Für Mensch & Umwelt

As at: 30 September 2022

# Report: Migration of Substances from Injection Moulded Components Produced by Different Companies

## 1 Objective

The aim of the study was to investigate, by means of GC-MS screening, the migrating substances from components produced by different companies in comparison with special test plates made by the granulate producers and to determine whether production at different production sites has an impact on the quality of the components with respect to the migration of substances.

The research was also aimed to gain experience about the use of the GC-MS screening method according to DIN EN 15768 to assess unexpected substances in framework of the certification of products intended to be used in contact with drinking water.

## 2 Sample description

Various injection moulded components used in assembled products were provided by different producers. Four different plastics materials were investigated: polyamide (PA), polyoxymethylene copolymer (POM-C), polyphenylenether (PPE) and polysulfone (PSU). Table 1 gives an overview about the provided components. It includes also details about the granulates (pre-product) of with the components are produced. For POM-C, PSU and PA the components were made of the same granulates. For PPE two components were made of two different granulates.

**Table 1 Overview of injection moulded components**

| **Sample** | **POM-C** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| **Granulate** | Disclosed confidentially – G.I* | | | | | | | | |
| **Injection moulder[a]** | F | G | H | G | A | B | I | J | PG[b] |
| **Sample** | **PSU** | | | | | | | | |
| | 1 | | | 2 | | | 3 | | 4 |
| **Granulate** | n.a. | | | | | | | | |
| **Injection moulder[a]** | G | | | C | | | G | | L |
| **Sample** | **PPE** | | | | | | | | |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| **Granulate** | n.a. | | | Disclosed confidentially – G.II* | | | | | |
| **Injection moulder[a]** | H | F | F | K | A | A | PG[b] | L | |
| **Sample** | **PA** | | | | | | | | |
| | 1 | | 2 | 3 | 4 | | 5 | | 6 |
| **Granulate** | Disclosed confidentially – G.III* | | | | | | | | |
| **Injection moulder[a]** | A | | B | C | PG[b] | | D | | E |

* All POM are made from one granulate: G.I, PPE-4 – PPE-8 are made from one granulate : G.II and PA are made from one granulate: G.III; [a] Each alphabetic character corresponds to one injection moulder; [b] Plates made by the producer of granulates; n.a. not available.

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# 3 Methods

## 3.1 Preparation of the migration waters

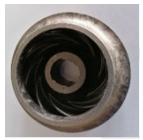
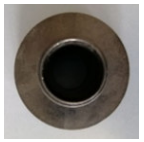
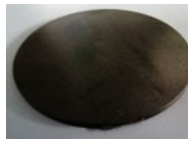
The migration waters were prepared according to DIN EN 12873-1 “Influence of materials on water intended for human consumption – Influence due to migration – Part 1: Test method for factory-made products made from or incorporating organic or glassy porcelain/vitreous/enamel materials”.

Previous to the migration the different test pieces were pre-treated as follow: (1) flushed for one-hour, (2) then put in contact with test water for 24 hours, (3) followed by one more one-hour flushing. The migration was then undertaken in closed glass chamber. In total 27 types of test pieces from four different materials (POM (9), PSU (4), PPE (8), PA (6)) were investigated and are presented in Table 2. The specific surface-area of the test pieces-to-the volume of test water (S/V) is given in Table 2.

Some migration tests were carried out in cold (23°C) and warm (60°C) water whereas others were prepared in warm water only (Table 2). The test pieces were put in contact with ultrapure test water for 72 h in case of cold water test and for 24 h in case of warm water test. The migration test was performed for 31 days (extended migration test). To obtain enough migration water for the analysis and to reach a required S/V-ratio of > 5 $dm^{-1}$ several test specimens were exposed to the test water in one glass chamber per migration period. At the end of each period the migration waters were analysed by means of GC-MS screening and for total organic carbon (TOC). For the determination of the threshold odour number (TON) according DIN EN 1420 the migration tests were carried out with unchlorinated drinking water and with a different S/V ratio (S/V = 1,5 $dm^{-1}$). The migration periods and the pre-treatment were the same as for the migration test to investigate the other parameters. In all migrations, test blanks were similarly prepared to check for any eventual external contamination.

For one material, PPE, dibutylamine (DBA) was determined specifically, for which 1 mL of the migration waters – same migration water as for GC-MS screening – was analysed using HPLC-MS.

**Table 2 Test pieces and testing parameters**

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Material: **POM** | POM-C-1  | POM-C-2  | POM-C-3  | POM-C-4  | POM-C-5  | POM-C6  | POM-C-7  | POM-C-8  | POM-C-9  |
| S/V (dm$^{-1}$) | 5,22 | 5,15 | 5,20 | 5,20 | 5,00 | 5,00 | 5,00 | 5,04 | 4,98 |
| Temp. (°C) | 23 / 60 | 23 / 60 | 23 / 60 | 23/ 60 | 60 | 60 | 60 | 60 | 60 |
| Material: **PSU** | PSU-1  | | PSU-2  | | PSU-3  | | PSU-4  | | |
| S/V (dm$^{-1}$) | 5,26 | | 5,28 | | 5,31 | | 5,30 | | |
| Temp. (°C) | 23 / 60 | | 23 / 60 | | 23 / 60 | | 23 / 60 | | |
| Material: **PPE** | PPE-1  | PPE-2  | PPE-3  | PPE-4  | PPE-5  | PPE-6  | PPE-7  | PPE-8  | |
| S/V (dm$^{-1}$) | 5,33 | 5,33 | 5,36 | 5,04 | 4,98 | 5,00 | 4,99 | 5,00 | |
| Temp. (°C) | 23 / 60 | 23 / 60 | 23 / 60 | 60 | 60 | 60 | 60 | 60 | |
| Material: **PA** | PA-1  | PA-2  | PA-3  | PA-4  | PA-5  | PA-6  | | | |
| S/V (dm$^{-1}$) | 5,00 | 5,00 | 5,00 | 4,99 | 4,97 | 4,98 | | | |
| Temp. (°C) | 60 | 60 | 60 | 60 | 60 | 60 | | | |

## 3.2 TOC determination

The determination of the total organic carbon in the migration waters was carried out following DIN EN 1484 “Water analysis – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)” using a TOC-L Analyser (Shimadzu Deutschland GmbH) (Table 3). The non-volatile part of the TOC, thus the non-purgeable organic matter (NPOC) was determined.

**Table 3 Parameters of the TOC device**

| | |
|---|---|
| **Oxidation** | Catalytic combustion (680 °C) |
| **System of detection** | Non-dispersive infrared detection (NDIR) |
| **Limit of detection** | 0,070 mg/l |

## 3.3 TON determination

TON values of migration water samples were determined in accordance with DIN EN 1420 “Influence of organic materials on water intended for human consumption — Determination of odour and flavour assessment of water in piping systems” and DIN EN 1622 “Water quality – Determination of the threshold odour number (TON) and threshold flavour number (TFN)”

The threshold flavour number (TFN) was not determined.

According to DIN EN 1420 for ancillaries or component of ancillaries the migration test has to be performed with S/V = 1,5 $dm^{-1}$.

## 3.4 GC-MS Screening

The analytical procedure was performed according to DIN EN 15768 “GC-MS identification of water leachable organic substances from materials in contact with water intended for human consumption” allowing the detection and the semi-quantification of contaminants leaching from the injection moulded test pieces. The parameters of analysis are presented in Table 4.

**Table 4 Parameters of the GC-MS device**

| | |
|---|---|
| **GC** | Agilent 6890N |
| **Detection** | Agilent 5973N Mass Selective Detector |
| **Column** | 60 m Zebron |
| **Temp. of injection** | 250 °C |
| **Oven temp.** | 40 °C bis 300 °C |
| **Carrier gas** | Helium |
| **Volume of sample** | 1 µl |

## 3.5 Determination of dibutylamine

Dibutylamine was determined using HPLC-MS (Table 5). A small sample volume of the migration water (max. 1.5 ml) was filled into vials, from which a volume of 10 µl was injected directly into the device. An 11-point calibration was carried out (0.1 µg/l; 0.2 µg/l; 0.4 µg/l; 0.6 µg/l; 0.8 µg/l; 1.0 µg/l; 2.0 µg/l; 4.0 µg/l; 6.0 µg/l; 8.0 µg/l; 10 µg/l).

