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Norwegian Institute for Air Research

NILU's Strategic Institute Initiatives (SIS)

2015

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ABSTRACT

Each of NILU's Strategic Institute Initiatives(SIS) is required to deliver a popular science report annually to the Research Council. This report contains all of NILU's annual SIS-reports for 2015.

NORWEGIAN TITLE

NILUs strategiske instituttsatsinger (SIS) - 2015

KEYWORDS

SIS

ABSTRACT (in Norwegian)

Alle NILUs strategiske instituttsatsinger (SIS) skal levere en populærvitenskapelig framstilling til Norges forskningsråd hvert år. Denne rapporten inneholder alle NILUs årlige SIS-rapporter for 2015.

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Preface

NILU receives basic funding from the Ministry of Climate and Environment through the Norwegian Research Council. 40 % of the basic funding is allocated to Strategic Institute Initiatives (SIS). After an initial process at NILU, the topic of each new Strategic Institute Initiative is discussed with the Norwegian Environment Agency before it is accepted as a SIS by the Norwegian Research Council.

Each SIS is required to deliver a popular science report annually to the Research Council. This report contains all of NILU's annual SIS-reports for 2015.

Contents

1 SACC - Strategic Aerosol Observation and Modelling Capacities for Northern and Polar Climate and Pollution

Annual report 2015 and final report

Duration: 01.01.2011 – 31.12.2015 **Project leader:** Markus Fiebig
Budget 2015: 1,667 MNOK **NILU project:** B-111011

Background
Atmospheric aerosol has a wide range of effects relevant not only for scientists, but also at the policy making level and for the general public. Atmospheric aerosol particles influence climate by scattering incoming solar radiation back into space (direct climate effect, cooling), and absorbing infrared radiation emitted by the Earth surface, thus heating the atmosphere (semi-direct effect, warming). They also influence climate by increasing cloud reflectivity and lifetime (indirect effect, cooling). In the net balance, atmospheric aerosol particles exert a cooling forcing on climate. The 5th IPCC assessment report identifies deficits in the understanding of the atmospheric aerosol climate effects as one of the most significant sources of uncertainty in climate predictions. Here, the deficits in understanding are significant for the direct aerosol climate effect, and even larger for the indirect aerosol climate effect. These uncertainties do not question the facts that climate has been warming, and that human activity is contributing significantly to this change. However, uncertainties in the magnitude of the atmospheric aerosol climate effect contribute significantly to the uncertainty in quantifying future climate change, and thus impact planning of mitigation measures.

Last, but not least, atmospheric aerosol affects human health by influencing the respiratory and cardiovascular system, leading to 300 000 premature deaths annually in Europe. While aerosol concentrations and properties are strongly influenced by local and regional sources in urbanised and industrialised areas, it is also transported on longer scales. Transport pathways go between the continents, but also pole-ward from the source regions at lower latitudes.

Strategic Relevance
The project answers the research needs specified in the relevant strategic documents, i.e. the “Prioritised research needs in the area of environmental management 2010 – 2015”, the 2009 – 2012 strategy of the Norwegian Research Council, and the Norwegian Parliament Announcement Nr. 30 “Klima for Forskning”:

- Better understanding of climate system, with focus on northern and polar latitudes, the effects of atmospheric aerosol, and changes in natural emissions
- Knowledge on long-range transported particulate matter (sources, chemical composition, effects) and consequences of climate change thereon
- Answer challenges on society posed by climate change, feed into national research focus on climate
- Foster international collaboration to meet challenges posed by climate change while underlining international excellence

- Extend capacities and competence in areas of strategic importance by building on areas where host institution is already strong
- Improve efficiency and international competitiveness by developing national and Nordic division of labour in climate research further while focussing on strong own areas of expertise/capacity building and national, Nordic, and international collaboration and networking
- Lasting effect of efforts by focussing on equipment and infrastructure (Forsk 2012), extend capacities for monitoring climate relevant parameters at Northern / polar latitudes for early detection of climate forcing and change signals
- Reduce uncertainty of climate predictions by focussing on largest uncertainty sources, aerosol-cloud interaction and the hydrological cycle

The project

The project-structure reflects the extreme range of atmospheric aerosol effects with scientific and social relevance. The project is organized in three work packages (WPs), each addressing a challenge identified as research priorities by the Norwegian Environment Agency and the Norwegian Research Council.

WP1: Observations Tailored to Assessing the Indirect Aerosol Climate Effect

To reducing the uncertainty of model-based climate predictions, where the uncertainties are caused by insufficient knowledge of the indirect aerosol climate effect, targeted, high-quality observations are needed. Corresponding observations are made by means of a Cloud Condensation Nucleus Counter (CCNC). Inside this instrument, an “artificial cloud” is generated, i.e. the air sample is exposed to conditions as it would experience by passing through a cloud. In this way, the influence of the aerosol particle phase on cloud formation can be studied even inside a surface in situ monitoring station. More specifically, the instrument counts the fraction of aerosol particles that are activated to cloud droplets, as a function of water vapour supersaturation the particles may be exposed to in a cloud. Data of this type are needed to test, verify, and improve the modules of climate models that describe the indirect climate effect of atmospheric aerosol in the model.

In the course of the project, CCNC measurements were established at Birkenes station, Norway’s atmospheric observatory in the South of the country, including operating procedures, quality assurance, and data reporting. In the frame of this project, it was also planned to collect observations from a corresponding instrument operated at Zeppelin station, Ny Ålesund, Spitsbergen, by the Korean Polar Institute, for archiving the data properly and making them available in the World Data Centre for Aerosol operated by NILU. This task revealed a shortcoming in the current data management infrastructure around Spitsbergen. A culture for open data sharing is not established in many research fields in Spitsbergen. Thus, collaborations depend critically on personal connections between scientists scattered around the globe, and means for enforcing an open data culture are lacking. This task will continue through NILU’s ongoing roles in the Svalbard Integrated Earth Observing System (SIOS) and Norwegian Scientific Data Network (NorDataNet).

The ability of an aerosol particle to act as cloud condensation nucleus depends on its size and chemical composition. Thus, observations of the aerosol particle cloud nucleation properties are combined with online measurements of the particle chemical speciation,

preferably at the same time resolution. In collaboration with NILU's ongoing Strategic Institute Project "Beskrive kilder, dannelse og transport av kortlevde klimadrivere ved bruk av nye avanserte målemetoder» (SCLF), this has been achieved by means of installing a novel instrument in parallel, an "Aerosol Chemical Speciation Monitor".

Feeding such advanced datasets on the indirect aerosol climate effect into a climate model to test and improve it is an elaborate process. Corresponding data from several stations need to be combined to derive systematic variations depending on aerosol type, and to give a systematic view of the dependence of cloud activation on particle chemical composition. To facilitate this, the project collaborates with partner stations in the EU-supported "Aerosols, Clouds, and Trace gases Research InfraStructure Network" (ACTRIS). The work on the result, an overview over the aerosol cloud activation properties in Europe and its dependence on aerosol chemical composition, will continue after the end of this project.

WP2: Global Transport Pathways of Particle-Bound Air Pollution with Focus on Southern Polar Latitudes

In order to calculate and predict the *anthropogenic* climate effect of atmospheric aerosol particles, climate models need to be able to distinguish between their contribution and the climate effect of *natural* aerosol particles. The lack of a reliable benchmark on the magnitude of the climate effect of atmospheric aerosol particles in the pre-industrial state, i.e. largely undisturbed by human activity, constitutes one of the largest contributions to the uncertainty of current climate predictions (Carslaw et al., 2013). As an approximation for pre-industrial aerosol, it has been proposed to study the aerosol processes in the remaining most pristine conditions, such as Antarctica.

To this end, this work package investigated the annual cycle exhibited by the physical and optical properties measured in the background aerosol at Norway's Troll station in Queen Maud Land, Antarctica (see Figure 2-1). By connecting the measured physical properties with the optical ones using scattering theory, it was shown that the annual cycles in both sets are closely connected, i.e. the annual cycle in the optical properties is due to the annual cycle in the physical properties. By comparison with corresponding data collected at other Antarctic stations (South Pole and Dome C), it was demonstrated that the observed annual cycle in the Antarctic background aerosol is a phenomenon common to the whole Central Antarctic Plateau and the air masses originating from there. The last step in the analysis made use of the Lagrangian transport model FLEXPART operated at NILU (Stohl et al., 2005). The model calculated the transport plumes backward in time for the air masses arriving at Troll station, and calculated the average light energy density the air masses were exposed to during transport. The light energy density was then correlated to the aerosol particle volume observed in the air mass to test the assumption that the aerosol particles in Antarctic background air are formed mainly by photo-chemical oxidation of gaseous pre-cursor substances. The analysis confirmed that the data are consistent with this theory. The transport calculations revealed also that Antarctic background air is transported upward either in tropical convective clouds or mid-latitude frontal systems to altitudes of the upper troposphere or lower stratosphere. From here, it is transported poleward at this altitude, and descends to the surface within the Antarctic high pressure system (Fiebig et al., 2014).

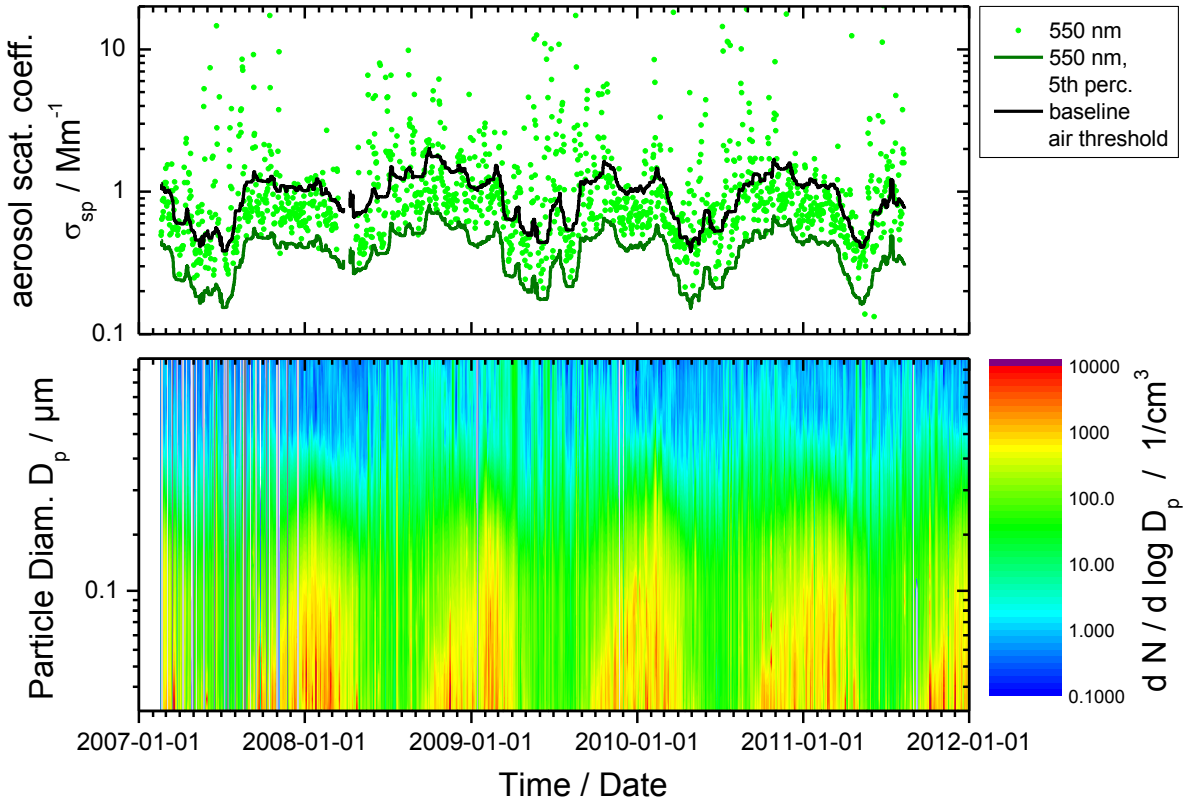

Figure 2-1: *Time series of the particle scattering coefficient (at 550 nm wavelength, top) and the particle number size distribution (bottom) measured at Troll station, Antarctica, in the years 2007 – 2011. The graphs illustrate the annual cycle in the background aerosol, which was subject of investigation in the project.*

The last task of the work package consisted of extending the analysis into the future, and to investigate how atmospheric transport patterns to Antarctica in general and Troll station in particular will change in a changing climate. The analysis again made use of the FLEXPART transport model in backward mode, this time driven by wind fields predicted by the Nordic Earth System Model (NorESM) until the 2070s. The analysis studied the footprints of the transport plumes, i.e. the regions where the air arriving at Troll station resided in the boundary layer where it is potentially exposed to aerosol sources. The result, displayed in Figure 2-2, shows surprisingly little change of the transport patterns on the annual average. Only autumn and winter show slight increases of the potential source strength over the Southern Atlantic Ocean when comparing the years 2050 – 2069 to the years 1990 – 2009. Thus, the Antarctic continent will likely retain its rather pristine atmosphere even in a changing climate.

