

# **Chlorinated paraffins in urban air in Nordic Countries**





# Content

|                                     |           |
|-------------------------------------|-----------|
| <b>Preface</b>                      | <b>3</b>  |
| <b>Summary</b>                      | <b>4</b>  |
| <b>1. Background</b>                | <b>5</b>  |
| 1.1 Selected compounds              | 5         |
| 1.2 Selected sampling sites         | 8         |
| <b>2. Methods</b>                   | <b>11</b> |
| 2.1 Sampling                        | 11        |
| 2.2 Chemical Analysis               | 11        |
| 2.3 Limit of detection              | 13        |
| 2.4 Uncertainties                   | 13        |
| <b>3. Results and Discussion</b>    | <b>16</b> |
| 3.1 Chlorinated paraffins           | 16        |
| <b>4. Conclusions</b>               | <b>20</b> |
| <b>5. Acknowledgements</b>          | <b>21</b> |
| <b>6. References</b>                | <b>22</b> |
| <b>Appendix A: Sampling details</b> | <b>23</b> |
| <b>About this publication</b>       | <b>27</b> |

This publication is also available online in a web-accessible version at:  
<https://pub.norden.org/temanord2023-515>

# Preface

The aim of the Nordic Screening Group is to gather data that increases the knowledge on the occurrence and distribution of hazardous substances in the Nordic environment in order to provide supporting information that may serve as fundament or support for regulatory action. To this end, the group regularly plans screening studies to obtain a snapshot of the occurrence of potentially hazardous substances, both in regions most likely to be polluted as well as in some very pristine environments. The focus of the group is on less known, anthropogenic substances and their derivatives, which are either used in high volumes or are likely to be persistent and hazardous to humans and other organisms.

In 2022, the project steering group decided to perform a study on short-, medium- and long-chain chlorinated paraffins in urban air. This decision was taken based on results from a previous screening study from 2019. One matrix was selected for analyses (i.e. air – particle phase) and three capitals could perform sampling based on the criteria (i.e. Helsinki, Reykjavik and Oslo).

The Nordic screening project was run by a steering group with representatives from the Danish Centre for Environment and Energy, Aarhus University, Denmark, the Finnish Environment Institute, the Environment Agency of Iceland, the Environment Agency of the Faroe Islands, the Climate and Pollution Agency in Norway, the Swedish Environmental Protection Agency, and the Swedish Chemicals Agency. The project was financed and supported by the Nordic Council of Ministers through the Nordic Working Group for Chemicals, Environment, and Health and the Nordic Working Group for Oceans and Coastal Areas as well as the participating institutions.

The preparation of air sampling material and the chemical analyses in this project have been carried out by NILU – Norwegian Institute for Air Research. The participating Nordic countries organised selection of sampling sites, collection of air samples and transport of samples based on sampling guidelines provided by NILU.

# Summary

In 2022, the Joint Nordic screening group decided to perform a Nordic study on short-, medium- and long-chain chlorinated paraffins (SCCPs, MCCPs, LCCPs) in urban air. A previous study performed on behalf of screening group in 2019 observed higher concentrations of chlorinated paraffins (CPs) in air samples from an urban site than from remote sites (Schlabach et al. 2022). It was then suggested that tire wear particles could be the source for the elevated urban concentrations.

The focus of the study in 2022 was to collect data to improve the understanding of sources for CPs in air by: (1) comparing concentrations measured in wintertime when studded tires are used and in summertime when normal tires are used, (2) comparing data from three capitals in the Nordic countries, and (3) compare urban air concentrations to air concentrations in a car tire testing facility. All the member countries were invited to participate but based on the possibilities to collect active air samples in urban locations, it was decided to collect air samples from Helsinki (Finland), Reykjavik and Reykjanesbær (Iceland) and Oslo (Norway). Samples were collected in February–March 2022 and May–August 2022. The sampling time for each sample was 48 hrs and 3–6 samples were collected per site and season.

**Table 1:** Detection frequency (as %) of SCCPs, MCCPs and LCCPs in air samples from urban sites (URB) in wintertime and summertime.

| Matrix            | Air URB Wintertime | Air URB Summer-time | Air URB |
|-------------------|--------------------|---------------------|---------|
| Number of samples | 14                 | 16                  | 30      |
| SCCPs             | 71                 | 38                  | 53      |
| MCCPs             | 100                | 56                  | 77      |
| LCCPs             | 71                 | 81                  | 77      |

Detection frequencies from the air samples are shown in Table 1. Lower detection frequency was observed in summer than in winter. The measured concentrations were highest for MCCPs in Helsinki and LCCPs at the urban site in Reykjavik while the lowest concentrations were measured for SCCPs and LCCPs at the urban site in Oslo.



# 1. Background

In 2019, NILU together with NIVA performed a screening study of CPs, dechloranes and UV-filter in different environmental matrices from the Nordic countries, on behalf of the Joint Nordic Screening Group (Schlabach, 2022). That study included air samples from three remote sites in Finland, Iceland and Norway and one urban site in Iceland. The results showed that the urban site had higher concentrations of S/M/LCCPs in air than the remote sites. The higher concentrations in urban air were suggested to be caused by tire wear particles (TWP) based on findings of CPs in car tires and products containing recycled rubber granulates (Brandsma et al. 2019).

In 2022, NILU proposed for the Joint Nordic screening group to perform a follow-up assessment on CPs in urban air in a wider range of Nordic countries.

