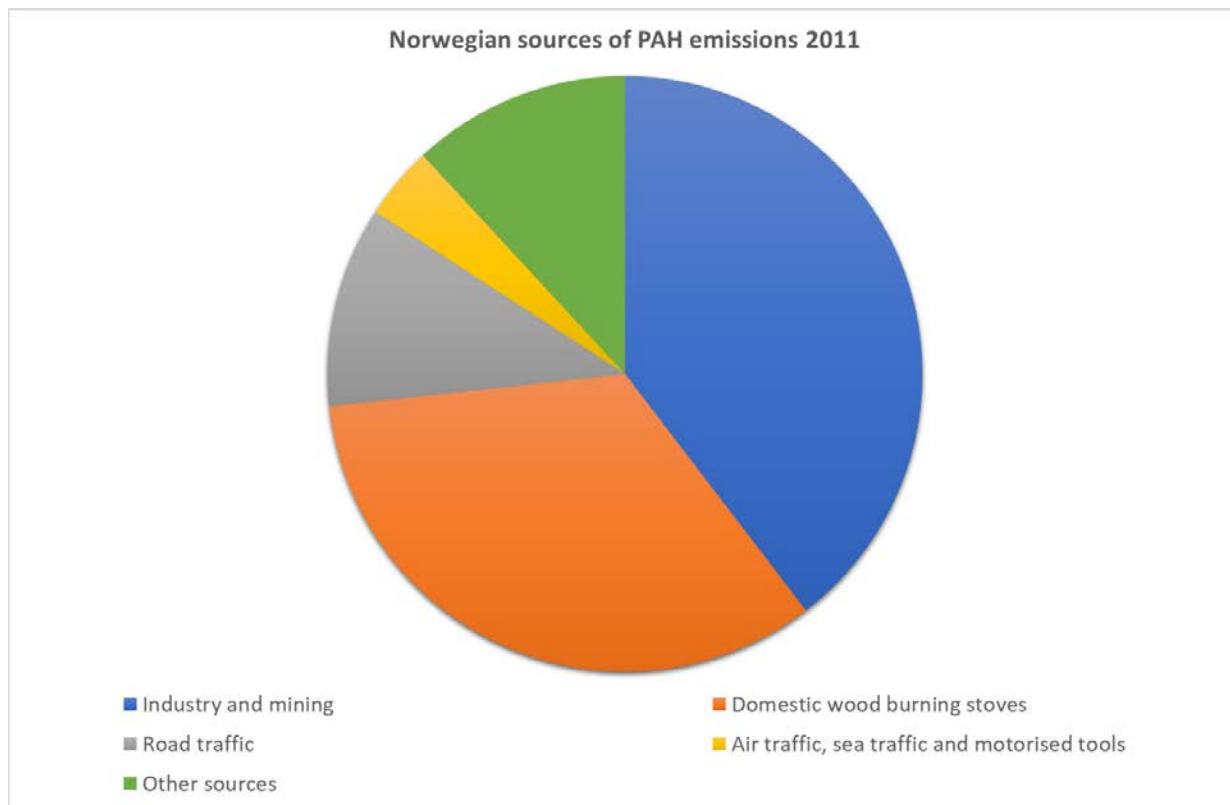
Figure 1.3: Norwegian sources of emissions to air in 2011. Source: NIPH [6]

1.3 Industrial sources of PAH

In different countries and regions, different industrial sources are of importance[7]. Two examples of traditionally and internationally recognised industrial PAH sources are aluminium and coke production. In Norway, the main industrial sources of reported PAH emissions have been the aluminium plants, followed by manganese ferroalloy smelters and silicon carbide producers[8]. Historically, the main reason for PAH emissions from the production of aluminium was the widespread use of a kind of electrodes, known as Söderberg electrodes. Söderberg electrodes contain coal tar pitch, which is a well-known source of PAH. Today, the Söderberg anode technology has been abandoned in most of the Norwegian aluminium plants. This has been recognised to have reduced the PAH emissions in Norway. [9]

The electrode materials are a text-book example of a material which contains PAH in itself. The PAH can become airborne during handling and transport, as dust forms at room temperature. The material is also heated in a process called baking, where the PAHs can evaporate and become airborne. Further, during consumption in the smelting process, the material itself or reaction gases from the metal producing reactions may combust in an non-ideal way, producing PAHs. Another way is that PAH-containing materials may be deposited and further exposed to weather and soil conditions. Then, PAH may be leached by water and/or by the pH-variations into soil and water systems.

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[6] Norwegian institute of national health website. https://www.fhi.no/nettpub/luftkvalitet/temakapitler/pah/
[7] Yang, H.H., et al. "PAH emission from various industrial stacks." Journal of Hazardous materials 60.2 (1998): p.159
[8] Statistics Norway and the Norwegian Environment Agency, available at https://www.norskeutslipp.no/
[9] Fadum, E. OSPAR Commission Background document on Polycyclic Aromatic Hydrocarbons (PAHs). Update 2009.

It is extremely important to understand however, that a material does not need to contain PAH to be the source of PAH. As mentioned before, PAH form during incomplete combustion. This means that any organic material can form PAH in a fire, furnace, or other hot industrial process. Think about an open flame, for example an ordinary candle. Sometimes, black soot forms in the flame. If the flame is behind glass, a black substance may deposit on the glass. This black substance is likely to contain significant amounts of PAH, even if the candle material itself (e.g. stearin) is completely free from PAH.

PAH can form when small organic gas-molecules combine into larger ones. For example, methane or acetylene can form benzene, which in turn grows into naphthalene (and/or even larger molecules, like soot). This requires some heat though, but a flame can easily provide the necessary heat. A process can also go the other way, and large organic molecules can be partly oxidised (burnt) and decompose into smaller molecules. Some of these may be PAHs. The two processes (formation and decomposition) may happen at the same time, in the same process. The exact dynamics and governing mechanisms of PAH formation and decomposition are still not known.

The amount of, and which, PAH molecules that form when, and where, in a process vary greatly. Many different factors are thought to be important, but not all factors are well understood. It is certainly important which type of material is being burnt or reacted. Other known factors are temperature, the amount of oxygen (for example air inlet) and the presence of compounds which contain hydrogen (such as water).