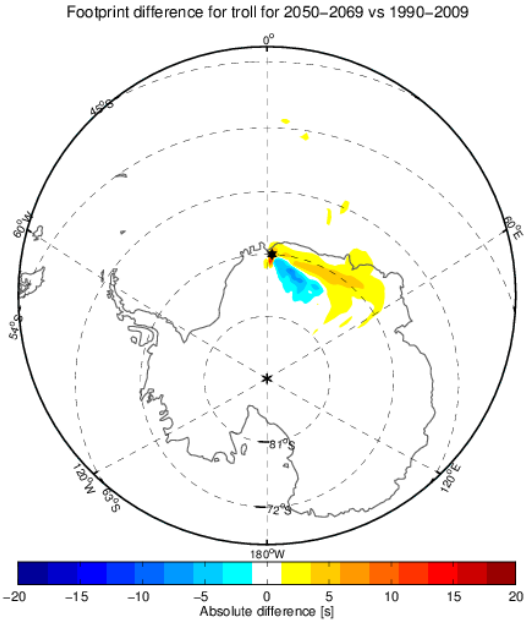

Figure 2-2. *Map of absolute difference in surface source sensitivity for Troll station, comparing the period 2050-2069 to the period 1990-2009.*

WP3: Past, Present, and Future Air Pollution Transport to Norway

Source attributions of climate forcing agents and pollutants are a prerequisite for emission policies. In Norway, there are two major stations monitoring a large spectrum of atmospheric trace constituents needed for a source attribution analysis: Zeppelin Observatory in Ny-Ålesund, Svalbard, and Birkenes Observatory at the southern tip of the Norwegian mainland. In the frame of this work package, the observatory at Birkenes was upgraded with observations of levoglucosan concentration, which is a tracer of biomass burning. It was intended to combine those with existing observations of microphysical, optical, and chemical atmospheric aerosol properties (EMEP supersite and WMO GAW station in 2009) in order to achieve the envisaged source attribution.

Data from the years 2010-2012 were analysed by means of clustering tools combined with calculations of back trajectories for the whole data provided again by the transport model FLEXPART. For the cluster analysis, NILU used the k-means modules (kmeans, kmeans2) offered by the Scipy/Python tool set, the first of which enables the user to find the optimum number of clusters, while the second provides cluster labels for each data point.

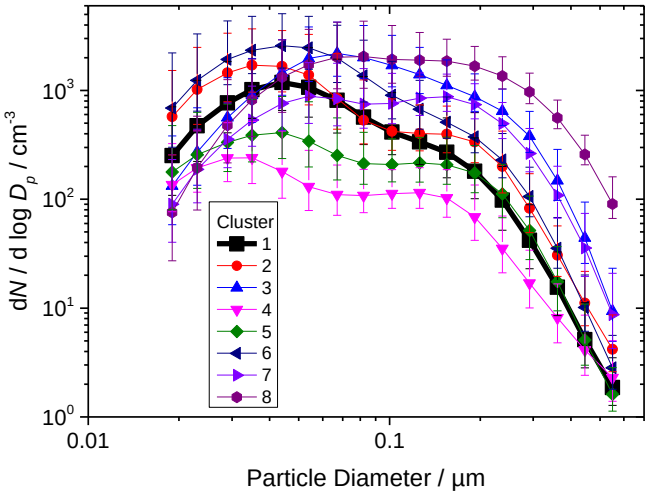

Figure 3-1: *Mean aerosol size distribution from all years included (2010-2012) for all clusters identified in the cluster analysis.*

Due to the largely differing time resolution of the aerosol data sets used (optical properties and size distribution: 1 hour, chemical compounds: 1 day), the analysis

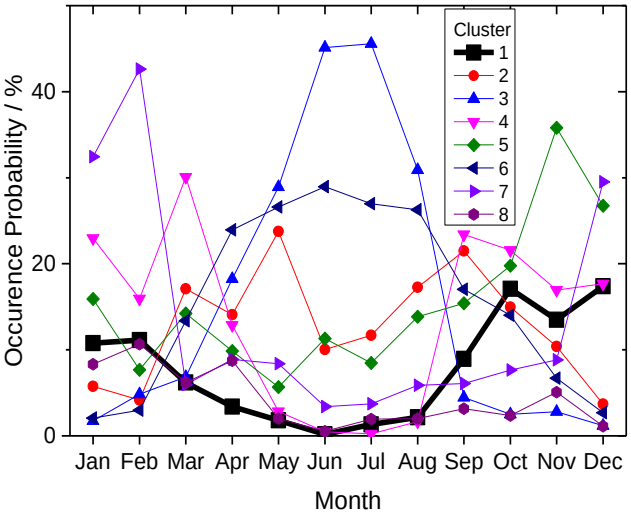

Figure 3-2: *Mean monthly occurrence probability [%] from all years included (2010-2012) for all clusters identified in the cluster*

was performed in two steps, first only including the high-resolution data and secondly with high-resolution data averaged over one day and chemical compounds data. The high-resolution data analysis, utilizing three optical aerosol properties (550 nm scattering coefficient, 522 nm single scattering albedo, 450nm-700nm-Ångstrøm coefficient) and the sub-micron particle number size distribution as physical aerosol property, resulted in the identification of 8 clusters. Figure 3.1 shows the size distribution for all 8 clusters, while Figure 3.2 shows the seasonal distribution of the frequency of the clusters. In the low-time-resolution data, 6 more parameters describing the chemical composition of the aerosol particles (SO_4, NO_4, Na, NH_4, K, and Ca) were included, while all data were gridded to a 1-day time resolution. Again, 8 clusters were identified at maximum, however, the residua from this analysis were larger. Our conclusion is, therefore, that adding information on the aerosol chemical composition at the expense of severely reduced time resolution does not provide additional information with respect to source attribution. This finding is significant since aerosol chemical composition is classically used by itself to attribute aerosol sources. At least for a boreal site such as Birkenes, online observations of physical and optical aerosol properties contain the same or even better information as chemical composition, just with much higher time resolution. The online observations have lately been made available in near-real-time, i.e. between 1-3 hours from the time of measurement. Thus, the findings open for new air mass source attribution products that could be made available on the same schedule.

In order to identify the source regions of the clusters, back-trajectories were calculated for each time point included in the analysis, using the FLEXPART trajectory model. This analysis yielded 8 air mass types, including some with very well defined source regions in continental Europe, but also polar marine air masses, and those dominated by domestic heating (winter) or biogenic aerosol production (summer).

Figure 3-3 shows two examples of source regions for clusters as derived by FLEXPART, one for an aerosol type with a well-defined source region of limited geographical extent (Eastern Central Europe) and one with a source region of (semi-)continental extent (boreal Europe, possibly also other boreal areas).

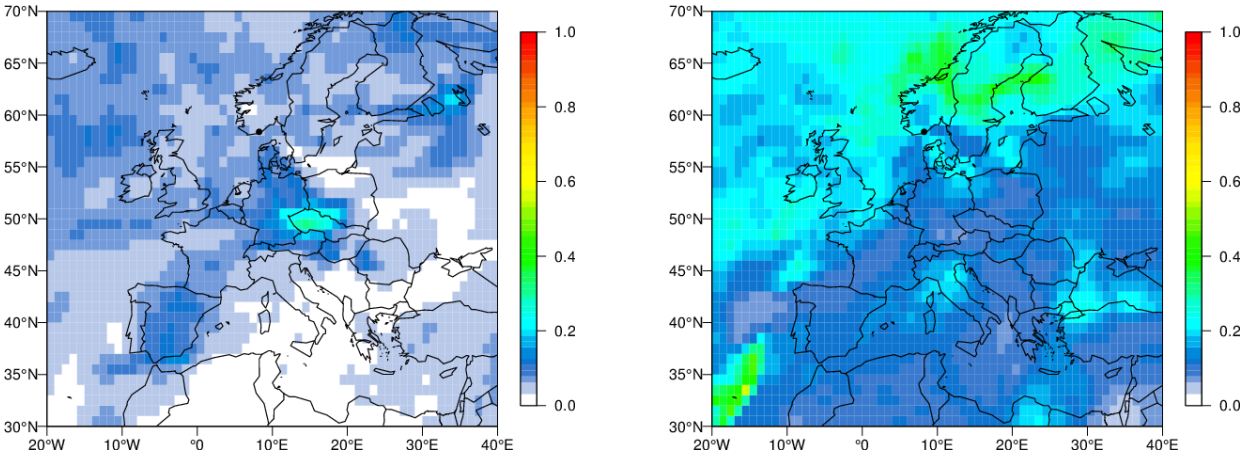

Figure 3-3: *Source region for cluster 1 (Estern Central European and regional winter pollution; left panel) and cluster 3 (aged boreal summer aerosol; right panel) as calculated with the FLEXPART model.*

This positive result of the combined cluster and back-trajectory analysis will enable us to perform a much more comprehensive analysis including many EMEP stations. At the same time it underlines that chemical characterization only can contribute to this process, if one implements measurement techniques with clearly better time resolution.

In the last step of the analysis, NILU investigated how the transport pattern to Birkenes, representative for Southern Norway, will change in the future. To this end, the combination of the FLEXPART transport model, driven by wind fields forecasted by the NorESM climate model, was used to compare the average footprints of 2050 – 2069 to those of 1990 – 2009. The footprint is the region where the backward plume resides in the boundary layer, and is potentially exposed to surface sources. Figure 3-4 shows the relative difference map of this comparison on the annual average, with areas of low sensitivity removed. It is apparent that the source sensitivity increases over the North Atlantic and part of the United Kingdom, and decreases over Sweden, Finland, and Eastern Europe (Figure 3-4). Increasing source sensitivity over the ocean, a region with few pollution sources, will thus likely work together with decreasing emissions due to stricter regulation elsewhere in decreasing pollution transport to Southern Norway.

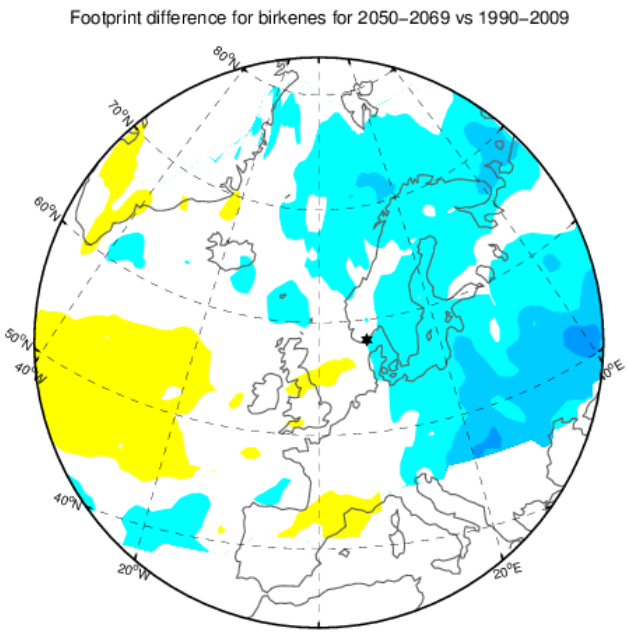

Figure 3-4: *Map of relative difference in surface source sensitivity for Birkenes station, comparing the period 2050-2069 to the*

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Peer-reviewed in preparation:

- Fiebig, M., G.H. Hansen, C.R. Lunder, A. Stohl, R.L. Thompson, K.E. Yttri, W. Aas (2016) Exploring air mass source identification using data from surface in situ aerosol monitoring stations.
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2 OrgSpec - Speciation and quantification of emerging pollutants

Annual report 2015 and final report

Duration: 01.01.2011 – 31.12.2015
Annual Budget: 1,7 MNOK

Project leader: Martin Schlabach
NILU project: B-111088

Background

Analysis of complex mixtures in environmental samples is an extremely difficult task. In most cases, sample matrices require a complex sample preparation. Following that, ultra trace analytical methods are developed for specific groups of substances. This traditional targeted approach provides excellent sensitivity and reliable identification and quantification of the analytes. However, unknowns and untargeted substances have been overlooked even when present at high concentrations. Therefore, suspect and non-target screening methods are increasingly realized as an important tool in environmental chemistry. For organic pollutants, two complementary techniques have shown to be important and relevant. For the lipophilic and non-polar compounds, GC-based techniques like GCxGC-MS-ToF and GC-QToF, are best suited, whereas for the more polar compounds, LC-techniques normally give the best results. Both approaches were tested for a long range of different compounds in the OrgSpec-SIS.