## 1.1 Selected compounds

### 1.1.1 Chlorinated paraffins

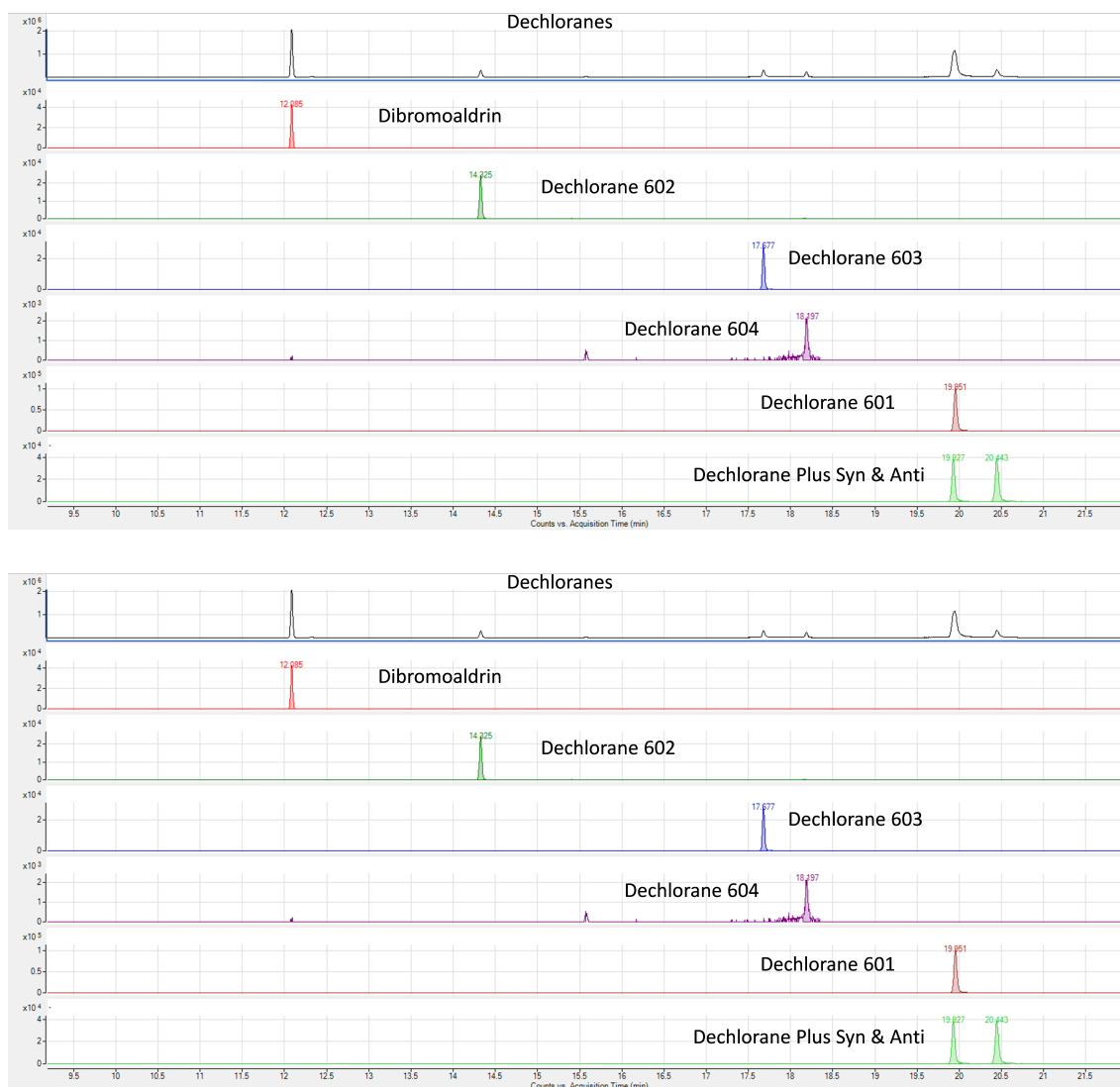
Chlorinated paraffins (CPs) are used and added to a wide range of applications as plasticizers or flame retardants; e.g. rubbers, paints, plastics, coatings, sealants and adhesives, or as high-pressure additives in metal working fluids. CPs are mixtures of congeners with different carbon chain lengths and number of chlorine atoms. Based on chain length, CPs can be divided into three groups: short chain (SCCPs: C10–C13), medium chain (MCCPs: C14–C17) and long chain (LCCPs: C18–C28). CPs are manufactured by radical chlorination of n-alkanes by treatment with ultraviolet (UV) light and/or high temperatures in the presence of chlorine gas. These reactions have low positional selectivity, and the different technical products are made up by innumerable individual congeners (Tomy et al., 1998).

CPs can be released into the environment during all life-stages from production to storage, transportation, use and finally disposal of products by runoff, leaching and/or volatilization from landfills, sludge and waste burning. CPs are of emerging concern due to their high production volumes (up to 600–1000 ktons/year in China), high persistency (half-life >1 year in sediment and >0.5 d in air), high bioaccumulation potential, and toxicity. Among CPs, short-chain CPs (SCCPs) have until now received the greatest attention.

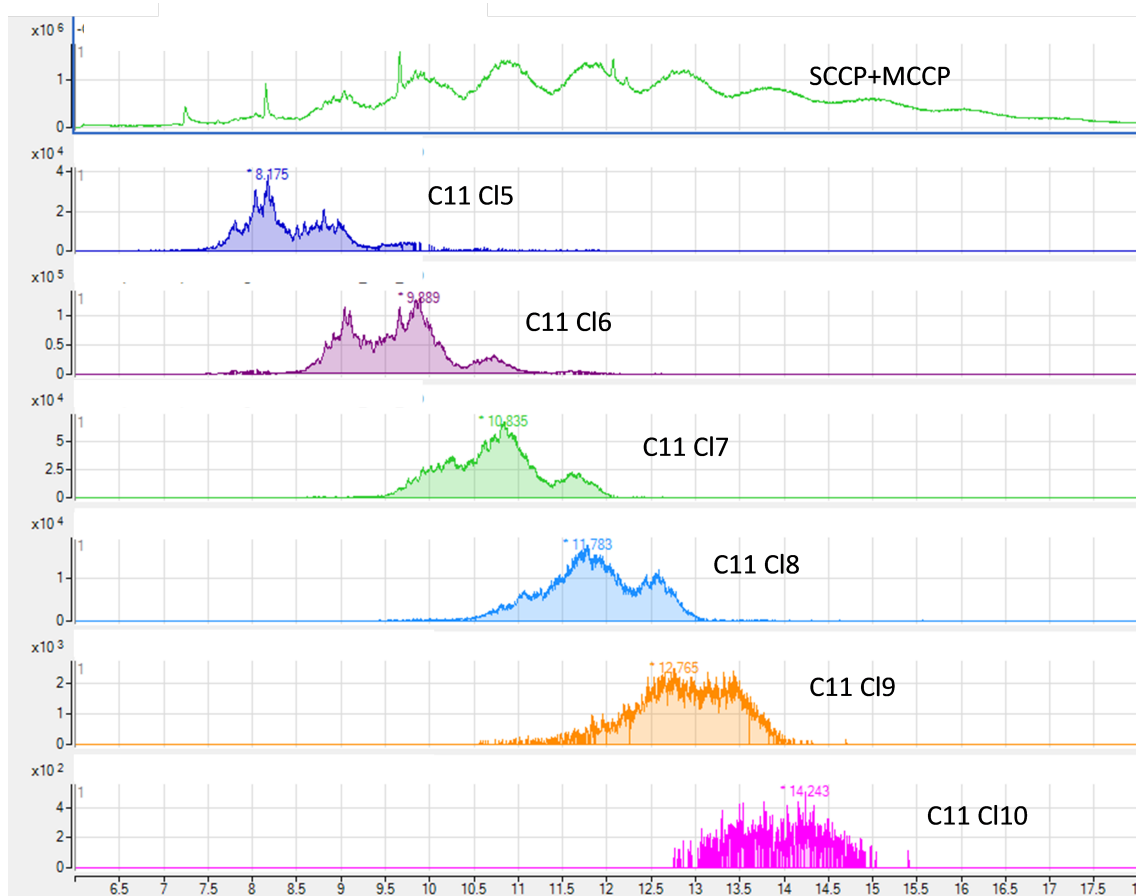
SCCPs are classified as substances of very high concern and are included on the list of the European water framework directive to be monitored in water (van Mourik et al., 2015). SCCPs are also restricted under the Stockholm Convention in Annex A (Elimination). UK has recently submitted a proposal to list chlorinated paraffins

with carbon chain lengths in the range C14-17 and chlorination levels  $\geq 45\%$  chlorine by weight as persistent organic pollutant (POP).