**Table 5 Parameters of the HPLC-MS device**

| | |
|---|---|
| **HPLC** | Agilent series 1200 |
| **Guard column** | Agilent Poroshell 120, EC-C18 (2,7 µm); 3,0 x 50 mm |
| **Detector** | AB SCIEX QTRAP 6500 Mass Detector |
| **Column** | Agilent Poroshell 120, EC-C18 (2,7 µm); 2,1 x 75 mm |
| **Pump** | Agilent 1260 G1312B |
| **Oven temp.** | 25 °C |
| **Eluent** | A: water (5 mM ammonium acetate, 0,1 vol% methanoic acid);<br>B: acetonitrile (5 vol% LC/MS-water, 5 mM ammonium acetate, 0,1 vol% methanoic acid) |
| **Volume of sample** | 10 µl |

| Step | Total time (Min) | Flow Rate (µl/min) | A (%) | B (%) |
|---|---|---|---|---|
| 0 | 0,00 | 300 | 90 | 10 |
| 1 | 3,00 | 300 | 90 | 10 |
| 2 | 8,00 | 300 | 30 | 70 |
| 3 | 10,00 | 300 | 30 | 70 |
| 4 | 15,00 | 300 | 90 | 10 |
| 5 | 18,00 | 300 | 90 | 10 |

# 4 Results

All the results generated were obtained under conditions that do not represent the real use of the end products in practice. Therefore, the concentrations determined in the migration tests are converted to the maximal estimated concentration at the consumer's tap ($c_{tap}$) following the KTW evaluation criteria document (https://www.umweltbundesamt.de/en/document/evaluation-criteria-document-for-plastics-other-1) and using a conversion factor Fc = 2 d/dm for ancillaries and fittings for pipes with ID < 80 mm (see Table 7 of the KTW-evaluation criteria document). The exact surface fraction of the tested components in the assembled end product is not known. In some cases, the surface fraction of the tested components might be less than 10% of the wetted surface of the assembled product. The conversion factor for these components is 0,2 d/dm, the presented concentrations will have to be divided by a factor 10.

## 4.1 TOC release

The TOC values measured in the migration waters of the different test pieces were converted to $c_{tap}$. For the following test pieces, the determined $c_{tap}$ did not exceed the acceptance criteria ($MTC_{tap,TOC}$ = 0,5 mg/l), neither in cold water tests (when applicable), nor in warm water tests:

- POM-C-1 – POM-C-9 (Figure 1),
- PSU-1 – PSU-4 (Figure 2) and
- PPE-1 – PPE-8 (Figure 3).

The concentrations do not show an increasing trend.

The TOC values determined in the migration waters tests (warm water) of PA-1, PA-2, PA-3, PA 4, PA-5 and PA-6 failed the $MTC_{tap}$ of 0,5 mg/l at the 10$^{th}$ day (relevant assessment day) (Figure 4). By extending the migration tests up to the 31$^{st}$ day (relevant assessment day), the TOC values of all the migration waters met the requirement. The concentrations do not show an increasing trend.