The project

In the first years of OrgSpec, a major focus was given to study of ambient air samples from the Arctic that were analysed on potential new persistent organic pollutants (POPs) by GCxGC/ToF-MS. The samples were analysed for contaminants (e.g. chlorinated and brominated organics, PAHs, PAH analogs and nitro compounds) by applying advanced data filtration tools (VB Scripts). This technique allows detecting of compounds without a commercially available library of known mass spectra. The mass spec library, however, was used either to identify the detected compounds or to determine if further investigation was needed to identify the detected compounds. In addition, the samples were also examined for potential new contaminants that were proposed by modelling approaches. By evaluating the model results, this can help to improve the quality of the available models, as well as develop highly sensitive non-target screening methods for the identification of hitherto unknown POP-like chemical residues in the environment.

In the later years, more focus was given to more polar compounds like pharmaceuticals, personal care products, and a huge range of industrial chemicals. Based on the application of LC/ToF and LC/Q-ToF techniques, a similar non-target screening approach was developed for these compounds of higher polarity. The separation capacity of even the most advanced LC-chromatography cannot be compared to GCxGC-separation. Furthermore, LC-MS-techniques are restricted by mass spectra with less structural information. Therefore, it is necessary to apply a more complex and time-consuming data treatment. In many cases, the structure of the compounds are only tentatively assigned and more research is needed to confirm the identity of the compounds.

During the last years, these techniques were used in a remarkable number of projects for Norwegian Environment Agency (Miljødirektoratet), Research Council of Norway (NFR), Norwegian Polar Institute, ØKOKRIM, other research institutes and different private organizations and customers. Non-target screening has proven to be a practical and useful tool for identification of unknown or new emerging environmental pollutants. It was possible to identify a huge number of new or earlier unrecognized contaminants in different environmental samples. The following compound classes were identified and partially quantified in these studies: pharmaceuticals and personal care products (PPCP) including perfumes and biocides, polymer additives and other compounds used in technical applications including bisphenols, phthalates/adipates, antioxidants, benzothiazoles/ triazoles, pesticides, halogenated compounds (prevailing chlorinated and brominated compounds), and flame retardants (both halogen and phosphorous containing FRs).

Many of these compounds have been classified as of environmental or health concern. These environmental or health concerns enforce reaction of the public, the marked and restrictions by national and international authorities. In most cases, however, these restricted compounds are replaced with compounds of similar technical properties, which often means also similar chemical, environmental, and health properties. Bisphenol A (BPA) for examples was recognised as an endocrine disruptor and there are concerns over its potential impact, particularly on the health of children and the environment. BPA was permitted for use in food contact materials in the European Union (EU). Recently, the restrictions on the use of BPA have forced the polymer industry to replace BPA with bisphenol S (BPS) in thermal paper and other products. Bisphenol F (BPF) and bisphenol B (BPB) are possible replacements in the production of epoxy resin and polycarbonate, and have already been detected in canned foods and soft drinks. In addition to these analogues, Bisphenol AF (BPAF) is used in the manufacturing of phenolic resins or fluoroelastomers. Based on analytical techniques developed under OrgSpec NILU in collaboration with NIVA studied replacements of BPA. Bisphenol F (4,4'-BPF and 2,2'-BPF), bisphenol AF (BPAF), bisphenol BP (BP-BP) and bisphenol S (BPS) were detected in comparable concentrations in effluent, sludge, leachate, sediment and biological samples. These bisphenols have a structural similarity to BPA and unfortunately, may have the same health effects as BPA.

Organophosphorous flame retardants and plasticizers (PFRs) are frequently used as additives in hydraulic fluids, lubricants, floor polishes and as an anti-foaming agent. Chlorinated PFRs have been shown to be carcinogenic. Negative effects on humans and also on aquatic organisms have also been shown for the aromatic PFRs such as TCP and DCP. PFRs have been detected in indoor and outdoor air, even in air in Arctic region such as Svalbard. PFRs are readily found in water from sewage plants, river water and sediments in close connection to urban areas. Analytical techniques were developed under OrgSpec NILU for 15 different PFRs, three chlorinated, 4 aromatic and 8 alkyl organophosphates for two different analytical techniques (GC-MSMS and LC-MSMS). Biota, water and sediments samples from the Arctic, terrestrial and urban environment have been reported were there have frequently been detected PFS such as TCEP, TCPP, TnBP and TBEP.
New techniques developed under the OrgSpec-SIS qualified NILU in performing a screening study for Norwegian Environment Agency for contaminants of emerging concern. The overall objective of these programs are to establish the occurrence and environmental impact of

these new persistent organic pollutants in marine and freshwater environments, with particular focus on their potential to bioaccumulate.

For a fast and effective development of the suspect and non-target screening approach, a strong international cooperation is required. NILU is collaborating in this field with other Norwegian, Scandinavian, and European universities and institutes. Most important during the last years, was the collaboration with NIVA in Oslo with common research projects, NMBU in Ås with common PhD students and with Umeå University. To improve the exchange of ideas, information, data, and mass spec libraries, NILU has also become a leading member of the European NORMAN network (Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances).

The OrgSpec-SIS has proven that non-target screening is a practical and useful tool for identification of unknown or new emerging environmental pollutants. It is possible to identify huge numbers of new or earlier unrecognized contaminants in different environmental samples.

3 SCLF - Beskrive kilder, dannelse og transport av kortlevde klimadrivere ved bruk av nye avanserte målemetoder

Årsrapport 2015

Varighet: 01.01.2013 – 31.12.2016
Budsjett 2015: 1,2 MNOK

Prosjektleder: Wenche Aas
NILU prosjekt: B-113006

Mål
Det overordnete målet med dette prosjektet er å karakterisere kildeopphav, transport, dannelse og prosessering av kortlevde klimapådrivere og deres forløpere ved å utnytte nye avanserte målinger på Birkenes kombinert med statistiske beregninger og modeller.

Bakgrunn
Kortlevde klimadrivere, som partikler og ozon, og deres potensial for å påvirke den globale oppvarmingen de førstkommende 20 år, har hatt stor oppmerksomhet de senere år. Disse komponentene er også viktige for effektstudier relatert til helse og terrestrisk natur. Effektive utslippsreduksjoner forutsetter god forståelse av hvor disse komponentene kommer fra og hvordan de omdannes og transporteres i atmosfæren. Det er store usikkerheter i dagens estimater av partikkelforurensning i Europa, spesielt siden en stor andel av partikkelmassen i stadig større grad ser ut til å bestå av karbonholdig materiale, som er dårlig karakterisert og som har et utall antropogene og naturlige kilder. Nyutviklede instrumenter gjør det mulig å spore kilder på en mer spesifikk måte enn tidligere, de gir kunnskap om andelen som er primært og sekundært dannet, samt til en viss grad fordelingen mellom naturlige og antropogene kilder.

Strategisk relevans
En bedre beskrivelse av kildeopphav for kortlevde klimadrivere er av stor nytte for fremtidig politikkutforming, spesielt knyttet opp mot UNECE LTRAP og EUs AQD.

Nasjonalt er dette også et strategisk viktig tema. Økt kunnskap om klimaendringene og reduksjon av utslipp er sentrale behov slik det er beskrevet i «Miljøforvaltningens prioriterte forskningsbehov 2010 – 2015» og i forskingsmeldingen «Klima for forskning», St.meld. nr. 30 (2008-2009). Av relevans er også Miljødirektoratet rapport med «Forslag til handlingsplan for norske utslipp av kortlevde klimadrivere» som beskriver tiltak for utslippsreduksjoner samt nasjonale overvåkingsbehov.

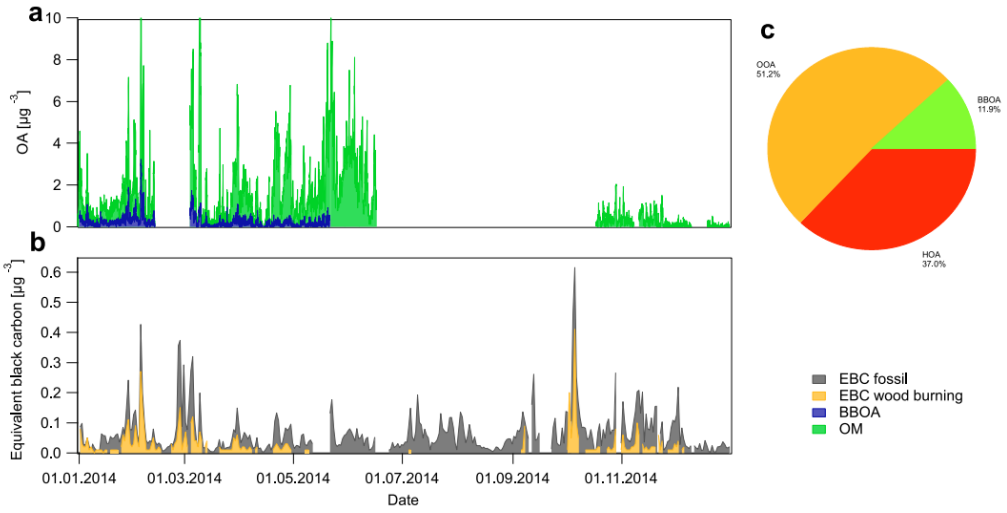
For NILU er overvåking og kjemisk analyse av luftforurensninger en av grunnpilaren i instituttets virksomhet. En strategisk satsning og videreutvikling innen dette feltet ved å utnytte nye avanserte målemetoder kombinert med bedre statistiske verktøy er essensielt for at NILU skal beholde sin sentrale posisjon på dette feltet i Europa.

Sammendrag av aktiviteter og resultater i 2015

Av nye avanserte instrumenter er det i hovedsak snakk om «Aerosol Chemical Speciation Monitor» (ACSM) som måler konsentrasjoner av partikulært nitrat, sulfat, ammonium, klorid og organisk karbon med høy tidsoppløsning og et «Proton-transfer-reaction mass spectrometry» (PTR-ToF-MS)-instrument som måler flyktige organiske forbindelser (VOC). En ACSM ble installert på Birkenesobservatoriet i 2012 for permanent drift, mens en PTR-ToF-MS har vært brukt i to målekampanjer på Birkenes, sommer 2013 og vinter 2013 (Langebner et al., 2014).

Det har vært stort fokus på å sikre høy kvalitet på målingene som har blitt etablert. Dette innebærer å delta i feltsammenligninger, etablere kalibreringsrutiner og rapportering av data. Det har vært et nært samarbeid med EUs infrastrukturprosjektet ACTRIS på dette. Oppsummering av ulike aktiviteter i 2015:

- I desember 2013 tok ACSM instrumentet fra Birkenes del i en europeisk interkalibrering i Paris med tretten andre laboratorier/stasjoner med tilsvarende instrument. To artikler med resultater fra denne interkalibreringen ble publisert i 2015 (Fröhlich et al. og Crenn et al., 2015).
- For å beskrive kildeopphav av forurensningen benyttes et statistisk verktøy spesielt utviklet for dette (Canonaco et al., 2013). Det har vært opplæring i bruk av verktøyet på en workshop i 2015 (Zürich februar 2015) hvor NILU deltok med to personer.
- Det har vært viktig å få på plass harmonisert europeisk datarapportering av ACSM observasjoner inkludert all relevant metadata. I samarbeid med Paul Scherrer Institute (PSI) ble det i 2014 utviklet et templat for innlevering av data, dette ble videreutviklet og forbedret i 2015.
- Resultater fra Birkensobservatoriet ble presentert på European Aerosol Conference i Milano i august (Platt et al, 2015). her ble det ble presentert de første resultantene på kildeallokering av organisk materiale, Figur 1. Denne viser at organiske partikler på Birkenes domineres av oksygenerte aerosol partikler (OOA)
- Analyse av levoglugosan fra filtre på Birkenes for 2014 og det er nå totalt 7 år med data. Tidsserien skal brukes til å gi et estimat av partiklmengden fra brenning av biomasse, og disse partiklenes relative bidrag til den total konsentrasjonen av karbonholdige partikler.
- Det ble installert et nytt ToF-ACSM instrument på Zeppelin høsten 2015 og er i kontinuerlig operasjonell drift. Videre tolkning av disse dataene vil bli viktig i 2016.