Due to the complex mixture of innumerable congeners in each technical product, environmental trace analysis of chlorinated paraffins is challenging. For the majority of POPs, a compound specific analysis can be used as they are analytically separated into single congeners/compounds and have isolated and purified standards for the single congeners/compounds (Figure 1).



**Figure 1:** Total ion chromatogram of dechloranes, together with chromatograms of all dechloranes completely separated. The complete separation and the existence of isolated C12 standard material for each compound allows for a **compound specific analysis**.



**Figure 2:** Total ion chromatogram of SCCPs and MCCPs, together with chromatograms of the congener groups C11-Cl5 to C11-Cl10. None of the possibly thousands of congeners could be isolated as single peaks. Limited separation and the non-existence of isolated C12 standard material for each congener allows only for a **mixture analysis**.

In contrast, CPs can only be separated into congener groups with the same chain length and number of chlorine atoms, and therefore the different individual congeners remain unresolved (Figure 2). In addition, there are only very few and little representative isolated single congener standards available, which can be used for identification and quantification. Thus, only a **mixture analysis** is possible and an accurate quantification is challenging. Different methods of highly variable quality have been developed during the last couple of decades (van Mourik et al., 2015). The method of Tomy (Tomy et al., 1997), has shown to be the most accurate but also most expensive for determination of CPs. It is based on the use of different technical CP mixtures and the application of GC-HRMS in ECNI-mode, and has been used by NILU for nearly 20 years. Due to the use of high mass resolution in GC/ECNI-HRMS little self-interferences between CPs and other POPs such as chlordanes, toxaphenes and PCBs occur, which otherwise is a common problem for GC/ECNI-LRMS.



Recently, an alternative technique based on APCI-qToF-HRMS and a deconvolution algorithm have shown promising results (Bogdal et al., 2015). Quantification using the deconvolution procedure has since been applied to other instrument techniques. However, this quantification method is highly complex, time consuming and the outcome is dependent on the availability and further selection of the right combination of technical mixtures used for calibration.

A worldwide intercalibration and certification study for SCCPs was conducted by the European Commission in 2019 with NILU participating as one of the leading expert labs. NILU was one of only five labs performing well within the accuracy and precision of the different methods.

## 1.2 Selected sampling sites

Chlorinated paraffins have previously been measured in various matrices in the Nordic environment, but a targeted study on urban air concentrations in winter and summertime has previously not been performed.

The main research questions justifying this study were collection of empirical data to improve the understanding of: (1) spatial variability of chlorinated paraffins in urban air in the Nordic countries, and (2) the importance of car tire wear for chlorinated paraffins in air. All countries were invited to participate in the sampling campaign, but the need for active air samplers in urban settings limited the participation to Finland (Helsinki), Iceland (Reykjavik and Reykjanesbær), and Norway (Oslo) (Table 2). Two sites were selected in Iceland (Reykjavik and Reykjanesbær) while one site was selected in Oslo and Helsinki (Figure 3). For comparison also one background site in Norway (Birkenes) and one car tire testing facility in Sweden (VTI) were included. The samples from Birkenes are a part of the Norwegian Monitoring programme for *Atmospheric Contaminants*, conducted by NILU on behalf of the Norwegian Environment Agency.

**Table 2:** Sampling sites and sample matrices for all participating countries.

| Country | Ma-<br>trix<br>acro-<br>nym | Loca-<br>tion<br>type | Loca-<br>tion     | Air sample<br>type                      | Lati-<br>tude | Longi-<br>tude | Samples<br>in<br>winter-<br>time | Samples<br>in<br>summer-<br>time |
|---------|-----------------------------|-----------------------|-------------------|-----------------------------------------|---------------|----------------|----------------------------------|----------------------------------|
| FIN     | AIR                         | URB                   | Helsinki          | Active air –<br>Particle<br>phase       | 60.19654      | 24.95179       | 3                                | 4                                |
| ICE     | AIR                         | URB                   | Reykjavík         | Active air –<br>Particle<br>phase       | 64.130115     | -21.874738     | 2                                | 3                                |
| ICE     | AIR                         | URB                   | Reykja-<br>nesbær | Active air –<br>Particle<br>phase       | 64.01466      | -22.57065      | 4                                | 3                                |
| NO      | AIR                         | URB                   | Oslo              | Active air –<br>Particle<br>phase       | 59.923        | 10.765         | 5                                | 6                                |
| NO      | AIR                         | REM                   | Birkenes          | Active air –<br>Particle +<br>gas phase | 58.38375      | 8.24997        | 3                                | 3                                |
| SWE     | AIR                         | IND                   | VTI               | Active air –<br>Particle<br>phase       |               |                | 1                                | 0                                |

Location type: URB: Urban sites; REM: Remote.



**Figure 3:** Photos of the four sampling sites; Helsinki (top left), Oslo (top right), Reykjavik Urban (Bottom left) and Reykjanesbær Urban (bottom right).

## 2. Methods

### 2.1 Sampling

Air samples were collected using two types of active air samplers available at the sampling sites: i) high-volume air samplers (Digitel, flow rate 20–25 m<sup>3</sup>/hr) in Oslo, Reykjavik, Reykjanesbær and Birkenes, and ii) low-volume air samplers (Comde Derenda, flow rate 2.3 m<sup>3</sup>/hr) in Helsinki. All samples from the urban sites were collected on filters only, that means that only the particle phase in air was collected and analysed. This sampling approach was selected based on the available active air samplers at the sites and to obtain comparable data between the sites. The use of filters only most likely underestimates the real air concentrations of SCCPs and to some extent MCCPs that are semi volatile and present in both gas phase and particle phase in air. Estimation of expected gas-particle distribution suggests that the bulk concentration can be up to ten times higher than the particle concentrations alone. The filters for the high-volume samplers were glass fibre filters with a diameter of 150 mm while the filters for the low-volume sampler were Fluoropore Membrane Filters with a diameter of 47 mm. The sampling time was 48 hrs with the high-volume sampler and 24 hrs with the low-volume sampler. In order to obtain samples with similar sample times, the filters from Finland were bulked in pairs before sample extraction. The samples from the background site were collected in accordance with the routine monitoring programme, that means with filter and Polyurethane foam (PUF) plugs collecting both particle and gas phase. This hampers the comparability to the urban sites but is even so included here.