Most industries clean their off-gas. The particle-bound PAHs in particular, tend to be collected in the dust cleaning units. As the distribution between gaseous and particle-bound PAH depends on temperature, the operating temperature of gas cleaning facilities often determines the distribution of PAHs being retained or emitted.

1.4 PAH impact and regulations

PAH concentration in air vary with the sources and the measurement locations. Once released into the atmosphere, some PAH compounds can travel for long distances with the wind. Some PAHs may also be changed by interactions with sun light and other gases in the atmosphere. For example, PAHs may decompose under solar radiation and also react chemically with nitrous oxide gases (NO_X) and ozone (O_3) in the atmosphere. Such processes are known as photodecomposition or aging.

When it comes to global cooperation for emission reduction, the United Nations (UN) are an important arena, and the UN Economic Commission for Europe (UNECE) [10] has an agreement[11] to reduce air pollution. In this agreement, 4-PAHs are considered Persistent Organic Pollutants (POP) together with a number of other organic pollutants[12] which are able to spread out over long distances in the atmosphere. POPs are monitored and reported across Europe. The practical work with monitoring and reporting is done by the European Monitoring and Evaluation Programme (EMEP). [13] [14] Figure 1.4 shows concentration levels across

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[10] The United Nations Economic Commission for Europe (UNECE) is one of the five regional commissions under the jurisdiction of the United Nations Economic and Social Council (UN ECOSOC)

[11] the 1998 UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP)

[12] The organic substances considered to be POPs are: polychlorinated biphenyls (PCBs), polychlorinated dibenzo(p)dioxins, and dibenzofurans (PCDD/Fs), hexachlorobenzene (HCB). The four PAHs are benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene

[13] The full name of EMEP is: co-operative Programme for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe. EMEP performs emissions modelling on national, European and global scales, and in-depth continuous monitoring at up to 67 sites across Europe to support the CLRTAP convention.

[14] https://www.emep.int/

Europe in 2020.[15] PAH concentrations in Europe vary from less than 0.1 ng/m^3 up to 3 ng/m^3 and higher and we can see that the levels in Scandinavia are relatively low compared to other parts of Europe.
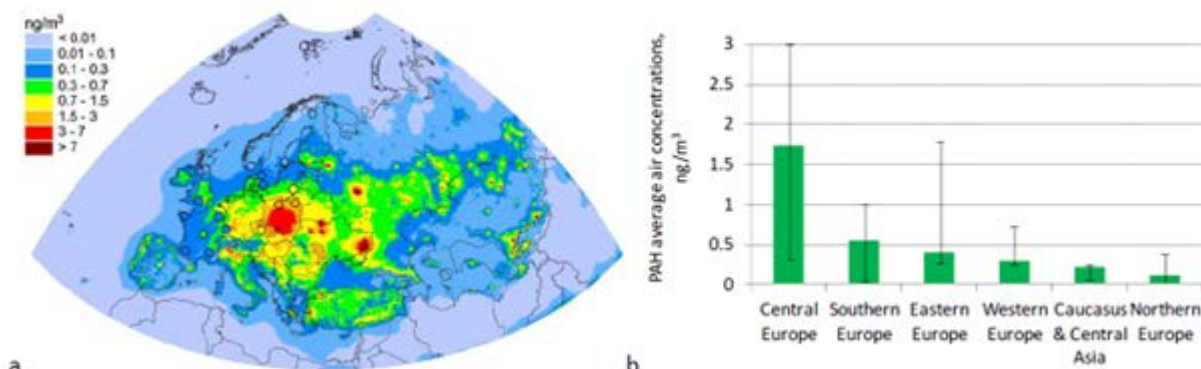

Figure 1.4: Annual mean air concentrations of 4-PAHs in Europe in 2020. a) The circles on the map show observed values, the other coloration is based on modelling. b) The whiskers on the graph show the range of concentrations in particular countries of each sub-region. Figure credit: EMEP Status Report 2/2022

It is always challenging to any discuss PAH as a single topic. The PAH category is so large that a proxy must be chosen but each proxy has its own uses, benefits and drawbacks and comparison between proxies is difficult even for experts. The different laws and guidelines of the many countries and regions of the world, the various proxies used by different disciplines of science and also the progress of knowledge and understanding through different historical periods makes it very challenging to compare and discuss PAH in a comprehensive manner.

1.4.1 Ambient air regulations

The main health concern for PAH exposure is cancer risk. One compound, Benzo(a)pyrene (B(a)P) in particulate matter (PM, dust[16]) is used to regulate PAH in ambient air. For other PAH compounds, B(a)P equivalents[17] may be calculated to indicate its contribution to cancer risk. Norway, as well as the European Union, have set target and guideline values of and 0.1 ng/m^3 B(a)P in PM$_{10}$, respectively. It is assumed that if a population is exposed to these levels over their entire lifetimes it will lead to one cancer death in 10 000 (1 ng/m^3) and in 100 000 (0.1 ng/m^3), respectively.

The EMEP model shown in figure 1.4 estimates that about 8 % of the population in 2020 resided in areas with annual mean B(a)P air concentrations which exceeded the EU target level, and 66 % live in areas exceeding the guideline level. However, if PAH-4 is used as a proxy for PAH instead of B(a)P, the percentage of population who resided in areas where the threshold levels are exceeded, is higher: 11 % of the population is exceeding the EU target value and the WHO reference level is exceeded for as many as 75% of the population.

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[15] I. Ilyin et al., EMEP Status Report 2/2022, Assessment of heavy metal and POP pollution on global, regional and national scales.

[16] Particulate matter (PM) is sampled in filters and the most common sampling procedures are PM10 and PM2,5 which collects particles with aerodynamic diameters smaller or equal to 10 and 2,5 μm, respectively

[17] Agency for Toxic Substances and Disease Registry [ATSDR]. 2022. Guidance for Calculating Benzo(a)pyrene Equivalents for Cancer Evaluations of Polycyclic Aromatic Hydrocarbons. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

PAHs are strictly regulated air pollutants, but the practice of how they are regulated varies between countries. The United States of America does not govern PAHs with a concentration limit in their National Ambient Air Quality Standards (NAAQS), although it is monitored in many places[18] and emissions of PAHs into the environment must be reported. Instead, the U.S. Environmental Protection Agency (EPA) has set lower digestion limits[19] (mass/kg body weight) for five PAH components which they consider safe.

