Short and medium-chain chlorinated paraffins (C10 – C17)

Background

Chlorinated paraffins (CPs) are manufactured on large-scale by chlorination of n-Alkanes (C_{10}–C_{30}); technical chlorinated paraffins usually consist of a mixture of straight-chain chlorinated paraffins with differing chain lengths and chlorination levels. Distinction is made between short (C_{10–C_{13}}, short-chain CPs, SCCP), medium (C_{14–C_{17}}, medium-chain CPs, MCCP) and long-chain (> C_{17}, long chain CPs, LCCP) chlorinated paraffins. The level of chlorination of technical products ranges between 15 % and 70 %.

Chlorinated paraffins are, among others, used as flame retardants and softening agents in PVC and varnish raw materials as well as an element of paints and lubrication fluids e.g. in the metal processing. Short-chain (C_{10–C_{13}}) chlorinated paraffins are primarily used in metallurgy, medium-chain (C_{14–C_{17}}) chlorinated paraffins as softeners and flame retardants in various PVC products such as floor coverings, cable casings and insulation materials.

The main path in which chlorinated paraffins (SCCP and MCCP) enter the environment is via emissions from metal and leather processing (in the form of waste water) and from waste treatment and the depositing of plastics (in the form of exhaust emissions and waste water). Short and medium-chain chlorinated paraffins have a toxic effect on aquatic organisms, very poor biodegradable qualities and enter the human and animal food chains. They have been identified in most environmental compartments at trace levels like in water, soil, biota and human tissue.

The eco-toxicological qualities of chlorinated paraffins depend on the chain length and chlorination level. Short-chain chlorinated paraffins (10-13 carbon atoms, 58 % chlorination level) may act as tumour promoters (carcinogenic) and reproduction toxic (teratogenic).

The German commission for setting maximum levels for hazardous substances in workplace air (MAK-Kommission) has classified various chlorinated paraffins into group III B: "Substances with justified suspicion of carcinogenic potential", although without giving any details.

C_{10–C_{13}} chlorinated paraffins are persistent, bio-accumulating, toxic compounds which are classified as priority hazardous within the Water Framework Directive (WRRL). According to EU guideline 2002/45/EC the circulation of substances with >1 % short-chain chlorinated paraffins has been banned in the metal and leather processing industry since January 2004. In addition, it is considered to include the short-chain chlorinated paraffins into the list of the Stockholm Convention on Persistent Organic Pollutants (POPs).

Analysis parameters

- Total of short-chain chlorinated paraffins (C10 – C13)
- Total of medium-chain chlorinated paraffins (C14 – C17)
Testing methods

Eurofins GfA Lab Service GmbH is accredited for determining short and medium-chain chlorinated paraffins (C10-C17) in air, exhaust gases, water, plants, dust, filter dust, ash, slag, soils, foods and human samples in accordance with DIN EN ISO/IEC 17025:2005.

The fundamental analysis steps in the case of all matrices are as follows:

- Extraction of the homogenised sample material by means of Toluene
- Addition of an internal standard (cis-Chlordane)
- Addition of a recovery standard (trans-Chlordane)
- Clean-up by means of sulfuric acid treatment and column chromatography
- Analysis by means of gas chromatography coupled with mass spectrometry (GC/MS-NCI)
- Quantification of the native chlorinated paraffins acc. to the method of the internal standard
- Calibration by way of technical C10-C13 and C14-C17 Cl paraffin mixtures: SCCP: 51.5 %, 55.5 %, 60 % and 63 % chlorine content; MCPP: 42 %, 52 % and 57 % chlorine content
- The calibration mixture is adjusted in line with the chloroparaffin pattern of the sample to be analysed.

Quantification limits, sample quantities and sample transport

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Quantification limit *</th>
<th>Sample quantity</th>
<th>Preferred sample containers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge, sediment, soil</td>
<td>1 - 5 µg/kg dry mass</td>
<td>100 g original sample</td>
<td>glass vessel</td>
</tr>
<tr>
<td>Liquids (watery matrix)</td>
<td>1 - 5 ng/l</td>
<td>2 x 1 l liquid</td>
<td>glass vessel</td>
</tr>
<tr>
<td>Biota</td>
<td>1 - 5 µg/kg</td>
<td>100 g original sample</td>
<td>glass vessel</td>
</tr>
<tr>
<td>Commodities</td>
<td>depending on matrix</td>
<td>after consultation</td>
<td>glass vessel</td>
</tr>
</tbody>
</table>

* The quantification limit varies with the chain length and chlorination level.

Quality assurance

Selection of interlaboratory comparison

<table>
<thead>
<tr>
<th>Time Frame</th>
<th>Organiser</th>
<th>Title</th>
<th>Parameter</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>April 2015 -</td>
<td>Ontario Ministry of the Environment and Climate Change (MOECC), CA</td>
<td>NCP III - Phase 9</td>
<td>OCP, PCB, OPFR, Chlorinated Paraffin (CP)</td>
<td>injection ready standards</td>
</tr>
<tr>
<td>April 2015 -</td>
<td>Interprofessional Bureau of Analytical Studies (BIP/Ea), Paris, FR</td>
<td>Waste Waters 202015 - 53 c,d, h</td>
<td>Alkylphenols, PBDE, OTC, Chlorinated Paraffin (CP)</td>
<td>waste water</td>
</tr>
<tr>
<td>August 2014 -</td>
<td>QUASIMEME Project Office, Wageningen UR, NL</td>
<td>Quasimeme Interlaboratory Study on the Analysis of Chlorinated Paraffins - Phase III</td>
<td>Chlorinated Paraffin (CP)</td>
<td>sediment</td>
</tr>
<tr>
<td>June 13 - August 13</td>
<td>Universitary Institute for Environmental Studies (IVM), Amsterdam, NL</td>
<td>Quasimeme Interlaboratory Study on the Analysis of Chlorinated Paraffins - Phase II</td>
<td>Chlorinated Paraffin (CP)</td>
<td>fish extract, standard</td>
</tr>
</tbody>
</table>
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References

Analysis of 27 peregrine falcon eggs within the POP monitoring for PBDEs, TBBP A, HBCD, Bisphenol A, Chloroparaffins, organotin compounds, perfluorinated chemicals and others on behalf of the Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg (LUBW; 2009-2014)

Examination of about 80 material samples for short and medium-chained chloroparaffins (SCCP/MCCP) subcontracted by the Eurofins Scientific AG Schönenwerd, Switzerland (2009)

Bussmann, P., “Development of an analysis procedure to determine short-chain chlorinated paraffins (C14-C17) in environmental samples”, Thesis at Münster Faculty, Department of Chemical Engineering, June 2006

Petersen, M., “Development of an analysis procedure to determine short-chain chlorinated paraffins (C10-C13) in environmental samples”, Thesis in the study course Environmental Technology of Hamburg Faculty, area of expertise: Scientific Technology, June 2002

National examination for organic trace pollution in running waters in Hesse, waste water and sewage sludge, HLUG, Umweltplanung, Arbeits- und Umweltschutz, 2001 and 2002

Publications


Petersen, M., Bussmann, P., Grümping, R., Lieck, G., Organohalogen Compounds 68 (2006) 2101-2104, Analysis of Short-chain (C10-C13) and Medium-chain Chlorinated Paraffins (C14-C17) in Norwegian Sediment and Water Samples by GC/ECNI-MS