Samples were collected in wintertime when studded tires are in use (January–April 2022) and in summertime when summer tires are obligatory (May–September 2022). The number of samples per season are presented in Table 2.

### 2.2 Chemical Analysis

#### 2.2.1 Sample extraction and clean-up

Prior to extraction, the samples had isotope labelled SCCP (1,5,5,6,6,10-hexachlorodecane) added for quantification purposes. The filters were extracted for 6 hrs in acetone:hexane (1:1) using Soxhlet extraction. The extracts underwent a clean-up procedure using concentrated sulphuric acid and a silica column to remove lipids and other interferences. Subsequently, solvent was changed to isooctane, and



extracts were concentrated using a gentle nitrogen flow. A recovery standard of 1,2,3,4-tertachloronaphthalene was added prior to analysis.

### 2.2.2 Analysis

Analysis of chlorinated paraffins covered SCCPs, MCCPs, and LCCPs. SCCPs and MCCPs were analyzed using an Agilent 7890B GC, 7200 QToF (GC/HRMS). To achieve a necessary separation, an HP-5MS UI 15 m×0.25 mm id, fused silica capillary column was used with a constant Helium flow of 1.2 mL/min. PTV injection was applied in solvent vent mode. The GC temperature program for SCCPs and MCCPs was: 55 °C (2 mins), 70 °C/min to 200 °C (1 min), 10 °C/min to 280 °C (1 min), 5 °C/min to 300 °C (0 mins), 70 °C/min to 320 °C, 1 min. The MS was operated in ECNI mode using methane as moderating gas. A selection of  $[M-Cl]^-$  or  $[M-HCl]^-$  ions for both SCCPs and MCCPs were extracted and the quantification was performed based on the deconvolution method described in Bogdal et al. (2015). Briefly, C10 - C13 standards with 51%, 55% and 63% Cl (w/w), and single chain length standards of C10, C11, C12, and C13 (50% and 65% Cl) were analysed for short chain CPs (SCCPs), and for medium chain CPs (MCCPs), C14 - C17 standards of 42%, 52%, and 57% Cl, and single chain C14 with 52% Cl were analysed. The resulting congener group patterns were used to reconstruct the congener group patterns in the samples. To do this we used the Lawson-Hanson algorithm (nnls package in R Studio) to obtain non-negative least squares estimates for the contributions of the individual standards. Separate calibration curves with four concentration levels were prepared for each of the included standards. All integrated areas from samples and standards were normalized using isotope labelled internal standard.

LCCPs were analyzed using an Agilent 1290 UHPLC, 6546 QToF (LC/HRMS). To achieve a necessary separation, an ACE Excel 5 Super C18, 75x2.1 mm column was used with a constant flow of 0.4 mL/min. The mobile phase was at start 70% water and 30% MeOH both containing 0.05mM of tetramethylammonium chloride. After 5 mins the mobile phase was adjusted to 100% of MeOH with 0.05mM of tetramethylammonium chloride. The MS was operated in negative ESI mode. A selection of  $[M+Cl]^-$  ions were extracted and the quantification was performed based on (Bogdal et al., 2015) as described above. For LCCPs, the availability of standards is more limited than for SCCPs and MCCPs. So, for LCCPs four technical mixtures of C18 – C30 with chlorination degree from 36% to 49% were used.

## 2.3 Limit of detection

Lab blanks and field blanks were analysed along with the samples. All samples including field blanks were corrected for the levels in the lab blanks from the same extraction batch. The limits of detection (LoD) for all chlorinated paraffins were calculated using 3 times the standard deviation for all lab blanks.

## 2.4 Uncertainties

When performing environmental screening studies for contaminants of emerging concern, all steps in the process, starting with study design, selection of the sampling sites, sampling frequency, time of sampling, performing the sampling, the transport and storage of samples, chemical analysis and data treatment, to some extent generate some degree of uncertainty (Thomas et al., 2014). To quantitatively estimate the contribution of all steps is challenging. However, we will discuss the relevance of the different contributions in a qualitative way.

Sampling and analysis of non- or recently regulated organic contaminants of emerging concern that are still in use (e.g., S/M/LCCPs) are associated with a bigger uncertainty than the well-established regulated legacy POPs. This is due to more diffuse sources in laboratories and sampling facilities (e.g., the use of CPs has increased again in a lot of different industrial, household products and consumer goods during the last years) that results in a larger risk for contamination. NILU is continuously taking actions to minimize this influence. Examples of such measures are improved pre-cleaning of analytical equipment, isolated work in clean cabinet facilities and removal of some materials and products where CPs are known to be present. However, samples cannot be sampled, stored, extracted and prepared for analysis without any physical contact with a lot of different materials and instruments. This raises the number of blank samples exceeding acceptable level, which in consequence raises the LOD for samples analysed in parallel with those blank samples. Therefore, all samples are corrected for the levels in the lab blanks. Further, samples are compared to the levels in the field blanks collected at corresponding locations to assess possibilities of contamination during sampling and transport.

Based on a 3-level categorization of quality and uncertainty in analysis of environmental samples, the quality and uncertainty of the analysis of the targeted S/M/LCCPs in this study fall into the lowest category:

**Category 3:** No or few reference materials or satisfying interlaboratory studies available. The methods are less reproducible, and the results have higher uncertainty.

The measurement uncertainty for the measurement of CPs is estimated to be much higher than for other POPs and probably higher than  $\pm 40\%$ .

There are international efforts to improve the analysis of CPs ongoing in which NILU is taking part. In 2021, NILU and nine other selected laboratories were invited by the European Commission to contribute to a certification and intercalibration study with the aim of certifying a reference material for SCCPs. The laboratories had to pass multiple quality assurance tests to be considered for the final evaluation of the material to be certified. NILU was one of five laboratories to pass the quality assurance tests, and thus providing data for the certification process of this reference material which became available in November 2022.