Figure 1.5 shows the annual mean concentrations of B(a)P in urban areas in Norway in 2008-2021. The levels comply with the air quality laws but sometimes exceed the guideline values. The annual concentration average for B(a)P has decreased in Norway over the last 30 years, but it is still higher than the guideline levels for B(a)P in the larger cities, like Oslo, Bergen and Trondheim. [20]
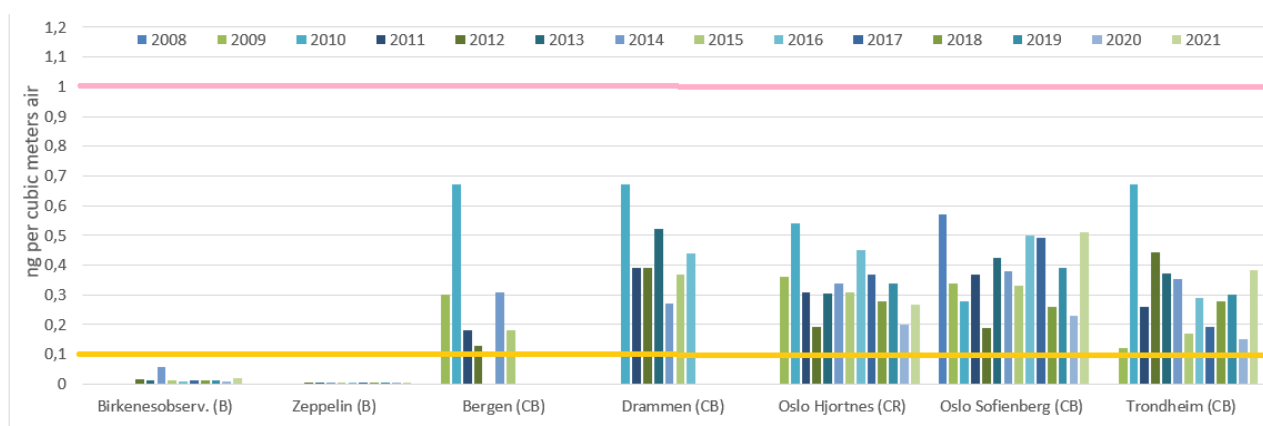

Figure 1.5: Annual mean concentrations of B(a)P in urban areas in Norway in the period 2008-2021 (ng/m^3) The orange line indicates the guideline level, and the pink line indicates the target value. (B) are background sites, (CB) City background sites, (CR) city road site. Data from Sentral database for luftovervåkningsdata[21]

1.4.2 Occupational exposure regulations

PAHs are also regulated in occupational health. The Norwegian Labour Inspection Authority (NLIA) governs the regulation of compounds with carcinogenic and mutagenic properties in working environments. About 50 materials containing such compounds are being regulated in the EU and in Norway.[22] In addition, the EU has limits for the content of B(a)P in certain special products, for example in the oil used for production of car tyres. [25]NLIA operates the total PAH concentration from PM filter samples of 21[23] compounds, sometimes referred to as total-PAH or PAH-21. It is important to understand that in spite of using the term "total", this subset of 21 compounds constitute yet another proxy parameter for PAH. In an 8-hour workday the upper limit is 0.04 mg/m^3 total-PAH. In addition, the two PAH compounds naphthalene and diphenyl are considered

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[18] https://www.epa.gov/criteria-air-pollutants/naaqs-table

[19] The lower digestion limits per kg bodyweight are: 0.3 mg anthracene, 0.06 mg acenaphthene, 0.04 mg fluoranthene, 0.04 mg fluorene, and 0.03 mg pyrene

[20] https://www.fhi.no/nettpub/luftkvalitet/temakapitler/pah/#kilder-og-luftforurensningsnivaaer-av-pah

[21] The websites for access to the central database for Norwegian air quality data is undergoing alterations at the time of writing of this report. Old websites: https://admin.luftkvalitet.info/ and https://luftkvalitet.nilu.no/historikk will be replaced by new websites: airquis.nilu.no, api.nilu.no and luftkvalitet.miljodirektoratet.no

[22] Arbeidstilsynet (NLIA), Grunnlag for fastsettelse av grenseverdi Polysykliske aromatiske hydrokarboner (PAH), 2021

[23] Antracene, benz[a]antracene, benzo[a]fluorene, benzo[b]fluorene, benzo[b]fluorantene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[e]pyrene, benzo[ghi]perylene, dibenzo[a,h]anthracene, dibenzo[a,e]pyrene, dibenzo[a,h]pyrene, dibenzo[a,i]pyrene, dibenzo[a,l]pyrene, phenanthrene, fluoranthene, indenol(1,2,3-cd)pyrene, chrysene, pyrene, and triphenylene

gaseous and sampled differently. Naphthalene and diphenyl have their own occupational concentration limits of 50 and 1 mg/m^3, respectively.[24]

1.4.3 Environmental PAH regulations

In Norway, the PAH proxies used to report industrial emissions to the environmental protection authority (Miljødirektoratet) have varied through the years. Historic emission records feature proxies referred to as PAH, PAH-4 and EPA-16, respectively[25]. Because these are not identical subsets of compounds, the numbers should not be compared and long-term trends are not available. Today, the European Union regulates Benzo(a)Pyrene equivalents and old emission inventories from the European Community sometimes use the Borneff-6[26] as a proxy for PAH. None of these are directly comparable to each other.

Today, the PAH-proxy used for environmental reporting in Norway is the EPA16 list. This proxy is one of the most widely used proxies for PAH in the world, especially when addressing PAH as pollution in environmental contexts and particularly where water pollution is concerned. It was created in the 1970's by the U.S. EPA. They listed 16 PAHs that, at the time, were considered most important for human health related to PAH in drinking water[27]. Since then, this list has become a standardized set of 16 PAHs compounds, most correctly named EPA16 [28,29].

Very often, when environmental samples are investigated for PAH content, the term "PAH" is used (and understood) as synonymous to the 16 compounds on the EPA list. The widespread use of the EPA16 have some significant advantages, for example that it allows comparison between countries and regions as well as time-series, allowing authorities to track the evolution of pollution and environmental trends.