Figur 1: *Kildeallokering av karbonholdig materiale målt på Birkenes i 2014. Organiske aerosoler (OA) er målt med en ACSM a) og Ekvivalent Black Carbon (EBC) er målt med en PSAP (sotfotometer) b) Sammensetning av OA er vist i c). OM= organisk masse, BBOA: organiske materiale fra HOA: hydrokarbonlignende organiske aerosoler.*

Videre planer og avslutning av prosjektet

- Det vil bli arbeidet videre med å bestemme kildekategorier ved å bruke observasjoner fra flere instrumenter kombinert med statistiske metoder.
- Trendstudier kombinert med transportmodellering for å bestemme kilderegioner for biomasse brenning ved å bruke levoglukosanmålingene som er gjort på Birkenes
- Beregne hvor stort bidrag lokale biogene utslipp har på sekundære organiske aerosoler (SOA) på Birkenes ved bruk av modeller og målinger fra blant annet PTR-MS-ToF.

Dette arbeidet vil forhåpentligvis resultere i to fagfellevurderte artikler i løpet av 2016 og det vil jobbes for å finne finansiering for å arbeide med tilsvarende studier på de nye observasjonene på Zeppelinfjellet i de neste årene.

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4 AMOM - Advanced modelling of organic contaminants/Avansert modellering av organiske miljøgifter

Annual Report 2015

Duration: 01.01.2013 – 31.12.2017
Budget 2015: 1,2 MNOK

Project leader: Knut Breivik
NILU project: B-113014

Main objective and key modelling tools

The overall goal of the AMOM SIS is to understand and predict relationships between sources and emissions of organic contaminants and environmental and human exposures. A particular emphasis is on the long range atmospheric transport of various organic contaminants. CoZMoMAN and FLEXPART are the two core modelling tools in focus in the AMOM-project (Figure 1). Main activities and results during 2015 are briefly summarized in this report.

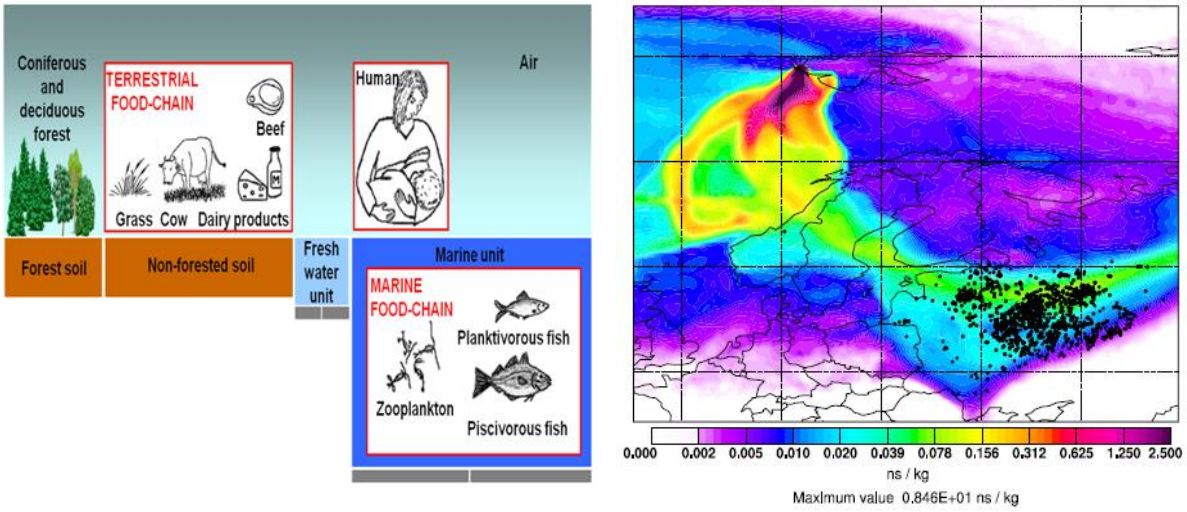

Figure 1*: Complementary modelling tools at NILU to study organic contaminants. Left: Model structure for the CoZMoMAN multimedia model [1]. Right: Illustrative output from FLEXPART whereby record high levels of PCBs measured at Zeppelin (Svalbard) in combination with satellite data (black dots) are traced back to biomass burning events in Russia [2].*

Main activities and results during 2015

During 2015 the main activities have been on multimedia modelling activities, rather than FLEXPART which was prioritized in both 2013 and 2014. More specifically, the main emphasis has been on human exposure modelling, and new multimedia model developments as detailed below.

Human exposure modelling using CoZMoMAN

The CoZMoMAN model, which is at the core of AMOM, is a dynamic multimedia model which aims to describe mechanistically the link between changes in environmental emissions of organic contaminants (e.g. POPs) and the resulting concentrations and exposures of both the physical environment and in the human food-chain (Fig 1, left). It is thus designed to facilitate an evaluation of the environmental and biotic response to temporal changes in emissions (increase and/or decrease). In order to have confidence in model predictions it is however imperative to confront model outputs with observations. Initial model evaluation exercises have previously been carried out for selected polychlorinated biphenyls [1, 3] and short-chain chlorinated paraffins [4] in the Nordic environment, for which the model is currently parameterized. These evaluations have shown agreement between modelled data and measurements within a factor of 2 to 4 in the case of individual PCBs and within a factor of 6 for SCCPs across various environmental compartments (biotic and abiotic).

In 2015, research efforts have continued with support from AMOM in terms of parameterising, programming, applying and evaluating the applicability of the CoZMoMAN model to predict (observed) human exposures of individuals. This activity largely came about because colleagues at NILU were working closely with scientists at the University Hospital of North Norway (UNN), doing human biomonitoring studies of POPs. An initial collaboration showed that CoZMoMAN was capable of reproducing observed time trends of selected PCBs from 1979 to 2007 in men from Northern Norway. However, these first simulations were restricted to a hypothetical “average” person compared with the observed population means [3]. The scientific goal behind the more recent effort was to understand and predict mechanistically the steps in a molecule’s journey from initial release into the environment to its uptake and accumulation in individual Norwegians, using CoZMoMAN. The motivation was in part to further increase confidence in the model by comparing predictions against a new empirical data set, but also, if possible, to evaluate possible impacts of control strategies (emission reductions) and/or changes in lifestyle (e.g. diet) on human exposure at the individual level. For the human exposure modelling exercise, the CoZMoMAN model were adjusted, re-programmed and re-parameterized to facilitate predictions of time-variant person-specific concentrations from birth, based on two cohorts. These two cohorts for which empirical data (measurements of POPs in blood) existed were selected by scientists at UNN, are referred to as the MISA and NOWAC cohorts. In brief, the MISA cohort consists of pregnant women (n=515) in the Norther Norway mother-and-child contaminant cohort study, whereas the NOWAC cohort consists of postmenopausal women (n=311) from the Norwegian women and cancer study. The CoZMoMAN model was run one time for each person, provided with person-specific information (input data) from the two cohorts. This included year of birth of the woman, date of birth and breastfeeding duration for individual children, as well as dietary information (intake of meat, dairy products and fish) based on information from questionnaires. Model results (predicted concentration of selected PCBs in individuals) were stored corresponding to the time of blood sampling. The CoZMoMAN model was found to reproduce all measurements within a factor of ten, and subject ranking and quartile assignments were largely consistent [5].

However, an important feature of the CoZMoMAN model is that it does not only predict concentrations at the time of sampling, but all the way back in time until the woman was

born. A key finding was that the predicted historical trend in exposure varied significantly between individuals, and particularly in the predicted timing of peak concentrations experienced in earlier years (prior to blood sampling). The dynamic feature of CoZMoMAN model thus makes it feasible to estimate past historical exposures of individuals, including possible sensitive time windows in terms of exposures in the context of potential health effects. This feature was further explored by colleagues at UNN [6] who predicted past exposures using CoZMoMAN in a study on the effect of POPs on Type 2 diabetes mellitus (T2DM) in individuals. However, these results did not support a simple association between T2DM and model predicted concentrations of PCBs[6].

New model developments

The CoZMoMAN model was developed at NILU in close collaboration with scientists from University of Toronto and Stockholm University. A deliberate restriction of this model in terms of complexity at the time of development and thereby also realism, is that it is non-spatially resolved and rather focussed on the complexity of accounting for all processes (abiotic and biotic) which are assumed significant for human exposure to POPs occurring through the environment. However, recognizing that POPs are global pollutants, the original CoZMoMAN suffers from not being able to explicitly account for long-range environmental transport and thereby differentiate between sources of POPs from within versus outside the model domain. From a policy perspective, this is a regrettable shortcoming as an evaluation of rational control strategies in Nordic countries calls for a better understanding of the relative importance of e.g. national emissions versus inflows by long-range transport in controlling contaminant burdens.

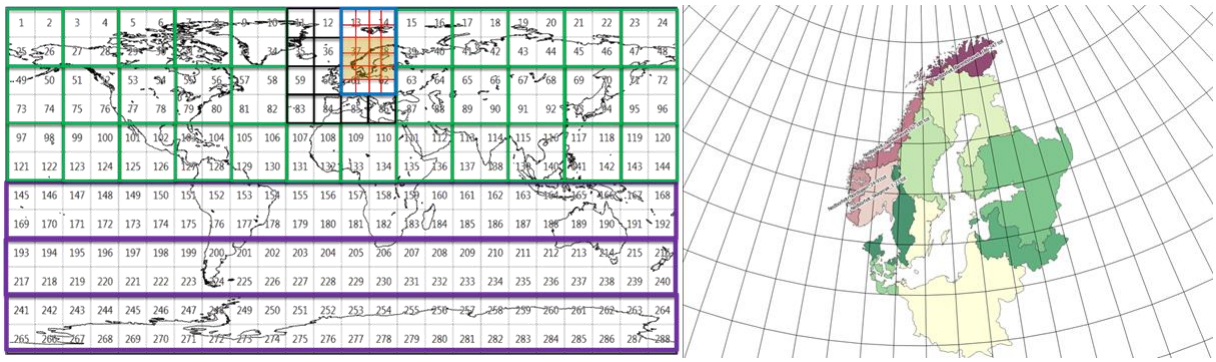

Figure 2: *Illustrative steps towards the new Nordic Exposure Model, which will build upon features from the BETR Global model to account for the global dimension [7], the POPCYCLING-Baltic model previously developed for the Baltic Sea drainage basin in a NILU-led EU project [8], as well as CoZMoMAN [1]. For the physical environment, enhanced spatial resolution will be explored for the Nordic region (left). While the atmospheric compartments will rely on a gridded structure with variable resolution (left), the terrestrial environment will reflect major drainage basins (right). Predicted concentration in exposure-relevant media will ultimately be used to predict uptake in the human food-chain.*

As AMOM represents a strategic research initiative, initial efforts were made to explore and evaluate opportunities for alternative modelling strategies to better account for the global behaviour of POPs while at the same time keeping a focus on the Nordic environment as our target region. In discussion with our international collaborators, this resulted in the

submission of a joint grant research proposal which received funding through the competitive "Økosystem" call (NFR 244298/E50). The new project aims to greatly expand and further improve the CoZMoMAN modelling tool in synergy with AMOM to explicitly account for possible global transport of POPs on environmental and food-chain exposures in the Nordic and Arctic region. Major efforts are currently ongoing on model development and parameterisation of the new modelling tool (Fig 2). It is our hope that the Nordic Exposure Model may be an important scientific tool for interpretation of observations of organic contaminants in both the abiotic and biotic part of the Nordic and Arctic environment, as well as a policy-oriented tool to help assess rational control strategies in the future for both legacy POPs as well as organic contaminants of emerging concern.

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5 TOXROS - Chemical and toxicological characterization of reactive atmospheric species

Annual Report 2015

Duration: 01.01.2013 – 31.12.2016
Budget 2015: 1,2 MNOK

Project leader: Elise Rundèn Pran
NILU project: B-113064

Background and objectives

There has been a need for a reliable and representative *in vitro* model for respiratory exposure to reduce animal testing. Thus, the impact of emerging indoor and outdoor pollutants and newly formed functionalized products on human health have never been comprehensively studied under controlled conditions that are close to the real situation. This require interdisciplinary expertise from tropospheric, analytical and quantum chemistry, as well as from cell biology and toxicology disciplines.