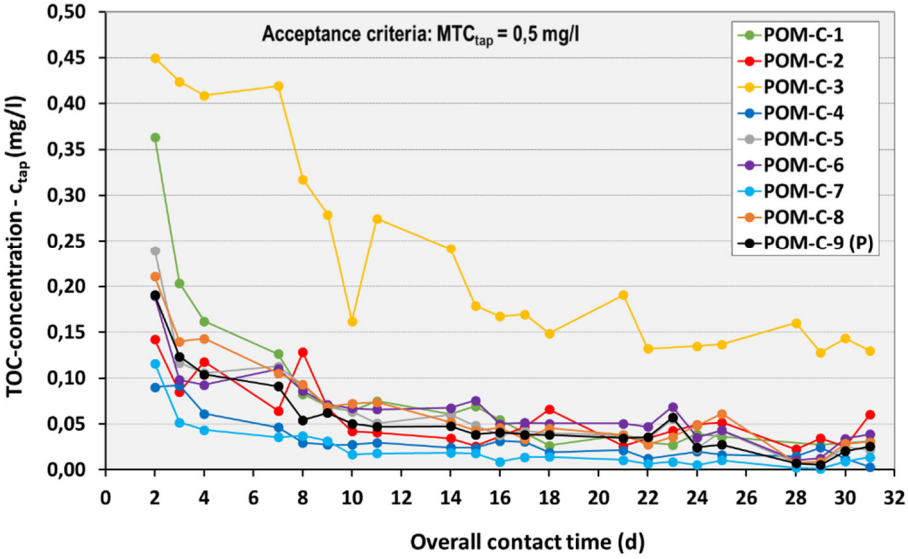



**Figure 1 TOC (POM-C1 – POM-C-9) of warm water test (60°C). *(P): plate***

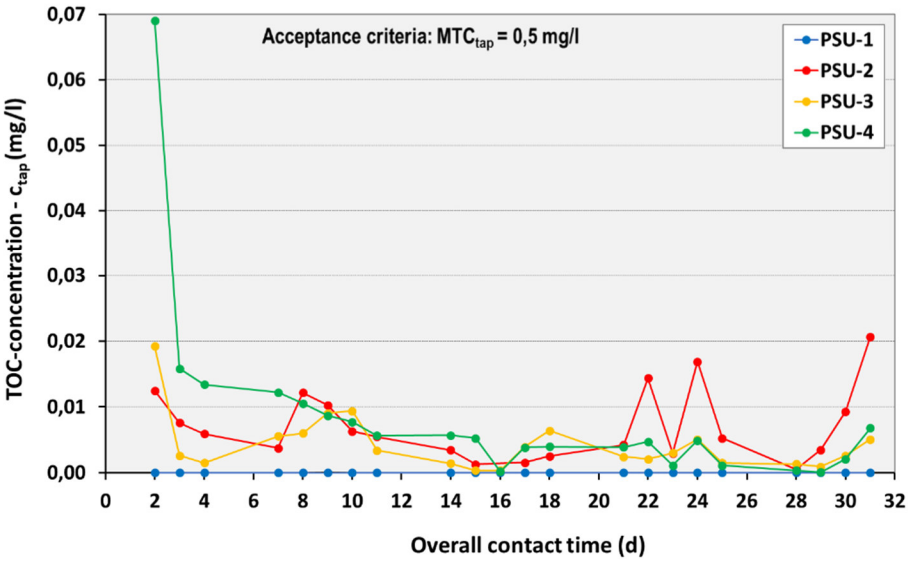



**Figure 2 TOC (PSU-1 – PSU-4) of warm water test (60°C)**

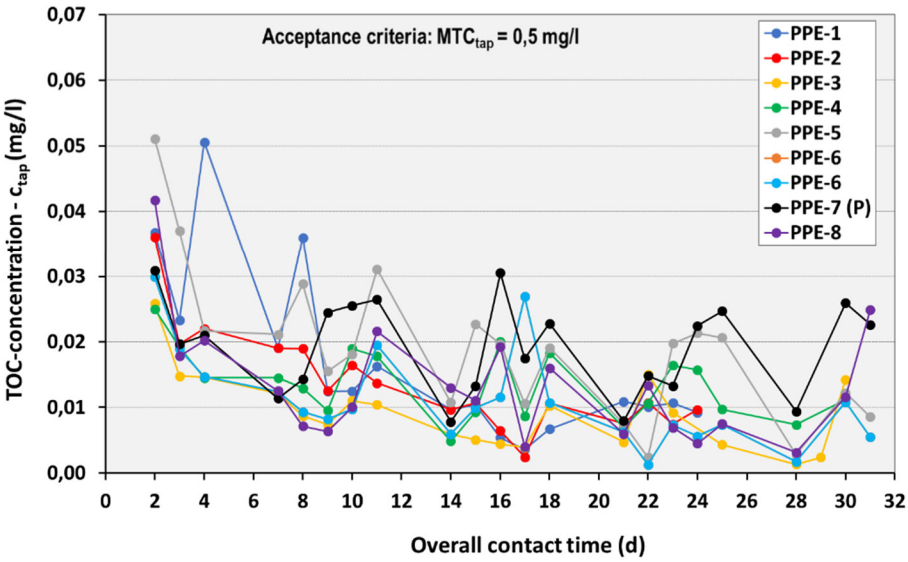



**Figure 3 TOC (PPE-1 – PPE-8) of warm water test (60°C). *(P): plate***

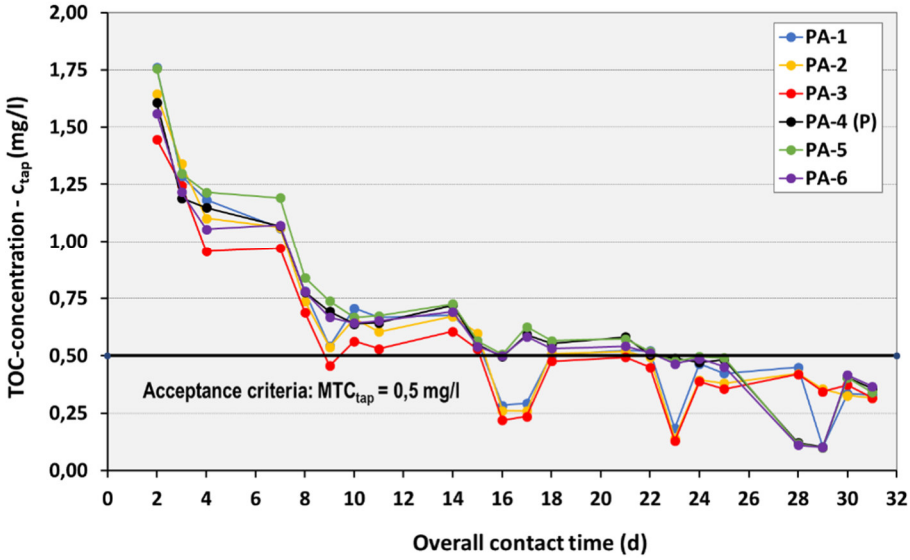



**Figure 4 TOC (PA-1 – PA-6) of warm water test (60°C). *(P): plate***

## 4.2 TON

Most of the tests were performed as warm water tests only, with the exemption of PPE, for which the TON values were determined in the migration waters of the cold and warm water test.

The results showed that all the materials – POM, PSU, PPE and PA – met the requirement of TON ≤ 4, and this already at the 10$^{th}$ day (relevant assessment day).

## 4.3 Detection of contaminants with GC-MS screening / HPLC

Analysis of the migration waters with the GC-MS screening detected and semi-quantified 69 compounds, of which 39 could be identified and 30 are reported as unknown. In this report we focus on selected contaminants with a minimum concentration of 0,1 µg/l (as $c_{tap}$) detected at the 10$^{th}$ day.

The substances were identified using the NIST 14 mass spectral library. To confirm these findings, some of the chemicals identified were also verified with individual standards.

The results for the different components are presented in the Table 6, Table 7 and Table 8. Not all the contaminants were detected in all the migration waters. Most of them were identified in warm waters, and most of these substances were specific for the granulates. Nevertheless 3 substances could be identified among two or three materials. For example, 1,2-Diphenoxy-ethane was detected in POM-C, PSU and PPE; Styrene in POM-C and PPE, and acetophenone in PSU and PPE.

**Table 6 Detected substances in the migration waters of different test pieces - warm water test (60°C)**

| | Compounds | Materials | | | | | | | | | | | | | | | | | | | | | | | | MTC$_{tap}$ (µg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | POM-C | | | | | | | | | PSU | | | | PPE | | | | | | | | PA | | | | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 1 | 2 | 3 | 4 | 5 | 6 | |
| 1 | 1,3-Dioxolane** | x | x | | | x | x | | X | x | | | | | | | | | | | | | | | | | | 250[a] |
| 2 | 1,3,5-Trioxane** | x | x | | x | x | x | x | X | x | | | | | | | | | | | | | | | | | | 250[a] |
| 3 | 1,3,5-Trioxepane | x | | | | x | x | | X | x | | | | | | | | | | | | | | | | | | 0,1[b] |
| 4 | 2-tert-Butyl-6-methylphenol | x | | | x | | | | | | | | | | | | | | | | | | | | | | | 0,1[b] |
| 5 | 1,2-Diphenoxy-ethane | x | x | x | x | | | | | | x | | | x | x | x | x | | | | | | | | | | | | 0,1[b] |
| 6 | 1,3-Diphenylpropane | | | | | | | | | | | | | | x | x | x | | | | | | | | | | | | 0,1[b] |
| 7 | Styrene | | | x | | | | | | | | | | | x | x | x | x | x | x | x | x | | | | | | | No limit[a] |
| 8 | Toluene | | | | | | | | | | | | | | x | x | | x | x | x | x | x | | | | | | | 60[c] |
| 9 | 2,6-Di-tert-butyl-4-hydroxy-4-methylcyclo-hexa-2,5-dien-1-on** | | | x | | | | | | | | | | | | | | | | | | | | | | | | | 0,1[b] |
| 10 | Chlorobenzene | | | | | | | | | | x | x | x | | | | | | | | | | | | | | | | 0,1[c] |
| 11 | Butyldiglycol | | | | | | | | | | | | x | | | | | | | | | | | | | | | | 0,1[b]/150* |
| 12 | Benzyl alcohol** | | | | | | | | | | | | | x | | | | | | | | | | | | | | | No limit[a] |
| 13 | Benzaldehyde** | | | | | | | | | | | | | | | x | | | | | | | | | | | | | No limit[a] |
| 14 | Acetophenone** | | | | | | | | | | | | | x | | | x | | | | | | | | | | | | 0,1[b]/ 0,7* |
| 15 | Phenoxy-ethanol** | | | | | | | | | | | | | x | | | | | | | | | | | | | | | 0,1[b] |
| 16 | 2,2′-Methylenbis(4-methyl-6-tert-butylphenol) | | | | | | | | | | | | | x | | | | | | | | | | | | | | | 75[a] |
| 17 | 2,3-Dihydrobenzo-furan | | | | | | | | | | | | | | x | x | x | | | | | | | | | | | | 0,1[b] |
| 18 | Nonanal | | | | | | | | | | | | | | x | x | | | | | | | | | | | | | 0,1[b] |
| 19 | Butanal | | | | | | | | | | | | | | | | | x | x | x | x | x | | | | | | | No limit[a] |
| 20 | 5-Methylene-4,5,6,6a-tetrahydro-3ah-pentalen-1-one | | | | | | | | | | | | | | | x | | | | | | | | | | | | | 0,1[b] |
| 21 | 2,4-Di-tert-butylphenol** (*Arvin IV*) | | | | | | | | | | | | | | | x | x | | | | x | x | | | | | | | 250[e] |
| 22 | Dioctylether | | | | | | | | | | | | | | | x | | | | | | | | | | | | | 0,1[b] |
| 23 | Isopropyl-palmitate | | | | | | | | | | | | | | | x | | | | | | | | | | | | | No limit[a] |
| 24 | Ethylbenzene | | | | | | | | | | | | | | | | | x | | x | x | | | | | | | | 30[d] |
| 25 | 2,6-Di-tert-butyl-4-hydroxy-4-methylcyclohexa-2,5-dien-1-on | | | | | | | | | | | | | | | | | | x | | | | | | | | | | 0,1[b] |
| 26 | Tetrahydrofurane | | | | | | | | | | | | | | | | | | | | | | x | x | x | x | x | x | 30[a] |
| 27 | Dimethoxybutane | | | | | | | | | | | | | | | | | | | | | | | | x | | | | 0,1[b] |
| 28 | Cyclopentanone** | | | | | | | | | | | | | | | | | | | | | | x | x | x | x | x | x | 0,1[b] |
| 29 | 2-Methylcyclopentanone | | | | | | | | | | | | | | | | | | | | | | x | | x | x | x | x | 0,1[b] |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 30 | 2-Methylen-4-pentennitril | | | | | | | | x | 0,1[b] |
| 31 | 2-Ethylcyclopentanone | | | x | x | | x | x | x | 0,1[b] |
| 32 | 2-Ethylhexan-1-ol** | | | x | x | x | x | x | x | 1500[a] |
| 33 | 2,2,6,6-Tetramethyl 3,5-heptandione | | | x | | x | x | | x | 0,1[b] |
| 34 | Caprolactam** | | | x | x | x | x | x | x | 750[a] |
| 35 | [1,1'-Bicyclopentyl]-2-one | | | x | x | x | x | x | x | 0,1[b] |
| 36 | [1,1'-Bicyclopentyliden]-2-one | | | | | | | | x | 0,1[b] |
| 37 | 2,6-Di-tert-butyl-p-benzochinone** | | | x | | x | x | x | x | 2,5[f] |
| 38 | Methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate** | | | x | x | | | x | | 50[f] |
| 39 | 7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-dien-2,8-dione** | | | | | x | | | | Under assessment |