The EPA16 is not without controversy, however. Some experts question the current relevancy of the EPA16 since the list was created on the background of the available knowledge and technology of the 1970's. It has not been updated to mirror the progress of either science, technology, or society. The criticism is often based on the fact that the list has gained such profound importance while seldom being scrutinized. Other important points of criticism are that the EPA16 may not adequately address toxicity, especially in light of modern knowledge of ecological systems. Some may argue that the EPA16 fall especially short with respect to air systems, since it was originally created to address water systems.

More comprehensive and modern alternatives to the EPA16 have been put forward, but none have been implemented in laws and guidelines (yet). One of the most science-based alternatives was suggested by Anderson and Achten[30] in 2015. It is a list of 40 PAHs combined with a number of other, related polycyclic compounds[31]. Andersson and Achten argue that a discussion of the current PAH analyses in environmental regulations is necessary and long overdue. They also point out that while there has been great scientific

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[24] https://www.arbeidstilsynet.no/en/laws-and-regulations/regulations/regulations-concerning-action-and-limit-values/8/

[25] Miljødirektoratet and Statistisk sentralbyrå (SSB): https://www.norskeutslipp.no/

[26] The Borneff 6 PAH compounds are: Fluoranthene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene and Benzo[ghi]perylene

[27] Lawrence H. Keith (2015) The Source of U.S. EPA's Sixteen PAH Priority Pollutants, Polycyclic Aromatic Compounds, 35:2-4, 147-160, DOI: 10.1080/10406638.2014.892886

[28] NS-ISO 28540:2011 Water quality — Determination of 16 polycyclic aromatic hydrocarbons (PAH) in water — Method using gas chromatography with mass spectrometric detection (GC-MS)

[29] NS-ISO 12884:2000, NS-ISO 11338-1:2003, NS-ISO 11338-2:2003

[30] Andersson and Achten's list contained 40 PAHs, 23 NSO-heterocyclic compounds, 6 heterocyclic metabolites, 10 oxy-PAHs and 10 nitro-PAHs.

[31] Jan T. Andersson & Christine Achten (2015) Time to Say Goodbye to the 16 EPA PAHs? Toward an Up-to-Date Use of PACs for Environmental Purposes, Polycyclic Aromatic Compounds, 35:2-4, 330-354, DOI: 10.1080/10406638.2014.991042

progress with respect to the traditionally acknowledged PAHs, there are several other categories of related compounds which we now know are equally important with respect to toxicity and environmental effect, for example heterocyclic compounds and substituted PAHs.

2 The PAHssion project

The industrial companies in the PAHssion consortium represents the Norwegian silicon, ferroalloy, titanium dioxide and silicon carbide producers. These companies all use different types of carbon materials as reductants, electrodes, lining materials etc. As a consequence, they emit PAH to a varying degree. The ultimate goal of the environmental efforts of all industrial companies is to minimize or eliminate process emissions. As a basis for decisions on process changes and investments aimed at mitigating the PAH emissions, the industry rely on costly PAH measurements to identify what to do as well as documenting the sought improvement. The experience in all of these industrial branches is that current PAH measurement methodologies give unacceptably varying results, despite them being in full compliance with standards and regulations. So much so, that the reliability and credibility of the results are questioned. Further, the results may not serve as a basis to understand, control and reduce the emissions. There is consensus in the industry that the road towards a zero emission goal must go via an understanding of the mechanisms of formation of the pollutant so that process improvements and other optimisation work can reduce and finally remove the source(s) of environmental pollution altogether.

2.1 Industry sources in the PAHssion project

Many industrial partners in the PAHssion consortium use Söderberg electrodes which contain coal tar pitch. These are typical PAH-containing materials which can generate PAH emissions even at low temperatures. Today, many producers and users of this kind of materials are trying to replace the coal tar pitch with new binders, not containing PAH. The motivation is often two-fold: one objective is to reduce the fossil carbon in the products, in which case they develop biologically sourced alternatives known as bio-binders. In other cases, it is the reduction of PAHs which motivates the efforts. In such cases, the alternative materials are typically marketed as *PAH-free*[32]. By introducing PAH-free materials, the emissions generated at room temperature can be significantly reduced. These types of PAH-emissions often represent a concern for occupational exposure but are typically less of an issue when it comes to emissions to the outer environment.

It should be noted that the term *PAH-free* means that the levels of EPA16 are below a certain level. Hence, other PAH compounds may be present in the material even at room temperature. Also, as previously mentioned, any organic material can be the source of PAH if incomplete combustion occurs and the PAH-free materials are no exception.

It is important to note, however, that the metal producers who have abandoned Söderberg technology still use other kinds of electrodes. Electrodes of the so-called "pre-baked" type also use binders which are removed in a baking process, but the baking takes place prior to its use in the metal production. Additionally, PAH emissions are generated in many metallurgical industries which do not use electrodes at all. An example is the iron production in blast furnaces where no electrodes are used. Instead, metallurgical coke is used both to provide energy and to remove oxygen from the iron ore. [33]

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[32] T. Eidet and Ø. Mikkelsen, PAH-free binders in metallurgical carbon pastes, in INFACON XV (Southern African Institute of Mining and Metallurgy (SAIMM), Cape Town, 2018).

[33] Yang, H.H., et al. "Profiles of PAH emission from steel and iron industries." Chemosphere 48.10 (2002): p.1061

2.1.1 A note on Söderberg electrodes

The electrode materials are very important industry-specific sources of PAH and many material producers have these in common. Among electrode technologies, the Söderberg is a special case of particular importance with respect to PAH.

The Söderberg electrode technology is a Norwegian invention, patented by Elkem in 1919. It is a so-called self-baking electrode which revolutionized the smelting industry in its time. Söderberg electrode mass can be fed continuously into a furnace and be baked through the heating from the process itself. Therefore it is sometimes referred to as self-baking electrodes. The Søderberg electrode technology is used for the production of a wide range of materials such as calcium carbide, pig iron, ferrosilicon, and ferromanganese. Some Aluminum producers also still use Söderberg electrodes. Today, Elkem's ELSEP™ Söderberg electrode pastes are produced from various recipes. Common for all, however, is that they contain calcined anthracite, but various carbon-containing raw materials can be blended with the anthracite to obtain specific properties. The main source of room or low temperature PAH emissions, however, is coal tar pitch. Coal tar pitch is the binding component in the Söderberg electrode paste. [34] The baking of the electrode serves to heat up the material so that most of the binding components are driven off (evaporated). Thus, PAH-rich pitch releases PAH by evaporation during the baking.