#### 2.4.1 Uncertainty related to chemical analysis

The uncertainty of the chemical analysis is governed by sample homogeneity, loss during extraction and clean-up, interference from other compounds, trueness of analytical standards, instrumental parameters, and contamination at all stages of sampling, transport, and laboratory work.

A normal approach to estimate and quantify these factors is the participation in a laboratory intercalibration. The uncertainty is expected to be larger for compounds which are analysed infrequently than for compounds which are analyzed commonly. For the CPs, where only a mixture analysis is possible the uncertainty is estimated to be higher than the normal 20%. SCCPs, MCCPs and LCCPs consists of a multitude of different congener groups. Furthermore, each congener group potentially consists of several thousand different isomers where complete chromatographic separation is impossible to achieve with present technology. Hence, single congener standards are not possible to isolate from a crude mixture and the ones available are very limited and rarely chemically representative. The individual instrumental response factors within the different congener groups will then not be possible to determine when the signals of the single congeners are overlapping. The responses will most likely depend greatly on the chlorine positions and are therefore subject to great variations. One of the most common approaches to quantification is to use average response factors from a number of standard mixtures with the closest resemblance to the samples as possible. Another approach which has been widely accepted during the last years, and has also recently been implemented at NILU, is the deconvolution method as first described by Bogdal et al. (2015). This method is based on the linear combination of several standard mixtures to determine response factors which is applied to the samples. The limitations are again the standard mixtures available, but most likely this

approach is by now the most promising way to quantify CPs in environmental samples. Another addition to the great uncertainty in GC/MS analysis of CPs is increasing response factors with increasing concentrations. This means that not only is it important to incorporate standards or a combination of standards with pattern resemblance, but also incorporate standards with responses within each congener group corresponding to the samples. The latter is much more important in CP analysis than traditional single compound analysis even when the responses are within the instruments linear area.

We consider the analytical uncertainty as adequate for a screening study. However, as for all other available CPs data, caution should be applied if using these results for future comparisons and time trend studies.

# 3. Results and Discussion

## 3.1 Chlorinated paraffins

### 3.1.1 Air

Air samples were taken in three Nordic capitals, one town in Iceland and at one background monitoring station in Norway in winter and summer 2022. Field blank samples were included for all sample types (i.e. filter types and PUFs). The levels of CPs in the field blanks depended on the size of the filters, and when converting to concentrations also on the total amount of air volume sampled for the representative filter. CP levels were higher in field blanks compared to lab blanks suggesting some degree of contamination during sampling and/or transport. However, most of the exposed samples had concentrations above the field blanks. Exceptions were LCCPs from Helsinki for which 71% of the samples were below the field blanks, and SCCPs from Oslo in summer and winter for which 100% and 60% of the samples were below the field blanks.

Of the three CP groups, LCCPs were most frequently detected (97%) followed by MCCPs (80%) and SCCPs (67%). The reason for lower detection frequency of MCCPs and SCCPs is partly due to higher LODs than for LCCPs. MCCPs were measured at the highest concentrations in a majority of the urban samples (88%) with detectable concentrations. The concentrations of LCCPs were higher than both MCCPs and SCCPs in four samples while lower than both MCCPs and SCCPs in 67% of the samples. The individually highest concentrations were measured for MCCPs in Helsinki and LCCPs at the urban site in Reykjavik. The lowest concentrations and lowest detection frequency were found for SCCPs and LCCPs at the urban site in Oslo and LCCPs at the sub-urban site in Reykjavik and the urban site in Helsinki.

The concentrations of LCCPs and MCCPs were significantly lower at Reykjanesbær than at Reykjavik, both in winter and summer. For SCCPs no difference was found between the two sites in Iceland. The results for Oslo and Helsinki indicate higher concentrations of SCCPs and MCCPs in wintertime than in summertime but no difference was observed in Reykjavik (Table 4). In contrast, higher concentrations were observed in summer than in winter at the background site in southern Norway.

Comparison of the urban concentrations with background air concentrations from Birkenes shows no difference for SCCPs. For MCCPs, higher concentrations were



observed in Helsinki than at Birkenes while the other urban sites were similar to Birkenes.

Overall, the measured concentrations of all CP groups at all sites in this study are significantly lower than the concentrations measured at the urban site in Reykjavik in 2019 (Table 3). The reason for lower concentrations at the urban site in this study is unknown as identical sampling methods were used in both studies and the same blank treatment was applied for all samples. The concentrations of SCCPs and MCCPs at the background site (Birkenes) are similar to those previously measured at Birkenes for the Joint Nordic Screening Group in 2019 (Schlabach et al. 2022) and those from the Norwegian Monitoring Programme "Atmospheric Contaminants" (Bohlin-Nizzetto et al. 2022). This shows consistency in the analytical method.

**Table 3:** Average concentration of chlorinated paraffins in urban air from the three Nordic capitals (Reykjavik, Helsinki and Oslo), Reykjanesbær, the background site, and field blank samples. Presented are also the concentrations measured in Reykjavik in 2019.

\*Schlabach et al. (2022).

| Sample type (Number)      | SCCPs                                                              | MCCPs                                                              | LCCPs                                                              |
|---------------------------|--------------------------------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------------|
|                           | (Min – Max)<br>Average (pg/m <sup>3</sup> )<br>Detection frequency | (Min – Max)<br>Average (pg/m <sup>3</sup> )<br>Detection frequency | (Min – Max)<br>Average (pg/m <sup>3</sup> )<br>Detection frequency |
| Reykjanesbær – Urban Air  | (<50–205)<br><b>105</b><br>83%                                     | (145–276)<br><b>214</b><br>100%                                    | (2–54)<br><b>29</b><br>100%                                        |
| Reykjavik – Urban Air     | (81–206)<br><b>161</b><br>100%                                     | (494–966)<br><b>646</b><br>100%                                    | (283–1366)<br><b>734</b><br>100%                                   |
| Helsinki – Urban Air      | (253–433)<br><b>347</b><br>100%                                    | (732–1098)<br><b>954</b><br>100%                                   | (<LOD–159)<br><b>55</b><br>86%                                     |
| Oslo – Urban Air          | (25–127)<br><b>67</b><br>100%                                      | (63–463)<br><b>223</b><br>100%                                     | (<LOD–217)<br><b>75</b><br>82%                                     |
| Birkenes – Background Air | (149–279)<br><b>206</b><br>100%                                    | (186–693)<br><b>350</b><br>100%                                    | <b>NA</b>                                                          |
| Field blank – High-vol    | <b>100</b>                                                         | <b>161</b>                                                         | <b>7</b>                                                           |

|                                    |                                    |                                    |                                       |
|------------------------------------|------------------------------------|------------------------------------|---------------------------------------|
| Field blank – Low vol              | <b>239</b>                         | <b>740</b>                         | <b>67</b>                             |
| <i>Reykjavik – Urban Air 2019*</i> | (1792–3006)<br><b>2473</b><br>100% | (1160–1606)<br><b>1325</b><br>100% | (12452–33548)<br><b>21202</b><br>100% |

**Table 4:** Seasonal concentrations (pg/m<sup>3</sup>) of chlorinated paraffins in air samples from the urban and the background site presented as average and range for each season.