** Identified with individual standards

$MTC_{tap}$ : a) listed in regulation (EU) No. 10 /2011

b) not assessed

c) 4 MSI-lists (4 Member State Initiative)

* Butyldiglycol: used as a starting substance: 0.1 µg/l would apply, since this is not evaluated for plastics. There is only one rating for silicones and coatings with $MTC_{tap}$ = 150 µg/l. Acetophenone: used as a starting substance: 0.1 µg/l would apply, since this is not evaluated for plastics. There is only one assessment as a degradation product of a peroxide for elastomers with $MTC_{tap}$ = 0.7 µg/l.

d) listed in KTW-BWGL

e) 4MSI Draft Common Approach on Organic Materials– Part C

f) Evaluated as degradation product of stabilisers

**Table 7 Unknown substances detected in the migration waters of different test pieces - warm water test(60°C)**

| | Compounds | Materials | | | | | | | | | | | | | | | | | | | | | | | | | | $MTC_{tap}$ (µg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | POM-C | | | | | | | | | PSU | | | | PPE | | | | | | | | PA | | | | | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 1 | 2 | 3 | 4 | 5 | 6 | |
| 1 | U (43;141;84;70)156 | | | | | | | | | | | | | | | | | | | | | | | | | | x | | |
| 2 | U (61; 91; 90; 44)152 | x | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3 | U (61; 91; 90; 44)207 | x | | | | | | | | | | | | | | | | | | | | | | | | | | | 0,1[b] |
| 4 | U (61; 91; 121; 44)209 | | | | | x | | | | | | | | | | | | | | | | | | | | | | | |
| 5 | U (61; 91; 121; 89)209 | | | | | | x | | | | | | | | | | | | | | | | | | | | | | |
| 6 | U (61; 91; 121; 89)210 | | | | | | | | X | | | | | | | | | | | | | | | | | | | | |
| 7 | U (61; 91; 89; 121)239 | | | | | | | | | x | | | | | | | | | | | | | | | | | | | |
| 8 | U (161; 235; 250; 177)252 | x | x | | x | x | | | | | | | | | | | | | | | | | | | | | | | 0,1[b] |
| 9 | U (61; 91; 89; 121)281 | x | | | | | | | | x | | | | | | | | | | | | | | | | | | | |
| 10 | U (61; 91; 121; 151)239 | | | | | | | | X | | | | | | | | | | | | | | | | | | | | |
| 11 | U (61; 91; 121; 151)280 | | | | | x | | | | | | | | | | | | | | | | | | | | | | | |
| 12 | U (61; 91; 89; 121)239 | | | | | | x | | | | | | | | | | | | | | | | | | | | | | |
| 13 | U (61; 91; 89; 151)354 | | | | | x | | | X | | | | | | | | | | | | | | | | | | | | 0,1[b] |
| 14 | U (61; 91; 89; 151)239 | | x | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 15 | U (61; 91; 89; 151)280 | | | | | x | | | | | | | | | | | | | | | | | | | | | | | |
| 16 | U (61; 91; 89; 151)281 | | x | | | x | x | x | X | x | | | | | | | | | | | | | | | | | | | |
| 17 | U (61; 91; 89; 151)282 | x | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 18 | U (61; 89; 91; 151)283 | | | | | | | | | x | | | | | | | | | | | | | | | | | | | 0,1[b] |
| 19 | U (61; 91; 89; 151)355 | x | | | | x | x | x | | x | | | | | | | | | | | | | | | | | | | |
| 20 | U (61; 91; 89; 151)414 | | | | | | | | X | | | | | | | | | | | | | | | | | | | | |
| 21 | U (61; 91; 89; 151)415 | x | | | | | x | | X | x | | | | | | | | | | | | | | | | | | | |
| 22 | U (61; 91; 89; 151)429 | | | | | | x | | | | | | | | | | | | | | | | | | | | | | |
| 23 | U (73; 61; 44; 75)341 | | | | | | x | | | | | | | | | | | | | | | | | | | | | | 0,1[b] |
| 24 | U (73; 61; 44; 105)253 | | | | | | | | X | | | | | | | | | | | | | | | | | | | | |
| 25 | U (73; 61; 44; 105)280 | | | | | x | | | | | | | | | | | | | | | | | | | | | | | |
| 26 | U (73; 61; 44; 105)282 | | | | | | | | X | x | | | | | | | | | | | | | | | | | | | |
| 27 | U (73; 61; 44; 105)402 | | | | | | x | | | | | | | | | | | | | | | | | | | | | | |
| 28 | U (73; 61; 44; 105)415 | | | | | x | | | | x | | | | | | | | | | | | | | | | | | | 0,1[b] |
| 29 | U (161; 235; 250; 177)252 | | | | | | x | | X | x | | | | | | | | | | | | | | | | | | | |
| 30 | U (112; 55; 86; 98)281 | | | | | | | | | | | | | | | | | | | | | | x | x | x | x | x | x | |

$MTC_{tap}$: b) not assessed

**Table 8 Detected substances in the migration waters of different test pieces - cold water test (23°C)**

| | Compounds | Materials | | | | | | | | | | | $MTC_{tap}$ (µg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | POM-C | | | | PSU | | | | PPE | | | |
| | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | |
| 1 | 1,3-Dioxolane** | | x | | | | | | | | | | 250[a] |
| 2 | 1,3,5-Trioxane** | x | x | | x | | | | | | | | 250[a] |
| 3 | 1,2-Diphenoxyethan | x | x | x | x | | | | | x | x | x | 0,1[b] |
| 4 | Diethylhexyl-adipate | | | x | x | | | | | | | | 900[a] |
| 5 | Chlorobenzene | | | | | x | | | | | | | 0,1[c] |
| 6 | 2,6-Di-tert-butyl-4-hydroxy-4-methylcyclo-hexa-2,5-dien-1-on** | | | | | x | | | | | | | 0,1[b] |
| 7 | alpha-Bisabolol | | | | | | x | | | | | | 0,1[b] |
| 8 | Trichloroacetic acid, 3-tridecyl ester | | | | | | x | | | | | | 0,1[b] |
| 9 | Isopropyl-palmitate | | | | | | x | | | | | | No limit[a] |
| 10 | Styrene | | | | | | | | | x | x | x | No limit[a] |

** Identified with individual standards

$MTC_{tap}$: a) listed in regulation (EU) No. 10 /2011
b) not assessed
c) 4 MSI-lists (4 Member State Initiative)

Characteristic examples of contaminants released over contact time in warm water tests are presented in Figure 5 to Figure 14. The presented substances were detected in a minimum of three migration periods.

