Considerations on the time-dependent migration of cyclic polyamide-oligomers from PA-kitchen utensils - migration and exposition -

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Background

Polyamides are widely used for the production of kitchen utensils which are used as food contact material (FCM) at elevated temperatures. Beside the lower-cost product PA 6.6 also thermally stable polyamides like PA 6T/6I are in use. Cyclic polyamide-oligomers (cPAO) are formed during the manufacture of the polymer and can migrate into aqueous foods during cooking. Currently there are no published data on the toxicity of cPAO <1000 Da, which hampers a risk assessment.

Conclusion

The migration of cPAO from PA kitchen utensils can be described in approximation to a square-root function over the time and can be expected over the product life-cycle. Water can be used as worst-case simulant for cPAO, but migration also takes place into oil at frying temperatures. When using the TTC-concept, the exposition threshold will likely be exceeded by kitchen utensils of PA 6.6. PA 6T/6I exhibits a low-migration alternative to PA 6.6.

Method

Migration experiments were carried out using the simulants water, 20%-ethanol and sunflower-oil at temperatures up to 100°C for water and 20%-ethanol (in an autoclave pre-pressurized at 1 bar) and up to 200°C for sunflower oil using total immersion of the food contact part of a kitchen utensil. For the investigations in water and 20%-ethanol the internal standard caprylolactam was used. Water and ethanolic simulants were injected into a RP-HPLC-UVD(210nm)-CLND system (CLND – chemiluminescent nitrogen detector) after migration. Sunflower oil was extracted using acetonitrile-hexane. After removing the solvent of the acetonitrile-phase by means of a rotary evaporator, the residue was dissolved in a defined amount of trifluoroethanol and subjected to the LC-system **(Fig. 1).** Recovery rates of the cPAO from PA 6.6 during extraction were determined to 96% for cPAO n1+1 and n2+2 and 74% for cPAO n3+3 by spiking an aliquot to crude oil.

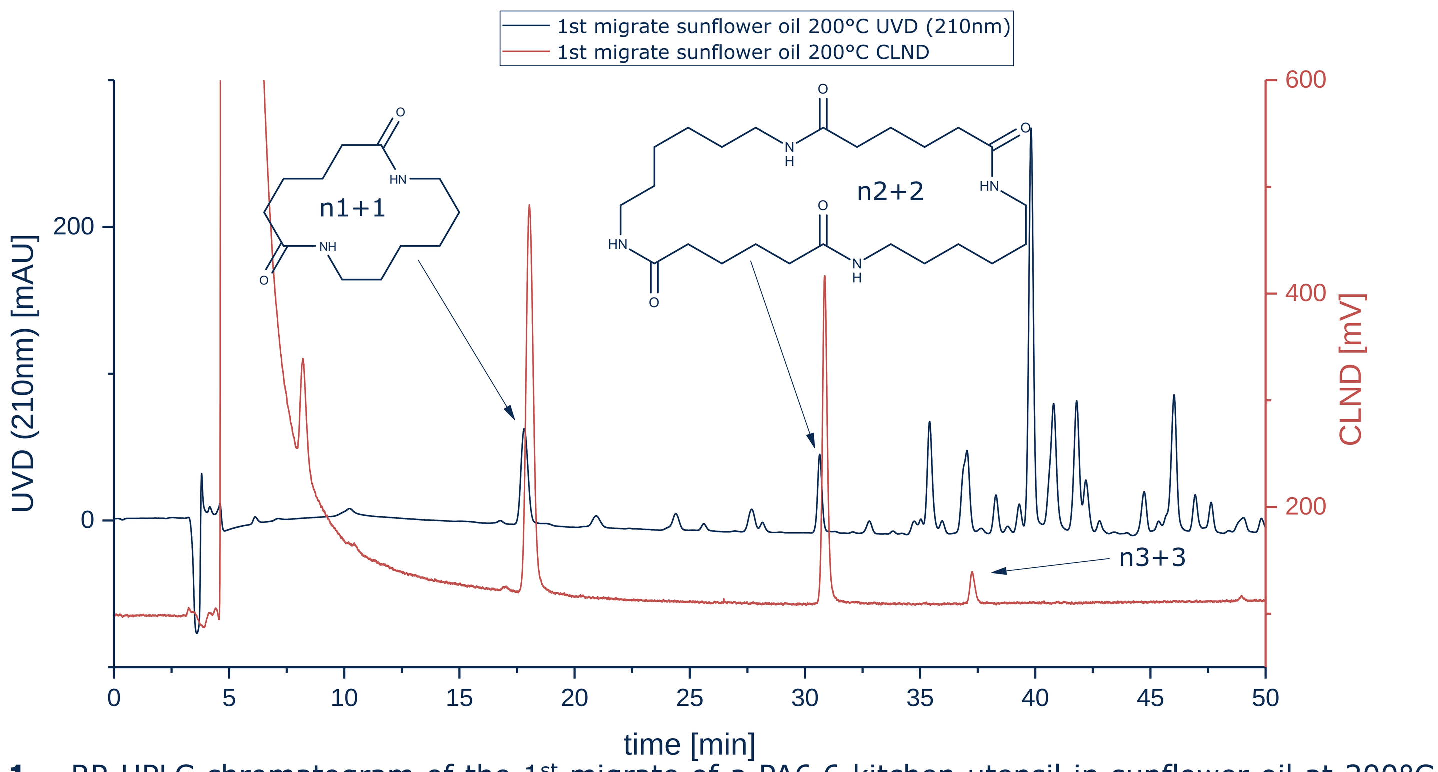

Fig. 1 – RP-HPLC chromatogram of the 1st migrate of a PA6.6 kitchen utensil in sunflower oil at 200°C for 30 min; **red:** Signal generated by CLND **blue:** UVD @ 210nm; structure of cPAO n1+1 and n2+2 included