The objective of this interdisciplinary project is to develop a realistic in vitro respiratory model for lung exposure. This model will be applied for toxicity studies by inhalation exposure to study effects of indoor and outdoor air pollutants for human health risk assessment. To obtain knowledge about health effects of emerging pollutants and functionalized mixtures of short-lived organic pollutants, it is essential to develop a combined exposure-effect model, mimicking real exposure on cells of first target, such as lung. The final aim is to develop a reliable model to investigate potential toxicity of various chemical pollutants related to human health by in vitro exposure of human cells in an air-liquid interphase (ALI) model. The cells will be exposed in a well-controlled manner to selected pollutants; functionalized particles, nanoparticles and reactive volatile and semi-volatile organic compound. Underlying mechanisms of toxicity and development of disease will also be explored.

Objectives

1. Develop an advanced *in vitro* human lung model for inhalation exposure that is as close as possible to the real situation (Air-Liquid Interphase (ALI)-model)
2. Develop an exposure system (controllable and measurable) for the lung model
3. Study toxicity and underlying mechanisms of toxicity of:
    a. emerging pollutants
    b. functionalized particles from reactive volatile and semi-volatile organic compounds
    c. Nanoparticles

Work progress

Development of ALI model for respiratory exposure

To reduce toxicity testing on animals and at the same time use models as close as possible to humans, in vitro human cell models are widely used in toxicology. For inhalation studies, a challenge has been that the cells are cultivated and exposed submerged in cell culture medium. However, in vivo, the lung epithelial cells are exposed to liquid on one side and air on the other. Thus, an in vitro respiratory model closer mimicking the in vivo situation would then be comprised of cells cultivated on the interface between air and liquid, as the lung cells are separated from the air only by a thin aqueous lining layer with a surfactant film at the air–liquid interface.

Therefore, our main aim was to set up an air-liquid interphase (ALI) model based upon CULTEX® exposure system for mimicking atmospheric, respiratory exposure conditions. The ALI-exposure model is technically challenging because: i) the cells must be adapted to new conditions, ii) a defined aerosol at constant composition and flow has to be generated, iii) exposure concentrations must be measurable, and iv) the temperature and humidity conditions for the cells should be at physiological level for the whole exposure period.

Cultivation of human lung cells on membranes at the air-liquid interphase

NILU has so far developed and validated protocols for cultivation of human lung epithelial cells under normal conditions, and we have also adopted the selected A549 human lung epithelial cells for cultivation on transwell membranes for the ALI-system. In this system, the cells are growing at the air-liquid interface (ALI), where the upper part of the cells is directly in contact with air and the basal part of the cells is directly in contact with liquid medium, similarly as in situ in the lungs (figure 1). This configuration mimics the conditions found in the human airway, and drives differentiation of the cells towards a mucociliary phenotype. NILU has investigated different media and semi-porous transwell membranes to find optimal conditions for cultivating cells at the air-liquid interphase and for the cells to exhibit morphological and functional characteristics similar to the human epithelium.

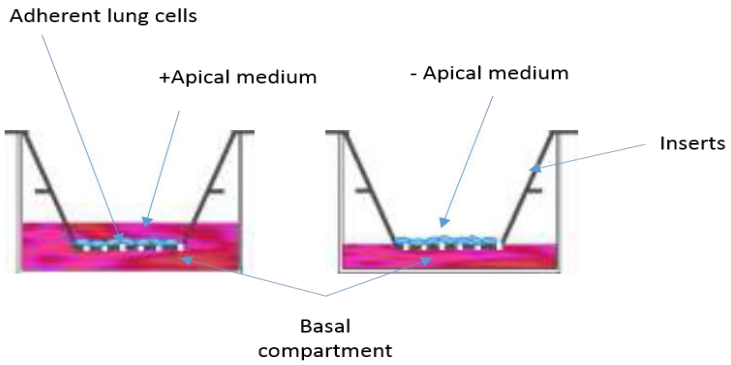

Figure 1: *Human adherent lung epithelial cells (A549) were seeded onto porous cell culture inserts (transwell) as submerged cells (medium in both basal and apical part) (left) or at the air liquid interphase (ALI) where cells were directly exposed to air from above (apical medium removed) and fed from the medium below (right).*

NILU has also designed a set up for exposure of the cells in the CULTEX chamber. The exposure part is challenging and many aspects has to be considered to have control of what the cells are actually exposed to, as well as the dose level.

CULTEX exposure system for ALI-cells

For exposure of the cultivated ALI-cells, a sort of cultivation chamber is needed. Therefore, NILU developed a protocol for cultivation of A549 cells in the CULTEX device. In this set-up, transwell inserts with cells were transferred from conventional 6-well cultivation plates into their corresponding position inside the CULTEX device (figure 2) before the testing.

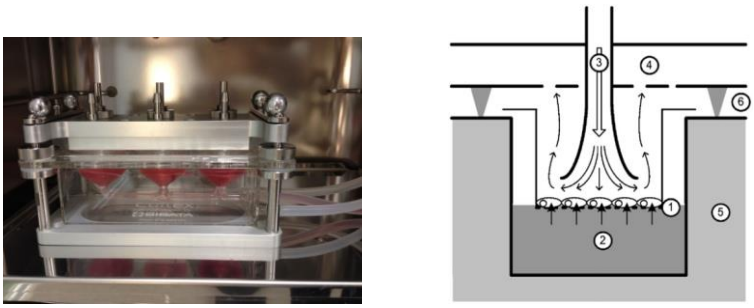

Figure 2: *CULTEX device for ALI exposure of lung cells. The nozzle shape ensure even distribution of the aerosol to the cell layer. Circulating water keeps temperature constant.*

For adaptation of the cells to ALI conditions before exposure, the cells were cultivated with reduced serum concentration to slow growth before removal of apical medium. In our testing, up to 6 hours, cells cultivated on transwell membranes without apical medium were found to tolerate these conditions, and their viability was above 80%. Cytotoxicity assays were performed and validated for the A549 cells both for conventional cultivation, submerged cultivation on membranes and for cultivation on membranes without apical media (ALI). NILU found no significant differences in cells viability with the different cultivation methods. Standard operating procedure was written for cultivation, adaptation before exposure, as well as for proper cytotoxicity assays.

Exposure of cells in the CULTEX system

The cells cultivated at the ALI needs to be exposed to the pollutants and compounds in a controllable manner. It is important to be able to measure what the cell are being exposed to, as well as the exposure concentrations. There are different possibilities for exposure systems for CULTEX, and NILU has visited other laboratories working with the ALI system for getting increased knowledge on this challenging aspect of the model. We have also attended an ALI workshop in Berlin, in which many issues and challenges connected to both cultivation of cells and exposure were discussed efficiently.

NILU has designed and are building an exposure system consisting of two main parts. One part is for exposing the cells to aerosolized nanoparticles and the other part is for exposing the cells to common indoor volatile- and semi-volatile organic compounds (VOCs/SVOCs).

Exposure to nanoparticles

For exposing the cells to nanoparticles, the nanoparticles firstly will be dispersed by sonication into solution. Calibration of the sonicator was performed to obtain optimal conditions for dispersing different nanoparticles. Then the nanoparticle dispersion will be aerosolized using an atomizer. When the particles are airborne, they are wet and charged. A diffusion dryer will be used to dry the particles so that only the pure, dried particles will continue in the airstream. As the particles are charged, it is possible to use an electric field for depositing the particles onto the cells. This is necessary as particles in the size range up to 300 nm have very low deposition efficiency. They are too large for diffusion deposition and too small for gravitational deposition or impaction.

Exposure concentration will be determined using an open source software quartz microbalance. The microbalance measures a mass variation per unit area by measuring the change in frequency of a quartz crystal resonator. The building of the system is ongoing. Using this approach, it will be possible to define specific exposure concentration using the output of the microbalance as input for the atomizer. The exposure system will additionally have a flow control and a calibration unit. The cells are exposed to synthetic air as a control (figure 3).

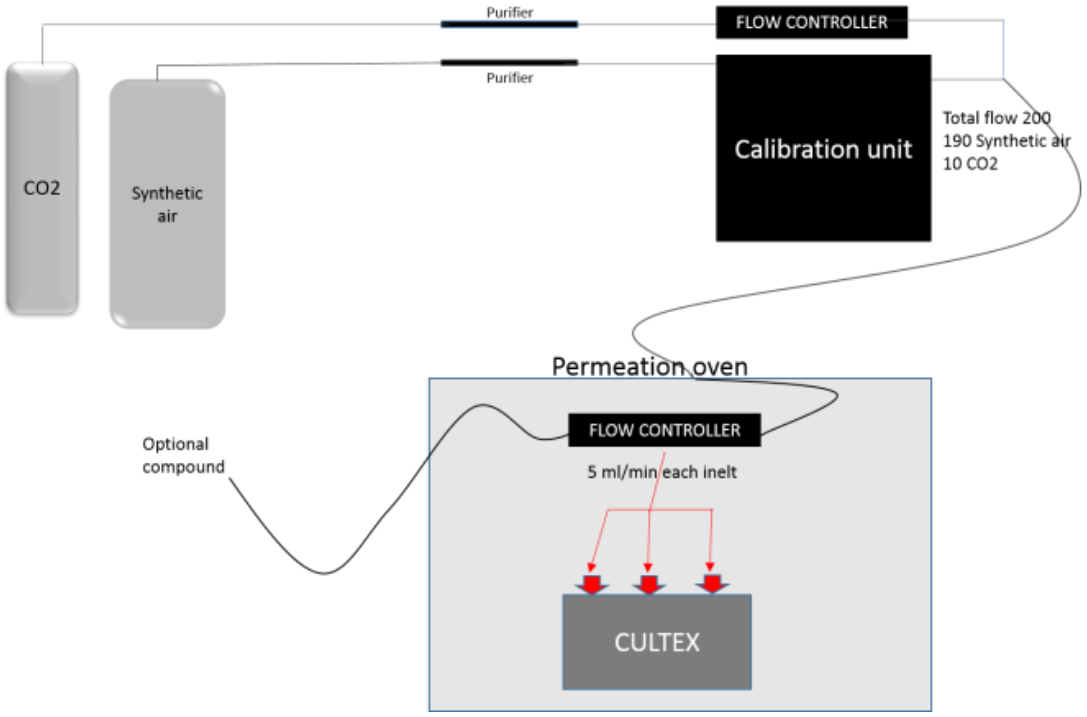

Figure 3: *Preliminary exposure set up for exposure of cells in the CULTEX system to aerosolized nanoparticles or gases.*

Exposure of the cells to volatile organic compounds (VOCs)

For exposing the cells to VOCs, NILU has built an exposure unit which consists of small vials containing a pure liquid VOC and a capillary. This setup utilizes the same principle as a permeation tube. By using a pure component there will be always some molecules in liquid phase and some in gas phase. The amount of molecules in gas phase is depending on the vapour pressure of the component and is highly influenced by temperature. The molecules in the gas phase will diffuse out of the capillary only by diffusion. The exposure concentration can thus be easily calculated and adjusted as long as the temperature is well monitored and easy to regulate. NILU is currently testing out different temperatures and systems for evaporation of the compounds to find a system that is compatible with exposure of the cells.

Toxicity studies

Cytotoxicity testing of nanoparticles on A549 human lung epithelial cells

NILU has, by submerged exposure, tested cytotoxicity of different engineered nanoparticles on A549 human lung epithelial cells. It is important to validate protocols for testing of potential toxicity of nanoparticles on these cells cultivated conventionally before moving on to ALI exposure. We have established a method and developed a protocol for cytotoxicity testing by colony forming efficiency (CFE), measuring cell survival by colony formation. NILU has tested seven different reference nanoparticles from the European depository (reference laboratory, Joint research Center – EC JRC) by CFE assay on A549 cells to standardize the protocol. Analysis is ongoing. Shown in figure 4 is a dose-response curve for NM300K nanosilver measured by colony forming efficiency. Nanosilver showed cytotoxicity also at low concentrations.