2.2 PAH emissions measurements

Measuring PAHs is more complicated than most other airborne emission types because the PAH category contains an almost unlimited number of compounds, and each compound has its own properties and behaviour. The measurement methods currently used have been developed with this in mind, trying to make it as simple as possible. The widespread use of the EPA16 is an attempt to harmonise the procedure(s) but, as described in the sub-chapters on PAH regulations, various PAH proxies are used for different purposes and a range of proxies have been used and reported historically.

In the PAHssion project, as a research project, we have typically analysed samples with a wider scope than the EPA16, covering 42 PAH components. Between 60 % and 94 % of the PAH found in our samples would have been covered by the EPA16. This varied greatly between the different sampling locations, but it indicates that up to 40% of the PAH present at certain sites would have been ignored by standard measurements. It is important to note however, that the 42 PAH components we analysed for do not represent the full PAH-picture either. It may be looked upon as a more comprehensive proxy though, which mirrors a rather common capability of a modern analytical laboratory.

There are a number of different standards for sampling and analysis of PAH. Here, we focus on the sampling procedures typically used in industrial stacks where PAH is present both on and as particles as well as gases. The measurement methods are designed with an ambition to collect all forms of PAH. Particle-bound PAH are typically sampled in a filter while the gaseous PAH are collected in some sort of sorbent. Examples of commonly used sorbent materials include an adsorbent identified by the commercial name XAD2 and glycol ether used as an absorbent solution.

2.2.1 Standardised sampling methods for PAH emissions

The standard for sampling of PAH (ISO 11338-1:2003) proposes three strategies for sampling of PAH from stacks. These methods are assumed to produce identical results, but it is quite obvious that each of the methods have its own pros and cons. Sampling of PAH is normally conducted over 2-6 hours, and this is

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[34] Elkem website. Available at: https://www.elkem.com/carbon/soderberg-electrode-paste/

assumed to ensure a representative average of the stack gas composition [35]. Conditions affecting the sampling are stack gas temperature, particulate matter concentration, and humidity. The three strategies are:

- PAH is collected on filter and absorbent mounted in series. As the sampled gas may be containing moisture, any water condensation is avoided by diluting the sample gas with filtered, dried, and cooled air.
- Particle-bound PAH is collected on a heated filter, used to separate the particles from the gases. Water is removed in a condenser inserted after the filter but before the absorbent. Finally a sorbent material is used to sample the gaseous PAH.
- A cooled and lined or inert sampling probe is used. Condensed moisture is collected in a condensate bottle or impinger. The particle-bound and gaseous PAH are collected on filter and solid adsorbent, respectively.

Once the samples arrive in the analytic laboratory, the particle-bound and gaseous PAHs are extracted from the filters and adsorbents into an organic solvent. Then, the solvent is analysed by gas chromatography with a mass spectrometry detector[36]

Sometimes it is important to know which PAHs are present as gases and which are particle-bound in an off gas. This is because the distribution of compounds between gas and particulate matter can be significant to the chemistry of the atmosphere, the efficiency of industrial off-gas filtration systems and also to human health. **It is very important to understand, however, that these standard sampling strategies are not designed to give an accurate distribution between the particle-bound and the gaseous PAH. The ambition of the standards is to give an accurate sum value for the total PAH-concentration.**

If the distribution between gaseous and particle-bound PAH is not important, it is possible to collect both particles and gas into a liquid phase. The liquid phase adsorbent is typically a solvent which adsorbs the gaseous PAH molecules and dissolves the particle-bound PAHs so that the analysis of the adsorbent/solvent liquid gives the total PAH concentration.

2.2.2 Non-standard method used in the silicon alloy industry today

In the silicon and ferrosilicon industry, it is often assumed that PAH emissions from normal operation of an open or semi-open submerged arc furnace can be ignored. Irregularities in the furnace operation on the other hand are still a concern with respect to PAH emissions to air. PAH emissions to air are therefore assumed to occur only/primarily if/when an emergency pipe must be used to evacuate furnace gases. Under such circumstances, the furnace off-gas is not filtered and both gaseous and particle-bound compounds may escape. The emissions of PAH during emergency pipe furnace operation are typically estimated based on a PAH-analysis of dust from the large industrial filters, known as *bag house* filters. This dust can be sampled regularly and frequently, using a grab sampling method. The PAH levels can thus be averaged over any time intervals. To estimate the total-PAH emissions, the analysis values are combined with measured data for the gas flow and dust concentration in the emergency pipe during the irregular furnace event. Importantly, grab sampling is very different from the standard methods described in the previous section and introduces other sources of uncertainty to the calculations.

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[35] Kero, I.T., et al. "Airborne emissions from Mn ferroalloy production." JOM 71.1 (2019): p.349
[36] A standard describing the analysis step is, for example, the Norwegian standard NS 9815

2.3 Key PAHssion project results

The PAH content in off-gas can vary greatly, but the root cause of the variations in the process is not understood. Therefore, the effect of process variation is often disregarded (ignored) when the uncertainty of measurements is discussed. As of today, PAH emissions are measured by discrete sampling for emission points, as described in chapter 2.2. Typical sampling times are a few (2-6) hours, and the samples are typically collected only a few (2-6) times per year at each industrial site.

Figure 2.1 illustrates the relative contribution of different factors to the total uncertainty of an annual emission estimate, based on a standard measurement program. More frequent or longer sampling periods would be beneficial e.g. for determining the yearly emissions. Unfortunately, the standard methods (as explained in section 2.2.1) for sampling and analysis of PAH are expensive and thus prevents such strategies from being practically feasible long-term solutions.