### 4.3.1 POM-C

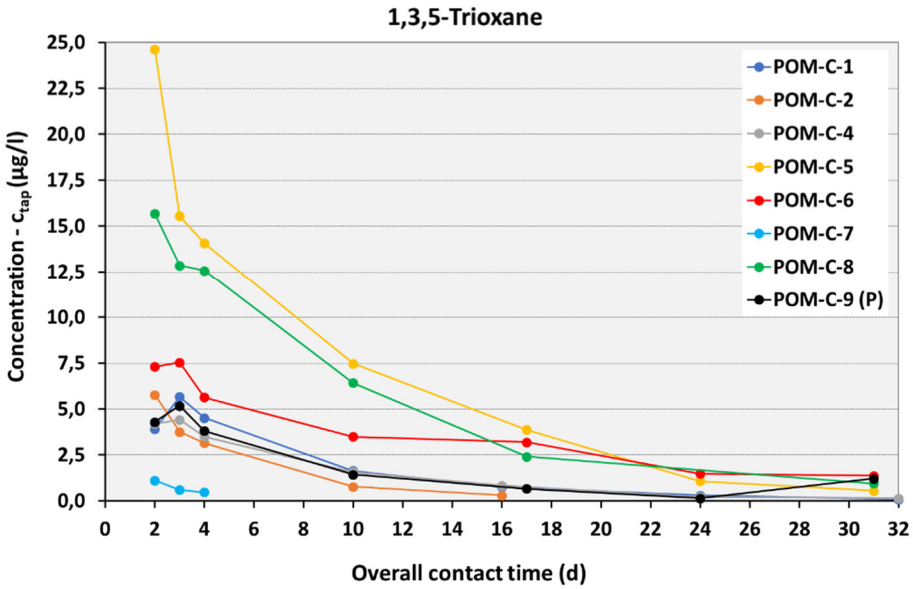



**Figure 5 Semi-quantitative concentrations of 1,3,5-Trioxane released over time for POM-C for warm water test**

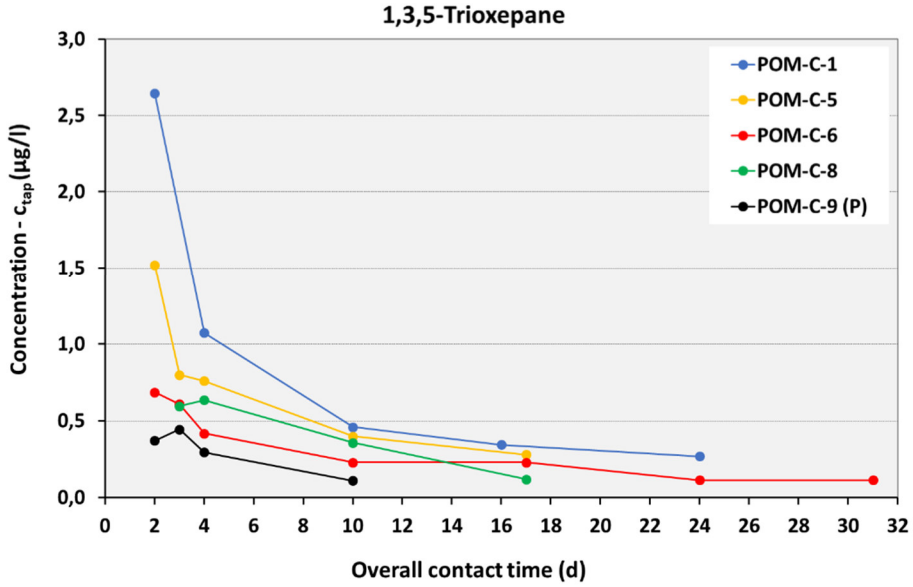



**Figure 6 Semi-quantitative concentrations of 1,3,5-Trioxepane released over time for POM-C for warm water test**

For POM-C the concentrations of all detected substances decrease considerably over time in the warm water test (60°C). Three substances: 1,3-dioxolane, 1,3,5-trioxane (Figure 5) and 1,2,3-trioxepane (Figure 6) were determined in most of the migration waters. For POM-C quite a lot of unknown substances were identified. For all tested components, except for POM-C-3, POM-C-5 and POM-C-7, at least one known substance was determined at concentration > 0.1 µg/l at the 31st day (relevant assessment day); for POM-C-1, POM-C-5, POM-C-6, POM-C-8 and POM-C9 significant amount of unknown substances were detected.

In cold water tests, only few substances were detected (Table 8).

There are some differences in the number of identified substances and the determined concentrations between the different components. However, the result for the specially produced test specimen in form of plates corresponds pretty good with the results for the real components.

### 4.3.2 PSU

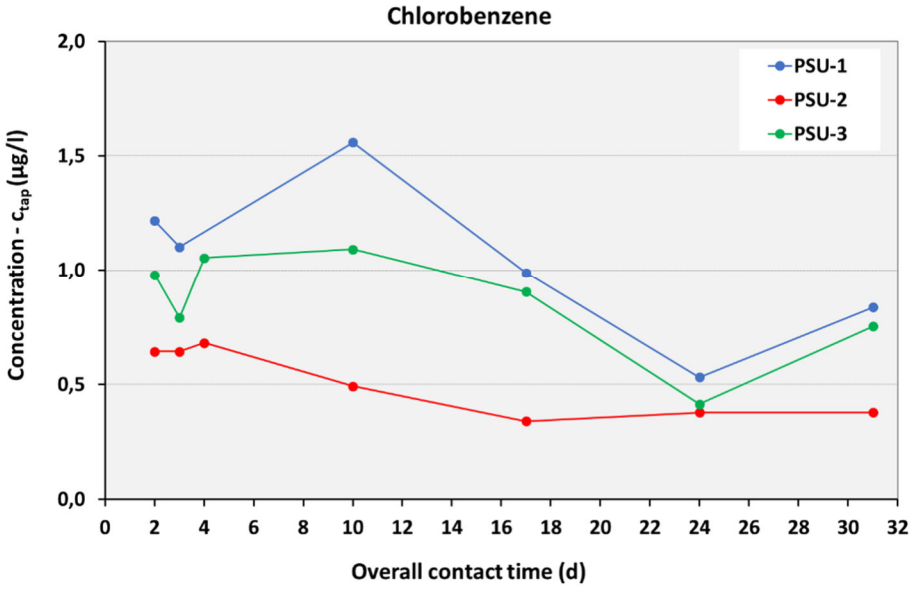



**Figure 7 Semi-quantitative concentrations of chlorobenzene released over time for PSU for warm water test**

Only few substances were released from components made of PSU in the warm water test. In most of the migration waters chlorobenzene was detected, for which the concentration remained at a constant level (Figure 7). Further identified substances are benzyl alcohol, acetophenone and phenoxyethanol. The identified substances were still detected at the 31st day (relevant assessment day) (Figure 7).

Five substances were detected in cold water tests, most of them only once. They are listed in the Table 8.