\*More than 66% of the samples below the field blanks.

|                            | SCCPs                                  | MCCPs                      | LCCPs                     |
|----------------------------|----------------------------------------|----------------------------|---------------------------|
|                            | Average pg/m <sup>3</sup><br>(Min-Max) |                            |                           |
| Reykjavik Urban Winter     | <b>197</b><br>(180–206)                | <b>578</b><br>(523–609)    | <b>914</b><br>(283–1366)  |
| Reykjavik Urban Summer     | <b>124</b><br>(81–178)                 | <b>714</b><br>(494–966)    | <b>554</b><br>(447–687)   |
| Reykjanesbær Urban Winter  | <b>126</b><br>(50–205)                 | <b>221</b><br>(145–276)    | <b>27</b><br>(2–47)       |
| Reykjanesbær Urban Summer  | <b>84</b><br>(57–115)                  | <b>207*</b><br>(148–251)*  | <b>30</b><br>(14–54)      |
| Helsinki Urban Winter      | <b>393</b><br>(362–433)                | <b>1063</b><br>(1016–1098) | <b>51*</b><br>(16–96)*    |
| Helsinki Urban Summer      | <b>313</b><br>(253–399)                | <b>873</b><br>(732–1059)   | <b>58*</b><br>(<LOD–159)* |
| Oslo Urban Winter          | <b>92</b><br>(69–127)                  | <b>378</b><br>(296–463)    | <b>88</b><br>(<LOD–210)   |
| Oslo Urban Summer          | <b>47*</b><br>(25–72)                  | <b>93*</b><br>(63–144)     | <b>64</b><br>(<LOD–217)   |
| Birkenes Background Winter | <b>178</b><br>(149–225)                | <b>238</b><br>(186–328)    |                           |
| Birkenes Background Summer | <b>234</b><br>(185–279)                | <b>462</b><br>(281–693)    |                           |

### 3.1.2 Car tire wear

Brandsma et al (2019) showed that end-of-life car tires contain high concentrations of CPs with dominance of MCCPs. One goal of this study was therefore to see whether mechanical car tire wearing release CPs to air. Active air samples were collected indoors at a research facility in Sweden (VTI) during mechanical wearing of car tires and while no wearing was performed. Unfortunately, the concentrations of all CPs in the field blank samples for this sampling campaign were elevated and at the same level as or even higher than the exposed samples. No conclusion can therefore be drawn from this side-activity.

## 4. Conclusions

SCCPs, MCCPs and LCCPs were found in most of the air samples from all three Nordic capitals. MCCPs were two to six times higher than the SCCPs in all samples. Lower concentrations of SCCPs may be due to the sampling approach, that underestimates the total concentrations of SCCPs in air. MCCPs were seven to 70 times higher than LCCPs in Helsinki while LCCPs were up to three times higher than MCCPs in Reykjavik. The highest concentrations were observed for MCCPs in Helsinki and LCCPs in Reykjavik.

The findings from this study show elevated concentrations of MCCPs and LCCPs at individual sites, but the concentrations at the urban sites were not consistently higher than at the background monitoring sites. The results from this study therefore show no clear relationship to traffic. Instead, sources may be more diffusive and local sources seem to differ.

# 5. Acknowledgements

## **Finland**

Thanks to Emmi Vähä, Finnish Environment Institute and Kati Loukkola and colleagues at Helsinki Region Environmental Services (HSY) for collecting and delivering the samples from Finland.

## **Iceland**

Thanks to Þorsteinn Jóhannsson, Environment Agency of Iceland, and Wojciech Sasinowski, Marine and Freshwater Research Institute, for collecting and delivering the air samples from Iceland.

## 6. References

- Bogdal, C., Alsberg, T., Diefenbacher, P.S., Macleod, M., Berger, U. (2015) Fast Quantification of Chlorinated Paraffins in Environmental Samples by Direct Injection High-Resolution Mass Spectrometry with Pattern Deconvolution. *Anal. Chem.*, *87*, 2852-2860.
- Bohlin-Nizzetto, P., Aas, W., Halvorsen, H. L., Nikiforov, V., Pfaffhuber, K. A. (2022). Monitoring of environmental contaminants in air and precipitation. Annual report 2021. (Norwegian Environment Agency, M-2317|2022) (NILU report, 19/2022). Kjeller:NILU.
- Brandsma, S.H., Brits, M., Groenewoud, Q.R., Van Velzen, M.J.M., Leonards, P.E.G., De Boer, J. (2019) Chlorinated Paraffins in Car Tires Recycled to Rubber Granulates and Playground Tiles. *Environmental Science & Technology*, *53*, 7595-7603.
- Schlabach, M., Borgen, A.R., Bæk, K., Kringstad, A. (2022) Screening of Chlorinated Paraffins, Dechloranes and UV-filters in Nordic Countries. *TemaNord* 2022:519.
- Thomas, K.V., Schlabach, M., Langford, K., Fjeld, E., Øxnevad, S., Rundberget, T., Bæk, K., Rostkowski, P., Harju, M. (2014) Screening programme 2013: New bisphenols, organic peroxides, fluorinated siloxanes, organic UV filters and selected PBT substances. Oslo/Kjeller, NIVA/NILU (M-176/2014) (NIVA-no 6696-2014; NILU OR 26/2014).
- Tomy, G.T., Fisk, A.T., Westmore, J.B., Muir, D.C. (1998) Environmental chemistry and toxicology of polychlorinated n-alkanes. *Rev.Environ.Contam Toxicol.*, *158*, 53-128.
- Tomy, G.T., Stern, G.A., Muir, D.C.G., Fisk, A.T., Cymbalisty, C.D., Westmore, J.B. (1997) Quantifying C 10 - C 13 polychloroalkanes in environmental samples by high-resolution gas chromatography electron capture negative ion high resolution mass spectrometry. *Anal. Chem.*, *69*, 2762-2771.
- Van Mourik, L.M., Leonards, P.E.G., Gaus, C., De Boer, J. (2015) Recent developments in capabilities for analysing chlorinated paraffins in environmental matrices: A review. *Chemosphere*, *136*, 259-272.  
doi:10.1016/j.chemosphere.2015.05.045