The measured PAH emission levels tend to have very large variations between results, even for samples taken back-to-back at the same sampling location. From these experiences, there is a clear suspicion that process variations strongly affect PAH levels. Unfortunately, the correlation between PAH emissions and process dynamics within the various industrial processes is not known. This knowledge gap of both the correlations and the causations constitutes a major barrier to efficient emission reduction through process improvements. Thus, any tool that can aid the learning and documentation of how PAH form during different types of processes and process conditions would be extremely valuable.
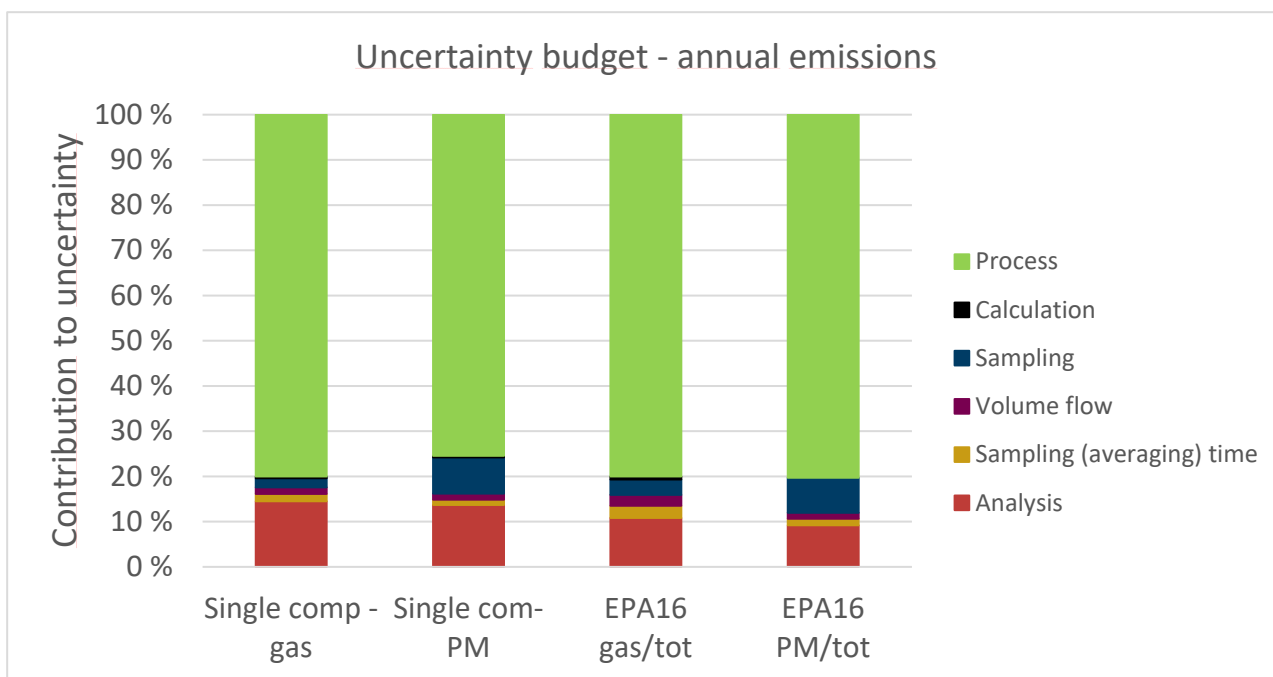

Figure 2.1: The relative contributions to the total uncertainty for estimated annual emissions. Note that this applies to industrial sites with standard measurement programs. Some industries have developed their own, alternative measurement/estimation procedures for which this budget is not valid.[37]

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[37] Eidem, Hunnes, Moen Strømsnes et al. SINTEF Report No 2022-00272: Kilder til usikkerhet ved måling av PAH i avgass - Polysykliske Aromatiske Hydrokarboner (PAH) (Restricted)

2.3.1 Proxy parameters for PAH

A potential proxy is a measurable quantity/parameter that correlates with the standardised measurement values, and the correlation must be established and documented to an acceptable degree. Then, the monitoring can be performed by indirect measurement of the new proxy parameter. By understanding how the PAH emission from a certain source distributes between individual PAH components, a correlation with a more easily measurable component can be made. The challenge lies in establishing the correlation to a scientifically acceptable degree in order to have a solid foundation for the new proxy approach. To this end, statistical and multivariate analysis of large amounts of industrial data is needed.

In the PAHssion project, most industrial sites investigated were dominated by the gas-fraction of PAH. And the gas fractions in turn were often dominated by Naphthalene in addition to other, light, non-EPA16 components, like the 1- methylnaphthalene and 2- methylnaphthalene.

Substantial data crunching led us to believe that no individual PAH compound constitutes a suitable PAH-proxy in this type of industries[38]. The gas-fraction may, however, be an acceptable proxy under certain circumstances. The most important condition is that the dust concentration is not too high (i.e. isokinetic sampling is not necessary).

2.3.2 Online monitoring

The global trend for emission measurements is towards more and more online monitoring. Modern sensor equipment tends to be small and relatively inexpensive. The potential for online monitoring of PAHs however, is currently limited to proxies. It is, for example, possible to monitor volatile organic compounds (VOC), which may be used as a proxy for the gas fraction of the PAHs. There is very limited instrumentation commercially available for online process monitoring of PAH and/or components relevant to PAH-estimations by proxy. Photo-ionization detectors (PID) provide an interesting option for online monitoring of PAH by proxy. It allows the user to see, in real-time, how organic off gas components vary with time in the process. Although a PID does not specifically detect the EPA16, many of the lighter PAHs are among the VOCs detected by the PID so the overlap is significant.

The PID seems to work well at industrial sites where manganese ferroalloys, silicon carbide and carbon materials are produced. It did not however, work equally well at silicon and ferrosilicon smelters because the PAH levels are extremely low, and therefore difficult to separate from signal background/noise. Also, the NOx concentrations in this industrial branch were often high enough to interfere with the PID signal. The SINTSENSE instrument, devised in the PAHssion project, is an example of this combined online-proxy approach based on PID.

The SINTSENSE[39][40] instrument has been deployed and tested for several months at different industrial sites representing different industrial branches. Figure 2.2, show the signals from an industrial site as logged by SINTSENSE during the PAHssion project.