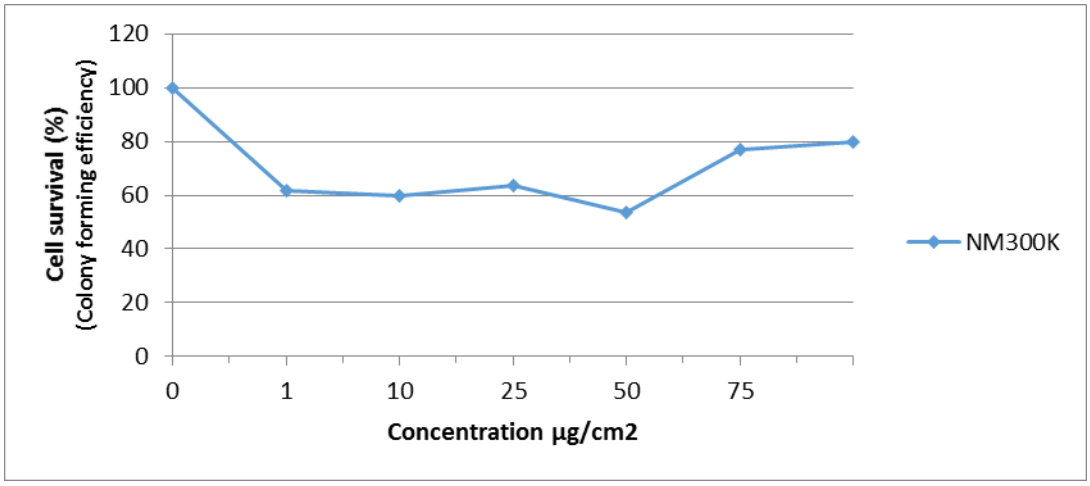

Figure 4: *Cytotoxicty of NM300K nanosilver on A549 cells measured as cell survival in % relative to negative control by colony forming efficiency.*

NILU has also tested the known toxin staurosporine on A549 cells cultivated conventionally, on transwell membranes with and without apical medium. Protocol for physio-chemical characterization of size, size distribution and stability of the nanoparticles in solution by NanoSight NS500 has been developed. All nanoparticles tested for cytotoxicity have also been characterized by NanoSight.

NILU has also tested removal of the cells from the membranes after exposure for testing of genotoxicity by the Comet assay. The Comet Assay detects strand breaks as well as oxidative base lesions. Specific DNA base lesions can be detected by application of lesion specific endonucleases. For high-throughput analysis, the assay has been miniaturized, testing small number of cells and 12 minigels per slide. The 12-gel comet assay has been shown to be applicable for testing of genotoxicity of nanoparticles, without significant interference between the nanoparticles and the assay (figure 5). Also, it works well with the A549 cells.

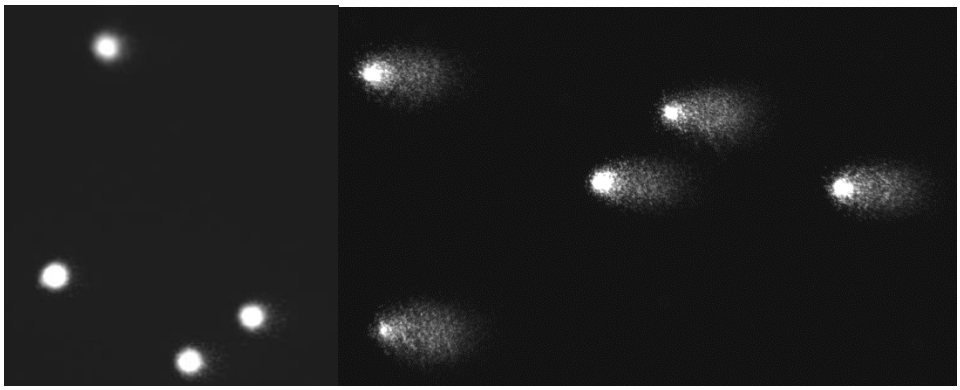

Figure 5: *The picture shows cells with high level of DNA damage, measured as tails (comets) by the Comet assay (right) compared to control cells (left).*

Studies of exposure and uptake of nanoparticles

For exposure of the cells with nanoparticles, uptake of the nanoparticles into the cells is an important issue. NILU performed some preliminary studies with submerged exposure of the A549 cells to e.g TiO2 nanoparticles, and studied uptake by our laser scanning microscope. We were able to visualize the nanoparticles, as well as intracellular uptake in some of them.

The A549 cells were clearly apoptotic after exposure, showing the cytotoxicity of the nanoparticles tested (figure 6). Procedure for both uptake of nanoparticles and measurement of oxidative stress (ROS production) by live cell imaging using Confocal microscope was developed.

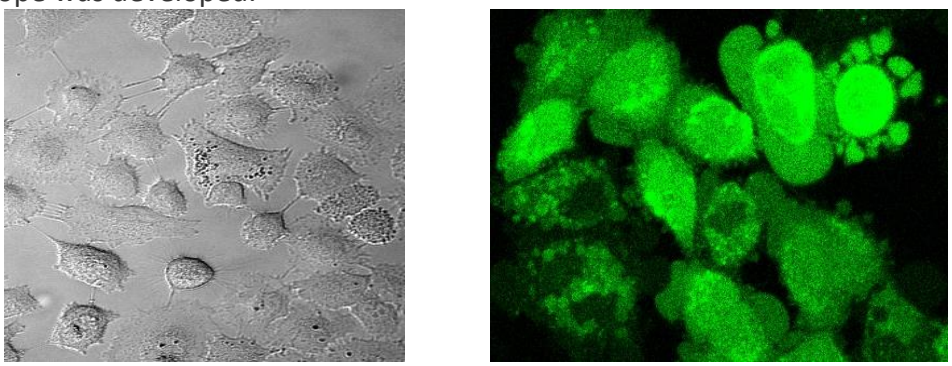

Figure 6: *Uptake of nanoparticles into A549 cells. Images obtained by laser scanning microscope (Zeiss LSM 500 confocal microscope). In the left image, TiO_2 nanoparticles can be seen as black dots on top of and around the cells. Also, it is seen how the cells stretch out filopodia to reach each other in a survival strategy. On the right, the cells are labeled with a fluorescent probe (cell tracker green), and are apoptotic (programmed cell death).*

Summary of results

- Protocols for ALI cultivation of A549 human epithelial lung cells were developed and validated
- Protocols for cytotoxicity assays, oxidative stress and genotoxicity were further developed and validated for A549 and for the ALI model.
- Different systems for exposure of the cells were studied, and exposure system was designed. Building of the exposure system is ongoing
- Exposure of A549 cells to different reference nanoparticles under conventional submerged system was performed. Both cell survival (colony forming efficiency) and genotoxicity were measured.
- Uptake of the nanoparticles into the cells as well as ROS production was studied by confocal microscopy
- Review paper on the ALI model for respiratory exposure was almost completed

Further progress

NILU wants to develop the culture model further, to even more closely resemble the in situ situation in the human lungs, by establishing an advanced and complex co-culture system. Thus, NILU wants to include immune cells (macrophages) in the model, and plan to set-up THP1 cell line (human peripheral blood model - monocyte-macrophage cell line) in co-culture with A549 to closer mimic the real situation. THP-1 cells have been received in the laboratory, and master cell bank is being created.

1. Complete building of controlled exposure system for ALI
2. Test the selected nanoparticles and also volatile pollutants on A549 cells in the ALI exposure system

3. Develop and validate protocols for cultivation of THP-1 cells and co-cultures of A549 and THP-1
4. Selection of atmosphere pollutants to test
5. Further cytotoxicity testing of different chemicals by the CULTEX system

6 REEs-PGM - Rare Earth Elements (REEs) and Platinum Group Metals (PGM): Application in new technologies and environmental and human health implications

Annual report 2015

Duration: 01.01.2015 – 31.12.2019
Budget 2015: 1,656 MNOK
Project leader: Kyrre Sundseth
NILU project: B-115009

Description of the project and objectives
The main objective of the SIS REEs-PGM project is to increase the understanding of environmental and human health implications of REEs and PGM used in new industrial technology applications. To reach its main objective, the SIS-project aims at generating knowledge on global and regional flows of REEs (Rare Earth Elements) and PGM (Platinum Group Metals) applied in technologies, how they are being released to the environment from their entire value chain (from extraction, processing, production, use, and end-of-life treatment) and how they subsequently affect environmental concentrations and risk of human health damage. Development of a methodology for Material/Substance Flow Analysis (MFA) of these materials, in combination with the development of sampling and analytical techniques for environmental studies of contamination levels, is central to the project. Baseline concentrations of these metals identified along the material flows will provide a basis for future studies of possible changes in environmental concentrations.

Background
REEs (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, scandium and yttrium) and PGMs (platinum, palladium, rhodium) are two groups of trace elements that are being used in industrial technology applications, such as in the electronics, magnet and battery production, satellite components, military devices, food and energy production, etc. High-technology and environmental applications of several of these metals have grown dramatically in diversity and importance over the last past decades. They are essential for global economic growth as modern technologies rely on these. At the same time, information is now becoming available on human health implications of production and use of these inorganic pollutants, particularly on their relation to infectious diseases (Pacyna et al., 2014; Ackland et al., 2014).

Since most of the global supply of PGMs and REEs originates from a few exploitable ore deposits, and further from the fact that most of them are difficult to extract in an economically viable and environmentally sound manner, most countries depend on their imports. China has become the major producer of many of the metals of concern, resulting from relatively low exploitation costs, particularly in terms of labour and regulatory costs, and in combination with technology transfer from industrialized countries. World economies at growth, particularly material-intensive emerging economies and heavy populated developing countries, will drive the demand for metals in the coming years and may lead to

a pressure on availability as well as to various product`s value chain, including waste handling systems. Increasing dependency is thus becoming an important issue for scientists and policy- makers as future market scarcity becomes an issue. The Norwegian debate on the possibilities for nationally extraction of minerals reflects this. In particularly, it is expressed interest in the mineral resources existing in Fansfeltet in Telemark (Nb, Th and REEs), Høgtuva in Nordland (Be and REEs) and Biggejavri in Finnmark (Be and REEs).

The methodology for assessing the charge of metals to the environment due to their production and various uses, has improved significantly the latest years. Current methodology leans on the application of life cycle methodologies such as MFA. Several research groups have formed to perform such analysis. An example is the Stocks and Flows Project (STAF) at the Centre for Industrial Ecology of the Yale University in the U.S. The STAF project has been involved in evaluating current and historical flows of specific technologically important materials, determining the stocks available in different types of reservoirs and the flows among the reservoirs, developing scenarios of possible futures of metal use, assessing metal supply and demand, and assessing the metal emissions to the atmosphere (e.g. Rauch and Pacyna, 2009). Although some studies exists on emerging elements (e.g. Graedel et al., 2013), such analysis is very limited for REEs and PGM as groups of trace elements.

Resent environmental concerns with REEs and PGM mainly links to mining activities. Little or no attention are being paid to their whole value chain and their environmental fate, i.e. all the way from mining (including by-products and tailings) to processing, production of products containing these metals, use, end-of-life treatment and environmental transport and fate. There is a need for a holistic system perspective for identifying and reducing environmental and human health risks of these elements. Before recommending any emission abatement options, it is necessary to establish methods for benchmarking environmental concentrations as well as for verification of the expected environmental benefits from introducing various sets of measures. At presence, this is a challenging task because determination of REEs and PGM in environmental samples links to concentration levels that are usually low and highly sensitive and selective analytical methods are required. In addition, environmental research involve analysis of a vast variety of samples with complex matrices making sample preparation very demanding. Inductively plasma mass spectrometry (ICP-MS) has a leading role as analytical technique for determination of REEs and PGM because of its high sensitivity (ppt level) and multi-element capability. Using ICP-MS, dissolution of the samples are furthermore most often required. This is not a straightforward process when it comes to PGM, which are difficult to dissolve. Accurate determination of REEs and PGM by ICP-MS is complicated from the low concentrations and the occurrence of many spectral and non-spectral interferences.

Activities performed and results achieved

The activities performed within the first year of the SIS-project have mainly focused at literature reviews on REEs and PGM global production and use, on environmental effects and on analytic methods. The work has in addition focused on methodology development. The following SIS-project activities and achievements can be reported for the period:

- Literature studies has been performed on the following:
    - Global mining, separation, fabrication, manufacturing, use and waste management of REEs and PGM. An historical overview of global rare earth oxides production and PGM can be observed in figure 1.
    - Environmental effects of REEs and PGM, -their attributes, mobility, bioavailability, toxicity, and bioaccumulation. The literature studies indicate the areas of environmental concern and help decide what type of samples that should be in focus throughout the project.
    - Analytical methods and sampling matrixes build-up as well as on various separation techniques. Sampling matrixes are tested on reference materials.
- A database is under development to accommodate collected- and estimated information on the global and regional occurrence, material flows, and technical applications of REEs and PGM.
- A systems perspective methodology for establishing global and regional MFA on REEs and PGM is developed and is further being designed for use in decision-making and environmental policy development.
- Work has been conducted on compiling baseline data of REEs and PGM concentrations from the national-wide moss survey, involving four decades of data collection. A geographical map has been made from the obtained information on the background concentrations of REEs (figure 2). From simplified statistical analysis, it was concluded that REEs to a large degree correlates with each other and to a certain degree with Lithium and Aluminium, -likely to originate from local ground particles. The analysis shows that Europium separates from the rest of the other REEs, but shows at the same time significant correlation with Barium.
- Fieldwork was conducted in form of moss sample collection nearby an industrial area in Kyrksæterøra.