### 4.3.3 PPE

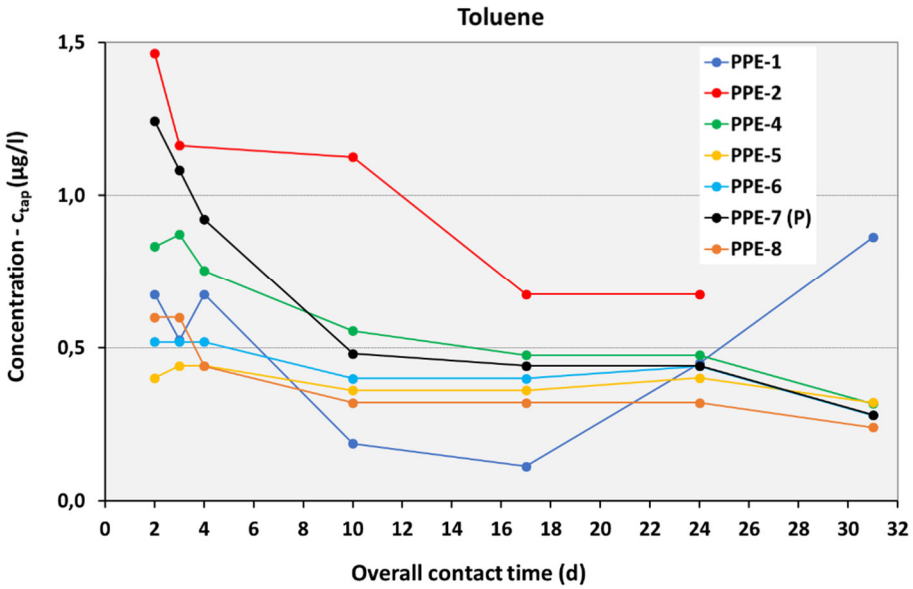



**Figure 8 Semi-quantitative concentrations of toluene released over time for PPE for warm water test**

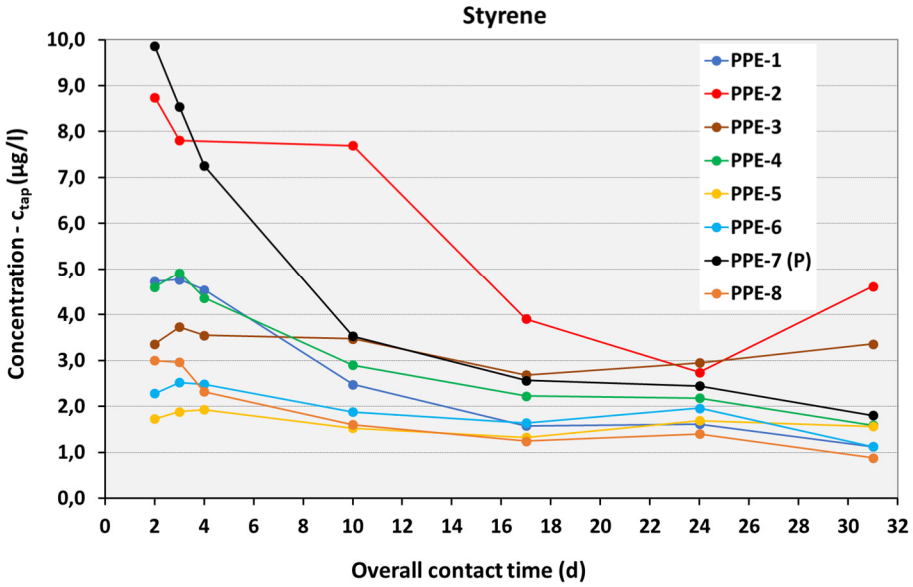
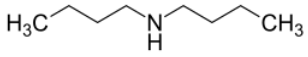



**Figure 9 Semi-quantitative concentrations of styrene released over time for PPE for warm water test**

Styrene was semi-quantified in all the migration waters (60°C) of the test pieces, at the highest concentration and up to 31 days contact time (Figure 9). Toluene was also present in the migration waters of most of the test pieces, PPE-1, PPE-2, PPE-4-8 (Figure 8). Except for PPE-2, toluene was detected up to 31 days contact time. Nonanal was released from the migration waters of PPE-1 und PPE-2, whereas butanal was released from PPE- 4-8. More substances were released and are specific to the individual test piece (see Table 6). At least three substances were detected up to the 31st day. However, a slight trend of decreasing concentrations can be observed.

Two substances were detected in the cold migration water of PPE-1, PPE-2 and PPE-3 (Table 8).

### 4.3.3.1 Investigation of dibutylamine

Dibutylamine (DBA; 

; CAS-Nummer: 111-92-2) was investigated in the warm migration waters of all the PPE test pieces, and in the cold migration waters for PPE-1, PPE-2 and PPE-3) using HPLC-MS. The release is shown in Figure 10 and Figure 11.

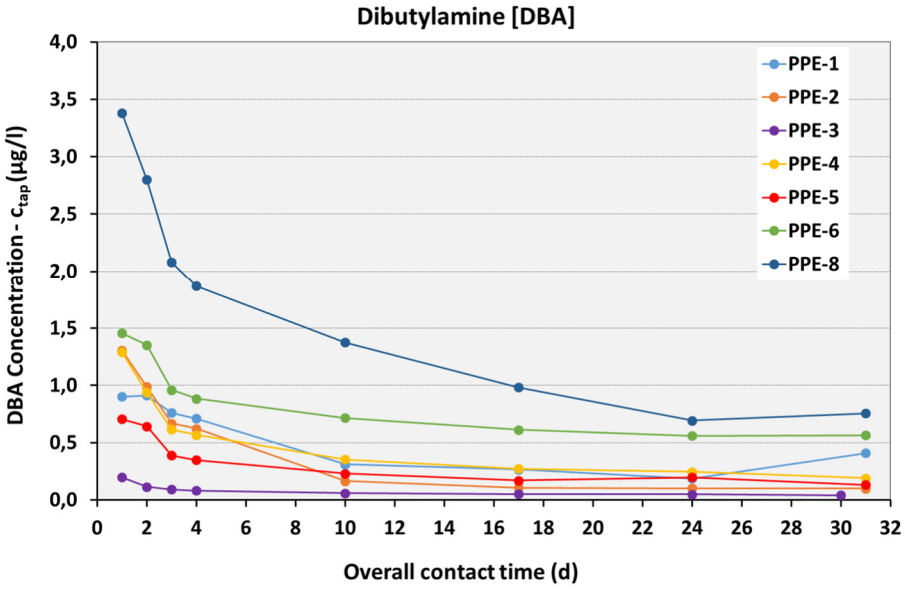



**Figure 10 Quantitative concentration of dibutylamine over time for PPE-1 to PPE-8 for warm water test**

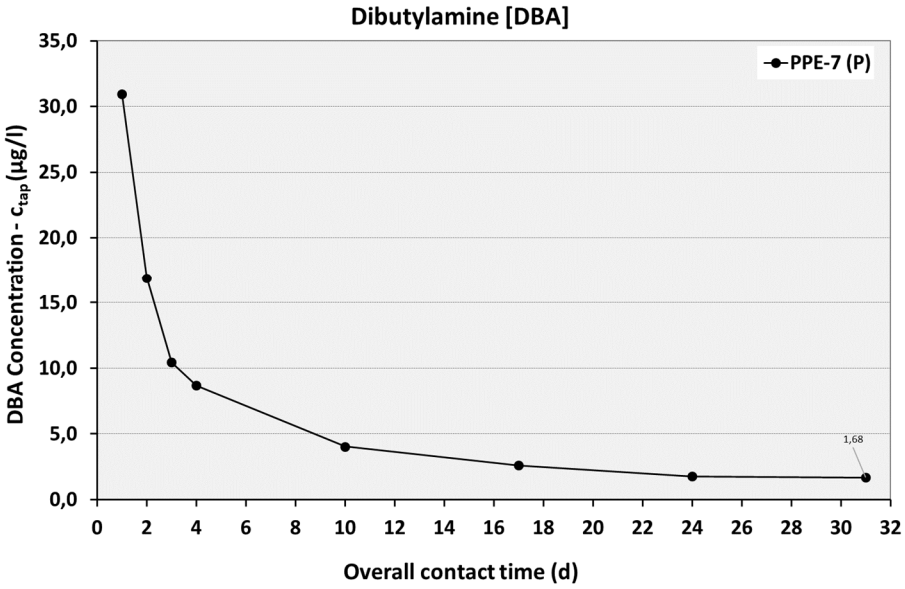



**Figure 11 Quantitative concentration of dibutylamine over time for PPE-9 (plates) for warm water test**

For the test pieces (plates) produced by the granulate producer the release is significantly higher.

As for the other substances release from PPE, a similar trend of decreasing concentrations over time can be observed. At the 10$^{th}$ day the concentration as $c_{tap}$ determined for almost all test pieces are below 1 µg/l. In PPE-7 (which is the plate of the granulate producer) and PPE-8 the concentrations determined at the 10$^{th}$ day were 4,05 µg/l and 1,38 µg/l, respectively, and exceed the $MTC_{tap}$ = 1 µg/l. In the extended test, the amount of DBA in PPE-7 remained above 1 µg/l.