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[38] Aarhaug & Eidem SINTEF Report 2021-01177 Aggregated measurement results and industrial data (Restricted)

[39] Aarhaug, T.A. et al., SINTSENSE: Low-Cost Monitoring of VOC Emissions from the Ferroalloy Industry (2021). Proceedings of the 16th International Ferro-Alloys Congress (INFACON XVI), Available at SSRN: https://ssrn.com/abstract=3926076 or http://dx.doi.org/10.2139/ssrn.3926076

[40] Aarhaug, T.A., SINTEF Blog 2020: SINTSENSE: VOC Sensor System for Air Quality Monitoring. Available at https://blog.sintef.com/industry-en/sintsense-voc-sensor-system-for-air-quality-monitoring/
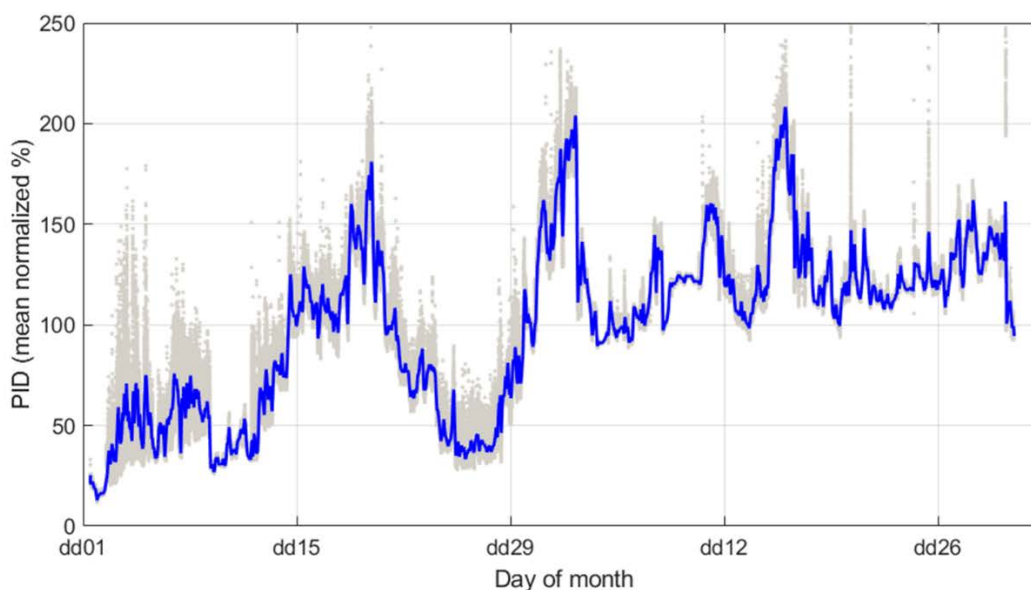
Figure 2.2: Normalised graph representing the PID signal logged over one month at a manganese ferroalloy smelter. 100% corresponds to the average level of that particular site and month. Blue line shows the PID data smoothened by 2h-averaging.

The online signal allows the industries to relate their own emissions to operational changes, for example to see if alterations in raw materials influences the emissions. They can learn which operational efforts have an impact on the emissions and then optimise the process accordingly. Thereby the sensor can actually support each company in their efforts to reduce emissions.

It should be emphasized though that the PID will not be able to replace the standard measurements any time soon, but it can be a very valuable complementing method. An online sensor can provide a context within which the results obtained less frequently by standard methods can be understood. A graph like the one in figure 2.2 offers a framework for the standard measurement results and its possible to see if the standard values were obtained at a peak, near the average baseline or at an abnormally low level. It is also possible to design better measurement programs for standard methods when the variations are known. If, for example, there are process cycles which should be covered by the standard samples.

2.3.3 Sampling time

The variation in PAH levels between standard samples taken back-to-back in an industrial stack can be high, (often > 50 %, as illustrated with the 2h smoothing in figure 2.2). When the annual emission estimates are calculated based on such samples (typically taken twice a year or so), it is uncertain how well the numbers represent the real emissions. As a consequence, a methodology allowing 24 hours sampling was suggested (and tested) in PAHssion.

The longer sampling time improve representativity because all variations occurring on time scales shorter than 24 h are evened out. This is an advantage for emission estimates based on few (2-6 measurements per year) and may thus support the task of emission reporting. However, neither 2h nor 24h samples can support process optimisation where much higher time-resolution is typically needed.

A sketch of a 24h-sampling setup tested in PAHssion is shown in Figure 2.3. Compared to the standard sampling methodology, the main changes are larger capacity of filter and sorbent (XAD2), necessary to capture the increased amount of PAH to be caught..

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When comparing the 24-hour samples with the standard 2-hour samples, there is relatively good agreement. The distribution of PAH components was the same for both sampling methodologies, and both methods showed that most of the PAH (>95 %) was in gaseous form. The 2-hour samples had more than 50 % variation between them, which is in the same order of magnitude as historic data at this site. The variation between the long-term samples was low in comparison. The results suggests that 24h sampling intervals are sufficient to average out a considerable part of the variations in PAH. It is important to remember however, that variations with a time constant of more than 24-hours still exist. [41] [42]

A. Heated sample lance
B. Heated filter-housing
C. XAD-2
D. Flow control unit
   - Silica gel drying-tower
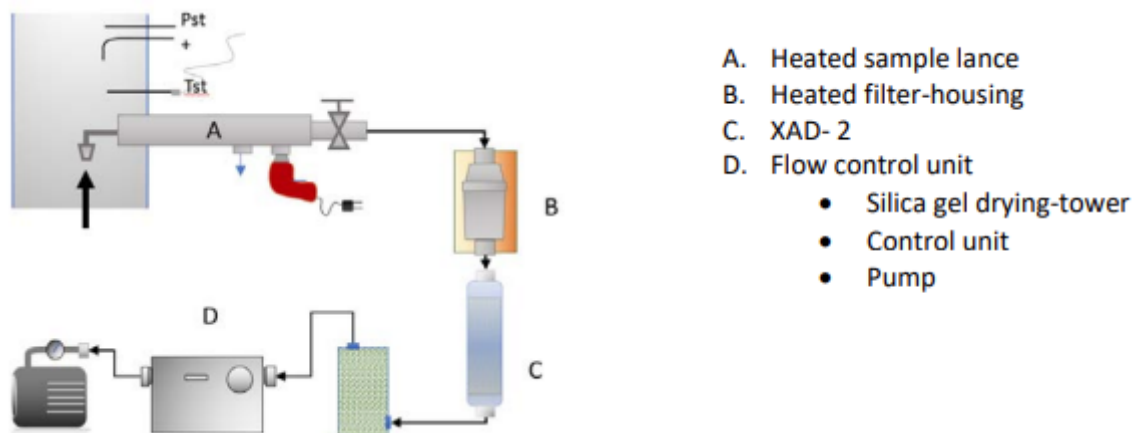   - Control unit
   - Pump

Figure 2.3: Sketch of PAH sampling line with sampling lance (A), filter (B) and XAD-2 absorption cartridge (C). Sample flow is control based on continuous temperature and flow measurement in the stack to ensure isokinetic sampling conditions with help of flow control unit (D).