With regard to dissemination, the main activities have included participation in the international Goldschmidt 2015 conference in Prague and the arrangement of a mini-seminar on REEs and PGM with invited scientists at the Norwegian University of Technology and Science (NTNU):

- Kyrre Sundseth, Jozef M. Pacyna and Elisabeth G. Pacyna. New Technologies Using Trace Metals of Concern. Goldschmidt 2015. Prague 20th of August, 2015. Environmental Geochemistry, Session 04e.
- NTNU mini-seminar at the Chemistry Department at NTNU. Trondheim, October 9, 2015.

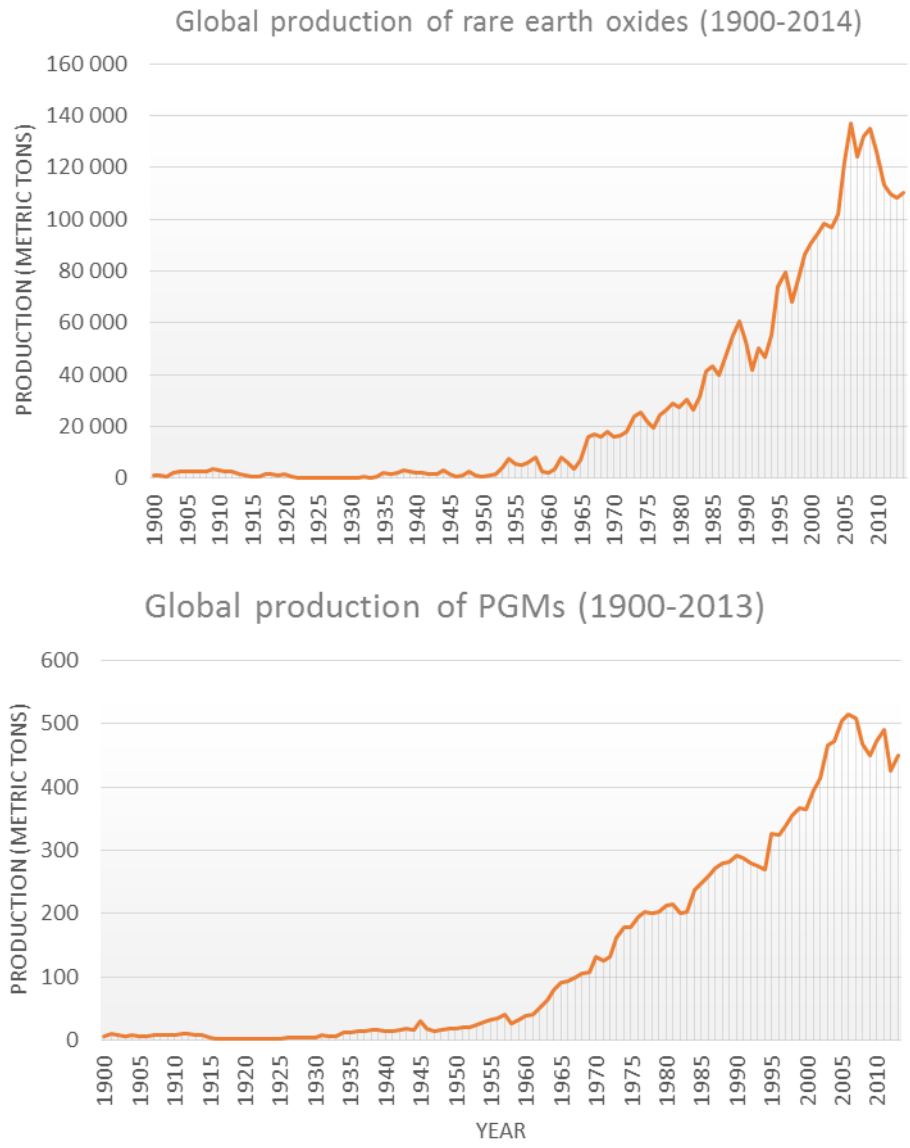

Figure 1: *Historical global production of rare earth oxides (upper image) and PGM (lower image), based on USGS data.*

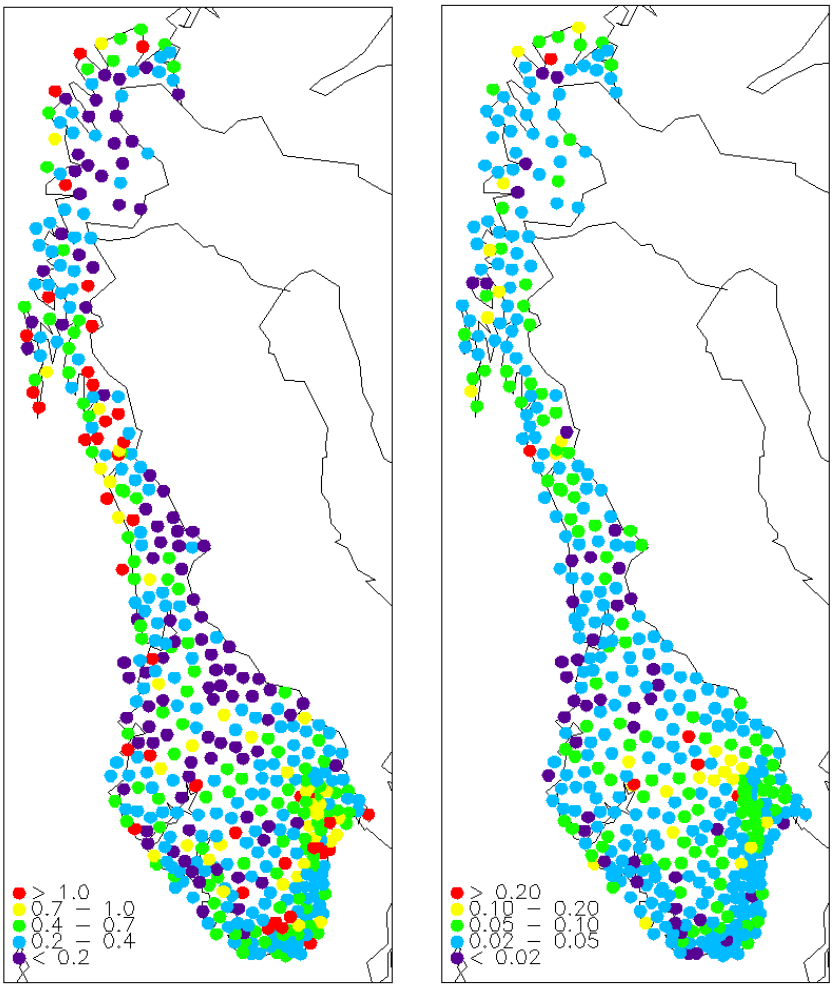

Figure 2: *Lanthanum (left) and Europium (right) analyzed in moss samples in Norway.*

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7 ChemInAir – Characterization of the Chemical composition of Non-industrial Indoor Environment

Årsrapport 2015

Varighet: 01.01.2015 – 21.12.2019 **Prosjektleder:** Britt Ann Høiskar
Budsjett: 1,5 MNOK **NILU prosjekt:** B-115019

Bakgrunn
Luftforurensning utendørs og innendørs representerer et betydelig folkehelseproblem. Verdens Helseorganisasjon (WHO) publiserte nylig nye resultater om overdødelighet knyttet til luftforurensning i verden. På verdensbasis kan 7 millioner dødsfall knyttes til felles effekter av innendørs og utendørs luftforurensning i 2012. Selv om risikoen er størst i andre land og verdensdeler, utløser også dagens nivåer av luftforurensning i norske byer og tettsteder betydelige helseeffekter. Luftforurensning kan både utløse og forverre sykdommer, først og fremst i luftveiene og hjerte-karsystemet. Nyere forskning gir stadig sterkere holdepunkter for at luftforurensning også kan påvirke nervesystemet og øke hyppigheten av sykdommer som diabetes og lungekreft.

Det har i lang tid vært stort fokus på utendørs luftforurensning både på forskningsfronten og blant beslutningstakere. Forurensende stoffer i innemiljø har derimot fått langt mindre oppmerksomhet til tross for at befolkningen i Europa oppholder seg 80-90% av tiden innendørs og forurensnings-nivåene innendørs i mange tilfeller er langt høyere enn utendørs.

Det foreligger lite systematiske målinger og studier av luftkvaliteten i norske bygg. Samtidig vet vi at den kjemiske sammensetningen i inneluften har endret seg dramatisk de siste 30-40 år, blant annet som følge av avgassinger fra nye bygningsmaterialer/produkter (for eksempel malinger, lim, sparkel, laminat, veggplate og isolasjonsmaterialer), ulike forbrukerartikler (rengjøringsmidler, tekstiler, kosmetikk) og interiør. Disse produktene inneholder både kjente kjemikalier og nye ukjente kjemikalier som kan ha helse- og miljøskadelige egenskaper. Flere studier viser at konsentrasjonen av en rekke helseskadelige stoffer er langt høyere innendørs enn utendørs. Det er derfor stort behov for å få bedre forståelse for den kjemiske sammensetningen i inneluften, både med hensyn til type stoffer, nivåer, kilder og variabilitet mellom bygningstyper.

I tillegg vil mange av de miljøgiftene vi finner i utemiljø komme fra produkter/materialer som brukes i byggsektoren og fra forbrukerprodukter. Dette betyr at mange nye potensielt helse- og miljøskadelige stoffer vil kunne oppdages og identifiseres på et tidligere stadium ved å gjennomføre screening studier i innemiljø.

Mål for prosjektet

Målet med ChemInAir-prosjektet er å utvikle metoder og verktøy for å:

- Få mer kunnskap om den kjemiske sammensetningen av innemiljø i boliger og yrkesbygg
- Studere kjemiske reaksjoner som finner sted i inneluft

Prosjektet vil fokusere på å utvikle målemetoder som egner seg til måling av kjemiske komponenter i inneluft og som kan benyttes i omfattende kartlegginger av innemiljøet og i epidemiologiske studier. Metodene som skal utvikles skal ta lite plass, være støysvake, rimelige og egnet til å kvantifisere en rekke komponenter som f.eks. flyktige organiske forbindelser (VOC), semi-flyktige organiske forbindelser (SVOC), polysykliske aromatiske hydrokarboner (PAH), flammehemmere og ftalater.

Sammendrag av aktiviteter og resultater i 2015 og planer for 2016

I 2015 er det fokusert på følgende hovedaktiviteter

1. Utvikling av en ny inneklimaparameter som mål på kjemisk reaktivitet
2. Metoder for prøvetaking og analyse av SVOC i inneluft

<u>Utvikling av en ny inneklimaparameter som mål på kjemisk reaktivitet</u>

Flyktige organiske forbindelser (VOC) er kjemikalier som brukes i bygningsmaterialer og i en rekke produkter som er vanlige i innemiljø fra møbler, rengjøringsprodukter, tekstiler og hygieneprodukter. "Flyktig" betyr at disse kjemikaliene fordamper eller kan lett komme ut i luft ved romtemperatur. "Organisk" betyr at disse kjemikaliene er karbonbasert. En viktig undergruppe av VOC-er er semi-flyktige organiske forbindelser (SVOC) som har høyere molekylvekt og høyere kokepunkt-temperatur enn andre flyktige organiske forbindelser.

VOC og SVOC i innemiljøet opptre dels i gassfase og dels på overflater innendørs eller på overflaten av små luftbårne partikler (Weshler et al. 2006). Mens VOC i stor grad opptrer i gassfase, vil SVOC finnes både i gassfase og på overflater i innemiljøet og på overflaten av små luftbårne partikler som kan pustes inn.

Både VOC og SVOC kan inngå i kjemiske reaksjoner som både kan fjerne enkelte forurensnings-komponenter, og være kilde til nye forurensningskomponenter (sekundære komponenter). Det er derfor viktig å få bedre forståelse for de kjemiske prosessene som involverer disse komponentene.