# Appendix A: Sampling details

| NILU number | Country | Location          | Location type | Matrix acronym | Species | Start date | Stop date  | Remark |
|-------------|---------|-------------------|---------------|----------------|---------|------------|------------|--------|
| 22/0592     | NO      | Sofienberg-parken | URB           | AIR            | Filter  | 07.02.2022 | 09.02.2022 |        |
| 22/0821     | NO      | Sofienberg-parken | URB           | AIR            | Filter  | 23.02.2022 | 25.02.2022 |        |
| 22/0822     | NO      | Sofienberg-parken | URB           | AIR            | Filter  | 04.03.2022 | 09.03.2022 |        |
| 22/0823     | NO      | Sofienberg-parken | URB           | AIR            | Filter  | 14.03.2022 | 16.03.2022 |        |
| 22/1264     | NO      | Sofienberg-parken | URB           | AIR            | Filter  | 16.04.2022 | 18.04.2022 |        |
| 22/1751     | NO      | Sofienberg-parken | URB           | AIR            | Filter  | 08.06.2022 | 10.06.2022 |        |
| 22/1758     | NO      | Sofienberg-parken | URB           | AIR            | Filter  | 21.06.2022 | 23.06.2022 |        |
| 22/2025     | NO      | Sofienberg-parken | URB           | AIR            | Filter  | 11.07.2022 | 13.07.2022 |        |
| 22/2029     | NO      | Sofienberg-parken | URB           | AIR            | Filter  | 19.07.2022 | 21.07.2022 |        |
| 22/2203     | NO      | Sofienberg-parken | URB           | AIR            | Filter  | 27.08.2022 | 30.08.2022 |        |
| 22/2493     | NO      | Sofienberg-parken | URB           | AIR            | Filter  | 10.08.2022 | 12.08.2022 |        |
| 22/1760     | FIN     | Backasgatan       | URB           | AIR            | Filter  | 15.01.2022 | 16.01.2022 |        |
| 22/1761     | FIN     | Backasgatan       | URB           | AIR            | Filter  | 10.03.2022 | 11.03.2022 |        |
| 22/1762     | FIN     | Backasgatan       | URB           | AIR            | Filter  | 13.03.2022 | 14.03.2022 |        |
| 22/1765     | FIN     | Backasgatan       | URB           | AIR            | Filter  | 27.05.2022 | 28.05.2022 |        |
| 22/1766     | FIN     | Backasgatan       | URB           | AIR            | Filter  | 30.05.2022 | 31.05.2022 |        |

|         |     |                     |             |     |                    |            |            |     |
|---------|-----|---------------------|-------------|-----|--------------------|------------|------------|-----|
| 22/1767 | FIN | Backasgatan         | URB         | AIR | Filter             | 02.06.2022 | 03.06.2022 |     |
| 22/1768 | FIN | Backasgatan         | URB         | AIR | Filter             | 05.06.2022 | 06.06.2022 |     |
| 22/2160 | ICE | Holmbergs-<br>braut | Sub-<br>URB | AIR | Filter             | 23.03.2022 | 25.03.2022 | Wet |
| 22/2161 | ICE | Holmbergs-<br>braut | Sub-<br>URB | AIR | Filter             | 30.03.2022 | 01.04.2022 | Dry |
| 22/2162 | ICE | Holmbergs-<br>braut | Sub-<br>URB | AIR | Filter             | 04.04.2022 | 06.04.2022 | Dry |
| 22/2165 | ICE | Holmbergs-<br>braut | Sub-<br>URB | AIR | Filter             | 23.03.2022 | 25.03.2022 | Wet |
| 22/2166 | ICE | Grensås             | URB         | AIR | Filter             | 30.03.2022 | 01.04.2022 | Dry |
| 22/2167 | ICE | Grensås             | URB         | AIR | Filter             | 04.04.2022 | 06.04.2022 | Dry |
| 22/3471 | ICE | Grensås             | URB         | AIR | Filter             | 24.08.2022 | 26.08.2022 | Dry |
| 22/3473 | ICE | Holmbergs-<br>braut | Sub-<br>URB | AIR | Filter             | 24.08.2022 | 26.08.2022 | Dry |
| 22/3475 | ICE | Grensås             | URB         | AIR | Filter             | 26.08.2022 | 28.08.2022 | Dry |
| 22/3477 | ICE | Holmbergs-<br>braut | Sub-<br>URB | AIR | Filter             | 26.08.2022 | 28.08.2022 | Dry |
| 22/3479 | ICE | Grensås             | URB         | AIR | Filter             | 28.08.2022 | 30.08.2022 | Wet |
| 22/3481 | ICE | Holmbergs-<br>braut | Sub-<br>URB | AIR | Filter             | 28.08.2022 | 30.08.2022 | Wet |
| 22/0212 | NO  | Birkenes            | REM         | AIR | Filter<br>+<br>PUF | 14.01.2022 | 15.01.2022 |     |
| 22/0490 | NO  | Birkenes            | REM         | AIR | Filter<br>+<br>PUF | 11.02.2022 | 12.02.2022 |     |
| 22/0776 | NO  | Birkenes            | REM         | AIR | Filter<br>+<br>PUF | 11.03.2022 | 12.03.2022 |     |
| 22/1726 | NO  | Birkenes            | REM         | AIR | Filter<br>+<br>PUF | 10.06.2022 | 11.06.2022 |     |

|         |     |          |     |     |                    |            |            |
|---------|-----|----------|-----|-----|--------------------|------------|------------|
| 22/1978 | NO  | Birkenes | REM | AIR | Filter<br>+<br>PUF | 08.07.2022 | 09.07.2022 |
| 22/2176 | NO  | Birkenes | REM | AIR | Filter<br>+<br>PUF | 12.08.2022 | 13.08.2022 |
| 22/1471 | SWE | VTI      | IND | Air | Filter             |            |            |