### 4.3.4 PA

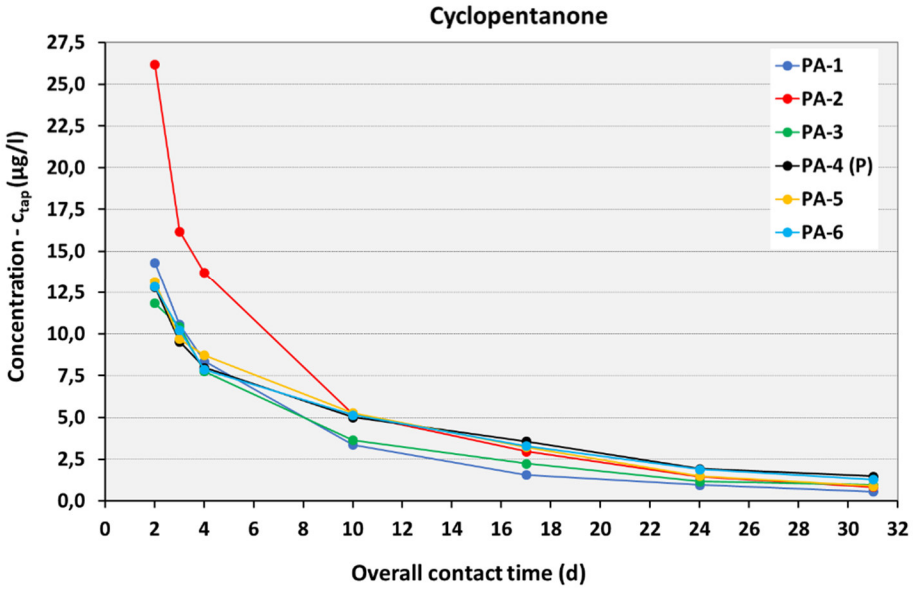



**Figure 12 Semi-quantitative concentrations of cyclopentanone released over time for PA for warm water test**

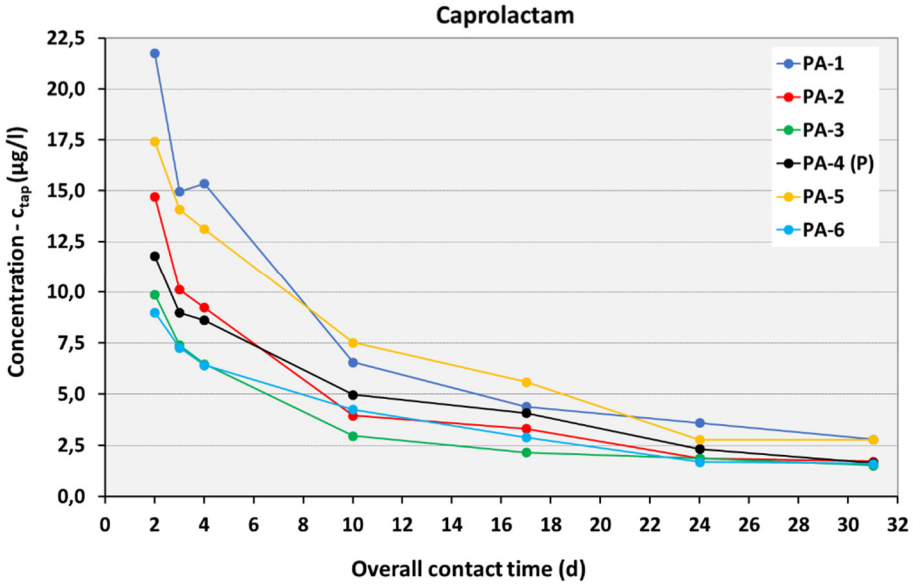



**Figure 13 Semi-quantitative concentrations of caprolactam released over time for PA for warm water test**

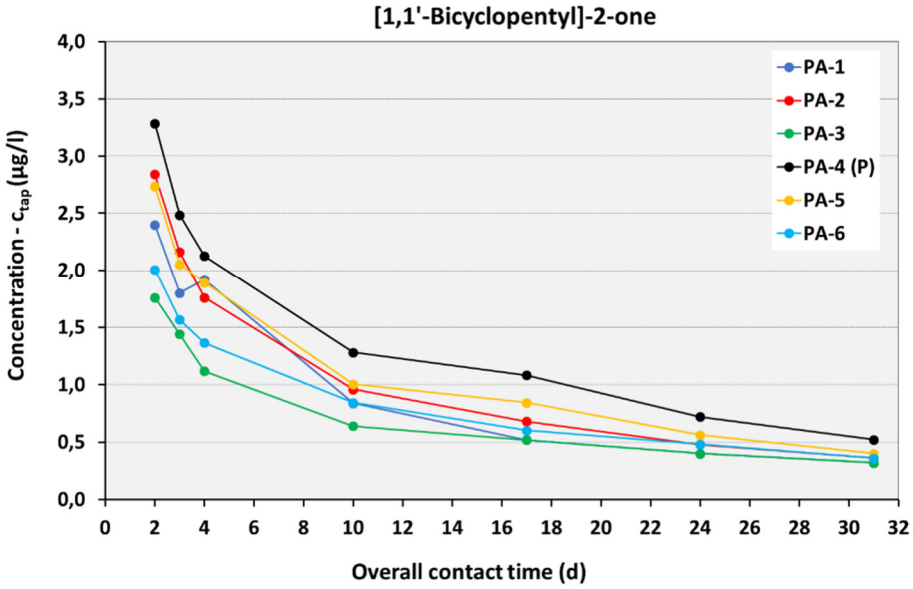



**Figure 14 Semi-quantitative concentrations of [1,1'-Bicyclopentyl]-2-one released over time for PA for warm water test**

Cyclopentanone (Figure 12), caprolactam (Figure 13) and one unknown substance were detected in a similar decreasing trend for all the PA test pieces. Their concentrations as $c_{tap}$ were first high, over 5 µg/l, but decreased rapidly over time. The substances can be still detected at the end of the extended migration of 31 days. At lower concentrations, 2-ethylhexanol and [1,1'-Bicyclopentyl]-2-one (Figure 14) were semi-quantified in all the PA test pieces. More substances were released and are specific to the individual test pieces (see Table 6). For all the substances, a decreasing trend can be observed. Four substance are detected in all the migration waters of the test pieces at the 31$^{st}$ day.

# 5 Discussion

## 5.1 Parameters

UBA was not aware of the formulation of the different components tested in the present study. For this reason, only TOC, TON as parameters of KTW evaluation criteria document were investigated. Additionally, a GC-MS screening method was applied to identify possible migrating substances and to semi-quantify the release of these substances. It can't be assumed that the applied screening method will cover all substances, which need to be determined in the migration waters as a result of the formulation review. It is very likely, that specific relevant substances might be present in the migration water but were not determined here.

The applied screening method according to DIN EN 15768 allows a semi-quantification. For this a one-point calibration of internal standards is used to estimate the concentration of the detected substances. The concentrations obtained by this can only be considered as rough estimations, which is especially important when compliance with acceptance criteria is discussed. However, for a comparison of different tested components or to identify trends over time the results are valid.

The applied GC-MS screening method (EN 15768) is discussed to become a mandatory testing method for unexpected substances in the framework of the new European system for the acceptance of materials in contact with drinking water according to Directive (EU) 2020/2184. The results of this report give an impression of the applicability of this testing method.

## 5.2 TOC

The acceptance criteria for TOC is considered as important for the limitation of the overall release of organic substances into the drinking water. The acceptance criteria according to the German KTW evaluation criteria document and the 4MSI common approach for organic materials is $MTC_{tap,TOC}$ = 0,5 mg/l. The TOC results for the different components and the test plates made of the same granulate are very similar. The only exception is the component POM-C3, for which a 2 to 4 times higher TOC release is observed than for the other POM-C components. This component was produced outside of Europe and it can't be ensured that the same pre-product (granulates) was used as for the other components.

The TOC release is material or pre-product specific as considerable differences can be observed for the different materials. The tested PSU and PPE components show a very low TOC release, POM-C a slightly higher. The results show that all POM-C, PSU and PPE components meet the requirement already at the 10$^{th}$ day. This is not the case for all PA components, for which the TOC values in the migration waters of the warm water test are high and failed consequently the requirement $MTC_{tap}$ of 0,5 mg/l at the 10$^{th}$ day. Nevertheless, the TOC values meet the requirement at the 31$^{st}$ day.

It was previously observed that only a small fraction of the TOC (< 15%) can be explained by the substances determined by the GC-MS screening method. For PSU, PPE and POM this is confirmed. However, for single migration waters up to 50 % of the determined TOC can be attributed to the substances determined by the screening. For PA the ratio is constantly lower than 3%. Especially for PA but also for POM it can be assumed that oligomers of the used monomers contribute considerably to the TOC.