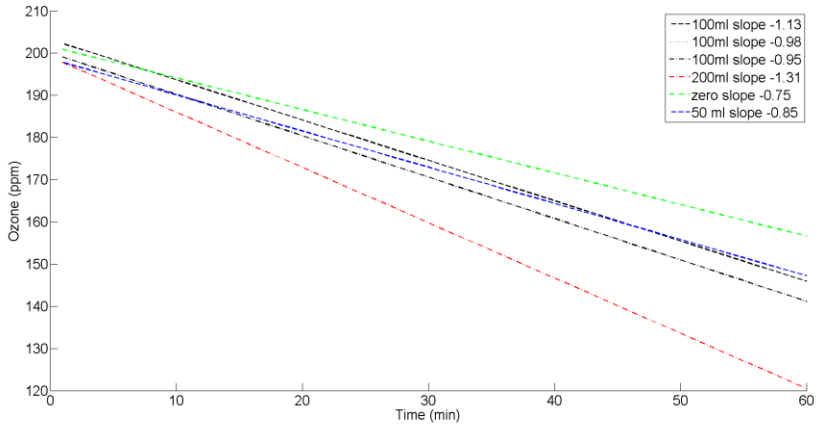
Den kjemiske sammensetningen av inneluften har endret seg mye de siste ti-årene etter innføringen av VOC direktivet (Directive 2004/42/EC) som regulerer bruken av VOC i malingsprodukter. Dette har medført økt bruk av mindre flyktige organiske forbindelser (SVOCs), som har bidratt til at det nå er større fokus på hvordan SVOC påvirker luftkvaliteten innendørs.

Fokuset på energisparing i byggsektoren gjør at de fleste nye bygg og boliger nå benytter mekaniske ventilasjonssystemer. Dette vil gjøre at ozon og nitrogendioksider i uteluften i større grad enn tidligere dras inn i byggene og medfører høyere nivåer av disse komponentene innendørs. Disse reaktive gassene kan reagere med både VOC og SVOC i inneluften og danne ultrafine partikler og ulike radikaler som kan være helseskadelige.

Siden det er dyrt og tidkrevende å kvantifisere enkeltkomponenter (både VOC og SVOC), er det ønskelig å se om man kan definere en enkel inneklimaparameter som kan være et godt mål på mengden VOC/SVOC i inneluften, og dermed et grovt mål på hvor reaktiv inneluften er.

I ChemInAir er det i 2015 gjort noen innledende forsøk for å undersøke om nedbrytning av ozon kan være en egnet parameter. Dette er gjort ved at man har tilsatt ulike konsentrasjoner av VOC inn i et kammer med kjent ozon-konsentrasjon og målt hvor raskt ozonkonsentrasjonene avtar ved hjelp av mikro-sensorer. Forsøkene viser at reduksjonen i ozon-konsentrasjonen avhenger av konsentrasjonen av de reaktive komponentene (VOC) som tilsettes, se Figur 1.

Siden resultatene fra testene i 2015 var så lovende, vil det i 2016 utvikles et automatisert oppsett for å variere mengdene av VOC inn i kammeret med kjent ozonkonsentrasjon. Dette vil gjøre det mulig å kjøre tilsvarende tester for de vanligste VOC-er i inneluft. Målet med forsøkene er å lage en «baseline» for den nye inneklima parameteren.



Figur 1: Figuren viser hvordan ozonkonsentrasjonen reduseres over tid når den eksponeres for ulike konsentrasjoner av metylbuten.

Metode for prøvetaking og analyse av SVOC i støvprøver

For å kunne gjennomføre systematiske målinger av den kjemiske sammensetningen av inneluften, kreves det målemetoder som egner seg for bruk i innemiljø. Mange av instrumentene som benyttes i dag er lite egnet for denne type studier fordi de er store, støyer mye, krever store luftmengder og er svært kostbare. Det er derfor behov for å utvikle standardiserte metoder som egner seg til bruk i omfattende målekampanjer for kartlegging av innendørs luftkvalitet.

Forskning på SVOC-er i innemiljøer begrenses i dag av mangelen på standardiserte prøvetakingsmetoder. Bruk av forskjellige metoder og målestrategier gjør det vanskelig å sammenligne datasett og resultater fra ulike studier.

Et hovedmål for ChemInAir er derfor å teste og validere prøvetakingsmetoder og målestrategier for måling av SVOC i luft og støv i innemiljøer. Metodene som skal testes skal være enkle og i liten grad forstyrrende for dem som oppholder seg i bygget/boligen. I tillegg

er det viktig å videreutvikle og validere eksisterende metoder som benyttes for å analysere luft- og støvprøvene for å oppnå tilstrekkelig følsomhet for nye SVOC-er. Det er et overordnet mål at arbeidet som utføres i ChemInAir vil bidra til å få etablert internasjonale standardiserte metoder for prøvetaking i innemiljø.

I 2015 er det gjennomført flere studier for å teste og validere metoder for prøvetaking og analyse av SVOC. I tillegg er flere nye studier påbegynt eller planlagt startet i 2016. Her gis en kort beskrivelse av de ulike studiene.

Studie I: Fordeling av SVOC i luft og støv

SVOC i innemiljøer forekommer både i luft (gassfase og partikkelfase) og i støv (gulv, vindu, andre overflater). Kunnskap om hvordan fordelingen er mellom disse matrisene er viktig for å kunne lage korrekte prøvetakingsstrategier.

For å studere dette har NILU sammen med RECETOX (Research Centre for Toxic Compounds in the Environment, Tsjekkia) gjennomført en studie i en bolig der man så på fordelingen av SVOC mellom luft og støv. I tillegg evaluerte man prøvetakingsstrategier for fem ulike SVOC-klasser, inklusive regulerte persistente organiske miljøgifter (POPs) og ikke-regulerte miljøgifter (som fortsatt er i bruk).

Prøvetakingen ble utført i 2014, mens dataanalyse og artikkelskriving ble utført i løpet av 2015. Prøvetakingen inkluderte lav/medium-aktive prøvetakere, polyuretan skum (PUF) passive prøvetakere, støvsugere og wipes (vindu samt overflater), se Figure 2.

Resultatene viste at de regulerte SVOC-ene var i likevekt mellom de ulike matrisene mens SVOC-ene som ikke er regulert og/eller er fortsatt i bruk ikke har oppnådd likevekt mellom matrisene. For prøvetaking betyr resultatene at en matrise kan brukes for å estimere nivåene i de andre matrisene for de regulerte SVOC-ene, mens en kombinasjon av støv og luftprøvetaking må brukes for SVOC-er som fortsatt er i bruk. Resultatene fra studien skal publiseres i det vitenskapelige tidsskriftet Chemosphere og artikkelen[1] er nå til sluttrevisjon (mindre endringer gjenstår).

[1] Melymuk, L., Bohlin-Nizzetto, P., Vojta, S., Kratka, M., Kukucka, P., Audy, O., Pribylova, P., Klanova, J. Distribution of legacy and emerging semivolatile organic compounds in five indoor matrices in a residential environment (to be published in Chemosphere)

Figure 2:Prøvetaking i studie 1: Fordeling av SVOC i luft og støv

Studie II: Test av passive prøvetakere med PUF

Passiv luftprøvetaking med PUF er den mest brukte prøvetakingsmetoden for SVOC-er i innemiljøer. Passiv prøvetaking gjør innemiljømålinger mye lettere og PUF er brukervennlig både i felt og i laboratoriearbeid. PUF enheten plasseres vanligvis i en metallbeholder som kontrollerer opptaket av miljøgifter i prøvetakeren. Dette er spesielt viktig i utendørsmiljøer der miljøfaktorer som vind, nedbør og sollys kan påvirke prøvetakingen. I innemiljøer er det bedre å ikke begrense luftbevegelser rundt PUF-enheten med en slik beholder. Til tross for dette har utendørsmodellen ofte blitt brukt i innemiljøer.

For å evaluere hvilken type beholder som bør brukes i innemiljø har NILU, sammen med RECETOX, utført en studie i ett kontorbygg. I dette studiet ble PUF-prøvetakere med tre typer beholdere testet: i) dobbel; ii) enkel; og iii) helt uten beholder (Figure 3).

I henhold til teorien bør opptaket av komponenter i gassfase øke når man går fra dobbel til enkel beholder og videre fra enkel beholder til ingen beholder. Motsatt bør opptaket av komponenter i partikkelfasen være størst når det ikke brukes beholder (Figure 3). Som referansemetode bruktes det aktiv luftprøvetaking. Studien inkluderte regulerte POPer som polyklorerte bifenyler (PCBs), klorerte plantevernmiddler, polybromerte difenyletere (PBDEs), polysykliske aromatiske hydrokarboner (PAHs), samt ikke-regulerte flamme-hemmere (bromerte (NFRs) og fosfororganiske (OPFRs)).

Data fra studien er under evaluering på NILU. Preliminære resultater viser at opptaket av komponenter fra gassfase øker med redusert beskyttelse, men at også variabiliteten/ usikkerheten øker med redusert beskyttelse – spesielt når man sammenligner enkel beskyttelse mot ingen beskyttelse. Dette tyder på at den optimale designen av PUF-PAS for innemiljømålinger er en enkel beskyttelse.

Resultatene fra studien skal publiseres i et vitenskapelig tidskrift. Publikasjonen er under utarbeidelse og planlegges innsendt i løpet av 2016.

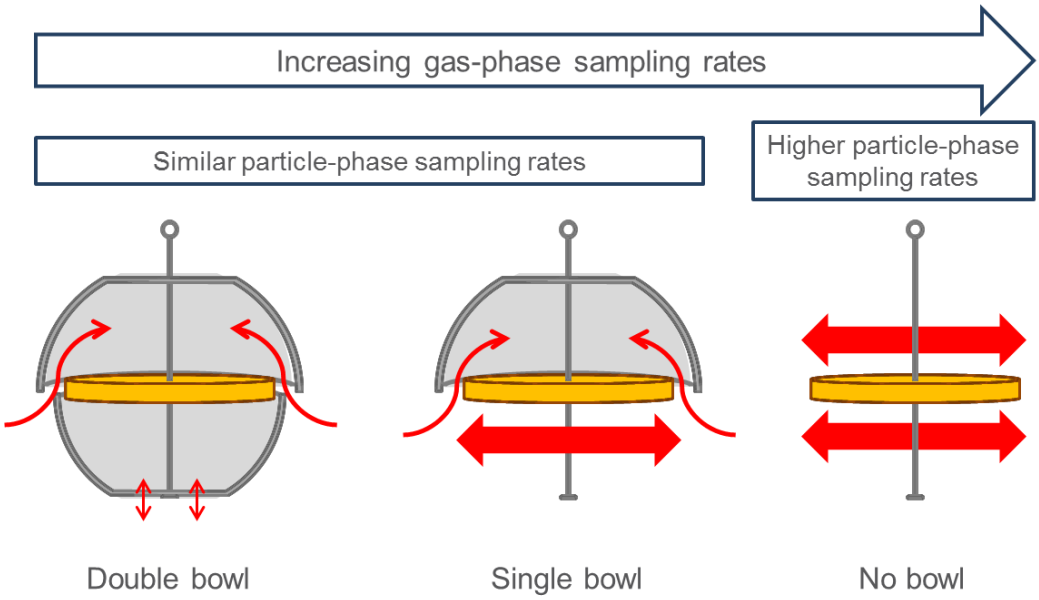


Figure 3: Figuren viser de tre typene beholdere som ble testet og illustrerer hypotesen for opptak av komponenter fra gassfasen.

Studie III: Test av to passive prøvetakere og to støvprøvetakere

I en pågående studie skal man teste og evaluere bruken av to typer passive prøvetakere (PUF og XAD), samt to typer av støvprøvetakere (støvsugere og wipes). Prøvetakerne skal brukes til å måle et større antall ikke-regulerte SVOC-er som er viktige i innemiljøer (fluorerte komponenter, bisfenoler, ftalater m.fl.).

Studien startet i 2015 med prøvetaking i kontor, laboratorier og lagerrom. Prøvene vil bli analysert i 2016, men analysen krever utvikling og validering av nye analysemetoder som er en del av arbeidet i ChemInAir-prosjektet.

Det er ønskelig å finne fram til en metode som kan anvendes på alle SVOC-klasser, inklusive regulerte POPs og ikke-regulerte SVOC-er (som er fortsatt i bruk). I 2015 ble en analysemetode for uttesting og validering av nye bromerte flammehemmere (NBFR) og fosforganiske flammehemmere (OPFR) utviklet. Som del av valideringen av denne metoden, ble en støvprøve fra en global laboratorie-interkalibrering (InterFlab II) analysert og rapportert. Resultatene fra interkalibreringen foreligger ikke enda, men vil bli verdifull for evaluering og videre utvikling av metoden.

Studie IV: Validering av støvprøvetaking

Denne studien vil se på hvordan man best tar støvprøver og det vil gjennomføres tester av en rekke ulike prøvetakingsmetoder. I tillegg vil man se på hvor man bør ta støvprøver for å få et representativt bilde på nivåene i et bygg. Denne studien begynner i sluttet av 2016 og skal også forgå i 2017. Dette arbeidet vil bli gjort i samarbeid med RECETOX og NORMAN nettverket (http://www.norman-network.net/) .

NILU – Norwegian Institute for Air Research

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