| NILU number | Country | Units             | SCCPs | MCCPs | LCCPs |
|-------------|---------|-------------------|-------|-------|-------|
| 22/0592     | NO      | pg/m <sup>3</sup> | 127   | 463   | 53    |
| 22/0821     | NO      | pg/m <sup>3</sup> | 72    | 296   | 4     |
| 22/0822     | NO      | pg/m <sup>3</sup> | 110   | 391   | 124   |
| 22/0823     | NO      | pg/m <sup>3</sup> | 81    | 354   | 210   |
| 22/1264     | NO      | pg/m <sup>3</sup> | 69    | 386   | 48    |
| 22/1751     | NO      | pg/m <sup>3</sup> | 52    | 144   | 19    |
| 22/1758     | NO      | pg/m <sup>3</sup> | 52    | 86    | 13    |
| 22/2025     | NO      | pg/m <sup>3</sup> | 42    | 92    | 217   |
| 22/2029     | NO      | pg/m <sup>3</sup> | 72    | 100   | 84    |
| 22/2203     | NO      | pg/m <sup>3</sup> | 25    | 63    | 19    |
| 22/2493     | NO      | pg/m <sup>3</sup> | 38    | 74    | 29    |
| 22/1760     | FIN     | pg/m <sup>3</sup> | 433   | 1016  | 96    |
| 22/1761     | FIN     | pg/m <sup>3</sup> | 362   | 1098  | 16    |
| 22/1762     | FIN     | pg/m <sup>3</sup> | 385   | 1075  | 40    |
| 22/1765     | FIN     | pg/m <sup>3</sup> | 399   | 883   | 59    |
| 22/1766     | FIN     | pg/m <sup>3</sup> | 300   | 818   | 16    |
| 22/1767     | FIN     | pg/m <sup>3</sup> | 300   | 1059  | 159   |

|         |     |                   |     |     |      |
|---------|-----|-------------------|-----|-----|------|
| 22/1768 | FIN | pg/m <sup>3</sup> | 253 | 732 | 0    |
| 22/2160 | ICE | pg/m <sup>3</sup> | 50  | 145 | 2    |
| 22/2161 | ICE | pg/m <sup>3</sup> | 123 | 276 | 32   |
| 22/2162 | ICE | pg/m <sup>3</sup> | 205 | 241 | 47   |
| 22/2165 | ICE | pg/m <sup>3</sup> | 180 | 602 | 283  |
| 22/2166 | ICE | pg/m <sup>3</sup> | 205 | 609 | 1092 |
| 22/2167 | ICE | pg/m <sup>3</sup> | 206 | 523 | 1366 |
| 22/3471 | ICE | pg/m <sup>3</sup> | 178 | 966 | 527  |
| 22/3473 | ICE | pg/m <sup>3</sup> | 115 | 251 | 54   |
| 22/3475 | ICE | pg/m <sup>3</sup> | 113 | 682 | 447  |
| 22/3477 | ICE | pg/m <sup>3</sup> | 80  | 223 | 21   |
| 22/3479 | ICE | pg/m <sup>3</sup> | 81  | 494 | 687  |
| 22/3481 | ICE | pg/m <sup>3</sup> | 57  | 148 | 14   |
| 22/0212 | NO  | pg/m <sup>3</sup> | 149 | 202 |      |
| 22/0490 | NO  | pg/m <sup>3</sup> | 161 | 186 |      |
| 22/0776 | NO  | pg/m <sup>3</sup> | 225 | 328 |      |
| 22/1726 | NO  | pg/m <sup>3</sup> | 279 | 281 |      |
| 22/1978 | NO  | pg/m <sup>3</sup> | 185 | 693 |      |
| 22/2176 | NO  | pg/m <sup>3</sup> | 239 | 412 |      |
| 22/1471 | SWE | VTI               | 288 | 841 |      |

*Italic: Below field blanks*

# About this publication

## Chlorinated paraffins in urban air in Nordic Countries

*Pernilla Bohlin-Nizzetto, Anders Røsrud Borgen, Maja Nipen*

TemaNord 2023:515

ISBN 978-92-893-7577-1 (PDF)

ISBN 978-92-893-7578-8 (ONLINE)

<http://dx.doi.org/10.6027/temanord2023-515>

© Nordic Council of Ministers 2023

Cover photo: Julius Jansson/Unsplash

Published: 11/5/2023

## NILU – Norwegian Institute for Air Research

NILU – Norwegian Institute for Air Research is an independent, non-profit institution established in 1969. Through its research NILU increases the understanding of climate change, of the composition of the atmosphere, of air quality and of hazardous substances. Based on its research, NILU markets integrated services and products within analysing, monitoring and consulting. NILU is concerned with increasing public awareness about climate change and environmental pollution.

*NILU's values: Integrity - Competence - Benefit to society\**

*NILU's vision: Research for a clean atmosphere*

NILU – Norwegian Institute for Air Research

P.O. Box 100, NO-2027 KJELLER, Norway

E-mail: [nilu@nilu.no](mailto:nilu@nilu.no)

<http://www.nilu.no>

## Disclaimer

This publication was funded by the Nordic Council of Ministers. However, the content does not necessarily reflect the Nordic Council of Ministers' views, opinions, attitudes or recommendations.

## Rights and permissions

This work is made available under the Creative Commons Attribution 4.0 International license (CC BY 4.0) <https://creativecommons.org/licenses/by/4.0>.

**Translations:** If you translate this work, please include the following disclaimer: This translation was not produced by the Nordic Council of Ministers and should not be construed as official. The Nordic Council of Ministers cannot be held responsible for the translation or any errors in it.

**Adaptations:** If you adapt this work, please include the following disclaimer along with the attribution: This is an adaptation of an original work by the Nordic Council of Ministers. Responsibility for the views and opinions expressed in the adaptation rests solely with its author(s). The views and opinions in this adaptation have not been approved by the Nordic Council of Ministers.

**Third-party content:** The Nordic Council of Ministers does not necessarily own every single part of this work. The Nordic Council of Ministers cannot, therefore, guarantee that the reuse of third-party content does not infringe the copyright of the third party. If you wish to reuse any third-party content, you bear the risks associated with any such rights violations. You are responsible for determining whether there is a need to obtain permission for the use of third-party content, and if so, for obtaining the relevant permission from the copyright holder. Examples of third-party content may include, but are not limited to, tables, figures or images.

**Photo rights (further permission required for reuse):**

Any queries regarding rights and licences should be addressed to:  
Nordic Council of Ministers/Publication Unit  
Ved Stranden 18  
DK-1061 Copenhagen  
Denmark  
[pub@norden.org](mailto:pub@norden.org)

**Nordic co-operation**

*Nordic co-operation* is one of the world's most extensive forms of regional collaboration, involving Denmark, Finland, Iceland, Norway, Sweden, and the Faroe Islands, Greenland and Åland.

*Nordic co-operation* has firm traditions in politics, economics and culture and plays an important role in European and international forums. The Nordic community strives for a strong Nordic Region in a strong Europe.

*Nordic co-operation* promotes regional interests and values in a global world. The values shared by the Nordic countries help make the region one of the most innovative and competitive in the world.

The Nordic Council of Ministers  
Nordens Hus

Ved Stranden 18  
DK-1061 Copenhagen  
pub@norden.org

Read more Nordic publications on [www.norden.org/publications](http://www.norden.org/publications)