## 5.3 TON

In the second part of the assessment, the threshold odour number (TON) of the different test pieces was investigated. All the materials – POM, PSU, PPE and PA – meet the requirement of TON ≤ 4 for the warm water test, and this already at the 10$^{th}$ day.

## 5.4 GC-MS-Screening

In the third part of the testing, the migration waters of the test pieces, were extensively investigated by GC-MS screening for their contaminants. In general, the number and the concentration (as $c_{tap}$) of the substances are significantly higher in the warm water tests than in the cold water tests, when the components were tested with cold water (POM-C-1 – 4, PSU and PPE-1 – 3). This is the reason, why for the successive tests only warm water tests were performed.

The results of the GC-MS-screening are very good comparable with respect to the detected substances and the concentrations for the different components and the respective plate made of the same pre-product (granulate). As for the TOC release for the components POM-C-3 differences to the other components and the plate made of POM-C-can be observed: Other substances are detected and in this case the concentrations of the POM-C specific substances are lower. This confirms that the granulate used for the production of the components POM-C-3 had a different quality.

It seems that if the quality of the pre-product (granulate) and the production parameters of the components at the different production sites are comparable, the components made at different production sites are very similar with respect to the hygienic properties. This seems also to be the case for plates made by the granulate producers.

In the following the results of the GC-MS-screening are discussed with respect to acceptance criteria for unexpected substances proposed for the new European system for materials in contact with drinking water. Unexpected substances in this context are substances that were not considered in the assessment of the respective starting substances.

In the migration waters of the warm water test, 39 compounds were identified for the different materials. In addition, 30 unknown substances were detected, 29 for the components made of POM-C and one for the components made of PA. Probably, these unknown substances are oligomers from the POM-C production, for which no requirement apply, when they are covered by the assessment of the monomers. However, as no information is available for these unidentified substances, a $MTC_{tap}$ of 0,1 µg/l would formally apply for non-assessed substances. For some of the POM-C components, this criterion is met, as no unknowns were detected at the 31$^{st}$ day. POM-C-6, POM-C-8, POM-C-9 and all the PA components would fail this requirement. For the new European system, a requirement for unexpected substances of 1 µg/l for the cold water test is discussed. The concentrations of unknown in POM-C-6, POM-C-8 and POM-C-9 are approximately in this range, for the tested PA components only PA-4 shows unknown concentration below 1 µg/l. However, the tests were carried out with warm water, and it can be assumed that the concentration for the cold water test of the PA test pieces would comply with the proposed requirement. In addition, the producer of the granulate recommends the use of PA only in cold water.

For the identified substances different requirements (Table 6 and Table 8) apply. Some of the identified contaminants are accepted starting substances in the *COMMISSION REGULATION (EU) No 10/2011* or in the *4MSI common approach on organic materials*. For these substances the

corresponding requirements (e.g. $MTC_{tap}$) of the positive lists apply. For non-assessed substance a $MTC_{tap}$ of 0,1 µg/l applies.

The semi-quantification of the identified substances in the migration waters of the POM-C test pieces, as well as in the plate, show a similar decreasing trend over the time. In general, the release of substances in terms of number and concentration can be considered as low, and meet the requirements for the identified substances at the 31st day.

In the migration waters of the PSU test pieces, almost all the identified substances meet the respective requirements. One substance, though, does not comply with the proposed requirement for non-assessed substances. Chlorobenzene, which is presumably used as solvent, occurs frequently in the migration waters, and for non-assessed substance an $MTC_{tap}$ of 0,1 µg/l applies. Neither PSU-1, PSU-2, nor PSU-3 complies with this requirement, and even with the extended test of 31 days, the proposed requirement is not met. It is probable that in the assessment of the PSU components the derogation for solvents (need not to be considered if the processing temperature is over the boiling point of the solvent) was applied. However, the results of this report show (as for toluene for PPE) that the solvents might be released into the drinking water and that general derogation for solvents needs to be reconsidered.

For the PPE components three substances were identified: styrene, which is used as a monomer of a second polymer used in a mixture with PPE, toluene used probably as solvent and 1,3-diphenylpropane which use is not known. The concentrations of the identified substances are significantly below or only slightly above the proposed requirements.

The concentrations measured in the migration waters of the PA test pieces at the beginning of the experiments were well above 5 µg/l for two identified and one unknown substances. The identified contaminants are caprolactam and cyclopentanone. Caprolactam is a monomer used for the PA-production and meets the respective requirement. The concentrations of cyclopentanone, for which the proposed requirement for unexpected substances of 1 µg/l in the cold water test might apply, are approximately in this range for all the test pieces. The other 11 identified substances comply with the proposed requirement. However, it is necessary for all the test pieces, as well as the representative plates, to carry the extended migration test up to 31 days, in order to meet all requirements.

The discussion on the concentrations is based on the semi-quantitative determination as described before. There is a quite huge uncertainty about the real concentrations. For the identified substances, for which concentrations near the proposed acceptance criteria are determined, substance specific calibrations might need to be applied. However, if this will become a general requirement the costs for testing will be much increased depending on the number of substances for which additional calibrations are needed.

## 5.5 Individual Substances

Dibutylamine (DBA) was expected to be used for the production of PPE. DBA was not detected by GC-MS screening but is accessible to HPLC-MS analysis. The use of a substance specific calibration allows an accurate determination of the concentration. Regarding DBA a provisional $MTC_{tap}$ of 1,0 µg/l is specified in the German evaluation criteria document for organic material in contact with drinking water. This value is met at the 10th day for PPE-1-6. The concentration measured in PA-8 was slightly above this requirement, but is met in the extended test. Interestingly the concentration measured in the migration waters of the plate made by the granulate producer (PA-7), is 5 to 10 times higher than of the other components and well above 1 µg/l at the 10th day, and slightly higher at the 31st day. As a conclusion the representative plate fails the actual requirement, whereas the test pieces comply with it. This is the only parameter,

for which a difference between the plate made by the granulate producer and the real components can be observed. In this case the plate of the granulate producer can be considered as the worth case test piece.

# 6 Conclusion

The producers of plastics granulates specify the process parameters for the injection moulding to produce the final products or components to be used in contact with drinking water. The results of this study support that the hygienic properties of the final products or components are comparable if the production follows the specification of the granulate producer. Test plates specifically produced by the granulate producers seems also to have comparable hygienic properties with real products or components. Only for one substance (dibutylamine) the specifically produced test plate (PA) showed a higher release than the real components.

The testing and assessment of specifically produced test plates and consequently the certification of the pre-product (granulate) seems to be an appropriate way to reduce the testing requirements for components produced in different sites. As a precondition the process parameters of the injection moulding will have to be monitored and considered in the certification process of the components. For certain components or products, a certificate of the pre-product (granulate) might be sufficient to demonstrate the fitness concerning the release of substances into the drinking water. For components or products with a possible stronger impact on the drinking water quality (larger surface in contact with drinking water) a reduced testing of the final components or products might ensure the quality of the final components or products. In this case TON and TOC might be appropriate test parameters to indicate the non-compliance of other parameters. Another advantage of this approach is that the formulation review has only to be performed once for the certification of the pre-product. The formulation review is a complex process for the assessment of products in contact with drinking water. Confidential information of multiple suppliers and pre-suppliers have to be provided to the certification body, which makes the process very time-demanding.

The use of the GC-MS-screening according to EN 15768 is a tool to identify and assess the leaching of unexpected substances and gives additional safety when certified products are tested accordingly. However, only a limited number of substances released into the drinking water will be detected by this method. Additionally, the identification of the substances and the assessment of the results requires well-experienced staff of the laboratory and the certification body. The assessment for the unexpected substances is time- and cost-demanding and can't be performed for all products or components made of the same pre-product. The assessment for the certification of a pre-product might be sufficient.

When results of the semi-quantitative analysis according to the mentioned screening standard are compared against acceptance criteria ($MTC_{tap}$) the high uncertainty of the determined concentrations has to be considered. It is recommended that a quantitative analysis will have to be performed additionally for identified substances in case the determined semi-quantitative is in the range of the acceptance criteria. For the new European system, a clear guidance is recommended when to perform a quantitative analysis of the identified substances.