2.3.4 Sampling frequency

Thermal desorption (TD) tubes could represent an interesting compromise between the standard measurement strategy and an online assessment. The TD-sampling procedure is fast, simple, and the analysis can be automated to a much higher degree than the standard methods. This in turn reduces the cost substantially compared to standard measurements and makes it possible to analyse many more samples for the same cost. A typical TD-sampling setup does not weigh more than ca. 500 g but it is mostly used to collect the lighter PAH components. The sampling times are also short (10-60 min). [43] [44] Figure 2.4 illustrates how the TD samples correspond to the online signal from a PID. The short sampling intervals increases the resolution to (almost) match the PID.

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[41] Kjos et al. SINTEF Report No 2021-00725: Eramet Porsgrunn Målekampanje-kun ekstraktiv måling (Restricted)

[42] Kjos et al. SINTEF Report No 2022:0094 PAHssion measurement campaign at Elkem Carbon (Restricted)

[43] Markes International, Application note 115: Simple and reliable quantitation of ppt-level PAHs in air by TD-GC-MS, 2016.

[44] Wallace, Whitaker and Oliver, "*Recovery and reactivity of polycyclic aromatic hydrocarbons collected on selective sorbent tubes and analyzed by thermal desorption-gas chromatograpy / mass specrometry*," J. Chromatogr A., 2019.
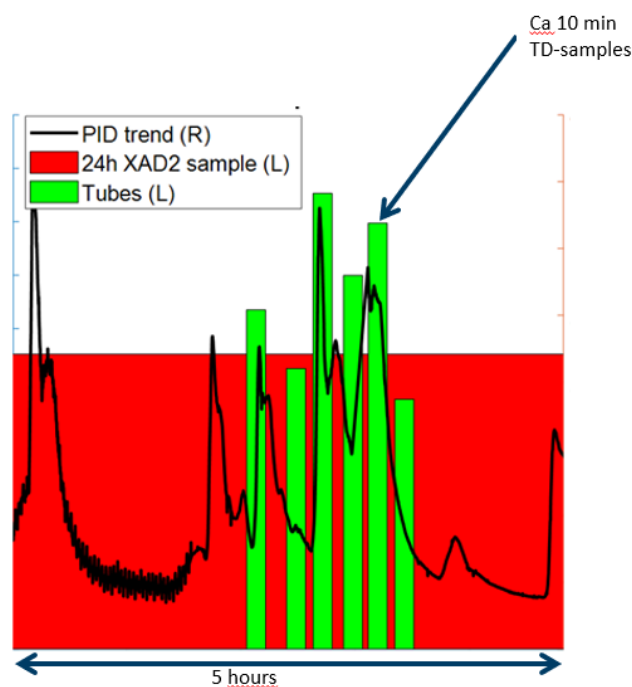
Figure 2.4: An illustration of the correlation between three different measurement methods trialled in the PAHssion project. The red field shows the result from a 24h sample of gaseous PAH sampled in XAD2. The black graph shows the PID signal over 5h as logged by the SINTSENSE instrument. The green bars illustrate the PAH concentration analysed by TD tube sampling (approximately 10 minutes per sample).

The use of TD tubes, however, can only be applied on the condition that isokinetic sampling is not necessary, that is when there is no (or not too much) dust. To establish that this is the case, it must first be ascertained that the emissions are dominated by the gaseous fraction or that there is a known correlation between the gaseous and particle-bound PAH fractions.[45]

2.4 Take-aways from the PAHssion project

PAH emissions vary greatly with the processes in which they are generated. The process variations contribute significantly to the uncertainty of the annual emission estimate. The variations and what causes them in industrial processes are not well understood. Since process variation is usually an unknown factor, it is not possible to quantify its contribution to total emission estimates. Instead, it is generally neglected.

Significant process variations occur over different time scales, from seconds to seasons. Annual emission estimates based on only a few standard measurements per year do not represent the process well, especially when the process variations are not known. Longer sampling periods up to 24 hours are possible and able to even out the variations which occur on a time scale shorter than 24h.

Representativity is improved by increased sampling time, but the sampling and analysis procedure remain time consuming and costly. An even better way to improve representativity is to increase the sampling frequency. Increasing sampling frequency while still using standard methods is often prohibited by costs (labour). In practice, increased sampling frequency requires that the cost per sample is reduced. This in turn is possible when PAH can be sampled by proxy.

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[45] Kjos et al. SINTEF Report No 2022:0094 *PAHssion measurement campaign at Elkem Carbon,* 2022. (Restricted)

The gas fraction dominates PAH in the industries examined in the PAHssion project. The gas fraction of the PAH can be a useful proxy for PAH if isokinetic sampling is not necessary, which is essentially when PM concentrations are low enough. Under such conditions, the volatile organic compounds (VOC) also represent a possible proxy for PAH. In such cases, thermal desorption (TD) tubes can be used for cost-efficient sampling and analysis for PAH or VOC. If VOC's can be accepted as a proxy, a photo ionisation detection (PID) can be used for online monitoring.

An online monitor allows the industries to relate their own emissions to operational changes, for example to see if alterations in raw materials influences the emissions. It shows which operational efforts have an impact on the emissions and allows the process to be optimised accordingly. Thereby the sensor can actually support each company in their efforts to reduce emissions.

An online sensor also provides a context within which the results obtained by standard methods can be understood. It is possible to design better measurement programs for the standard methods when, for example, the sensor can show if there are process cycles which should be covered by standard samples.