time-dependent migration into water

The time-dependent migration of cPAO from PA kitchen utensils into water can be described by a power function close to a square root function **(Fig. 2)**. The 3rd migrate of a PA 6.6 kitchen utensil at 70°C for 2 hours (warm holding conditions following BfR opinion 8/2008) shows a migration of cPAO of 0,62 mg/dm² into water, which constitutes one third of the migration at 100°C with 2,15 mg/dm² (worst case following EURL-guideline). PA 6T/6I exhibits a low-migration alternative to PA 6.6 with a migration value of 0,018 mg/dm² in the 3rd migrate at 100°C for 2 hours. The 10-fold repetition of the migration of cPAO from a PA 6.6 soup ladle into water at 100°C for 2 hours respectively shows an exponential decay of the migration level to about 0,7 mg/dm², which corresponds to about 0,7% of the initial content of cPAO in the kitchen utensil **(Fig. 3).** It can be estimated, that the migration potential of cPAO from PA kitchen utensils will not be exhausted during its product life-cycle.

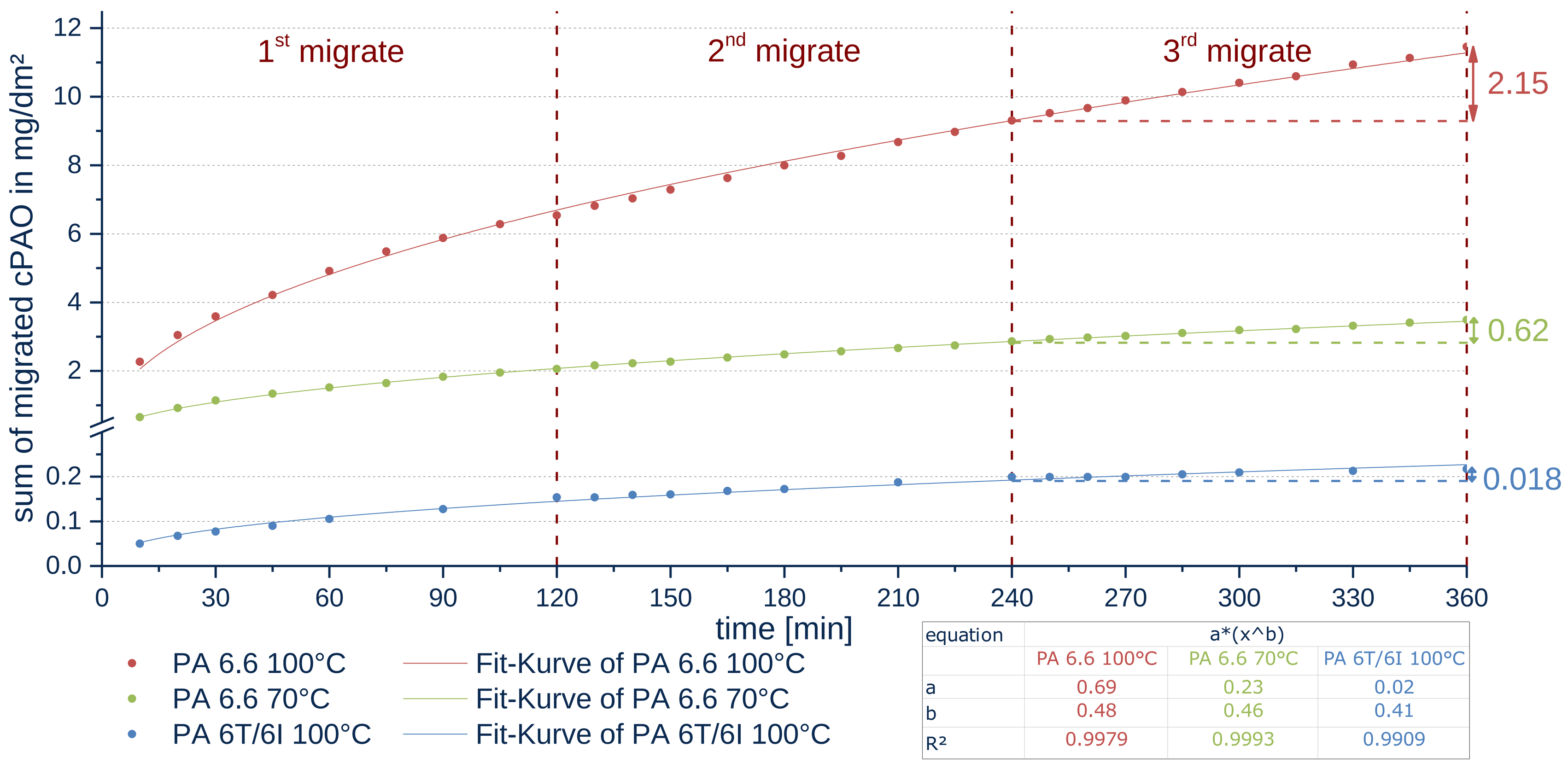

Fig. 2 – amount of migrating cPAO from spatulas into water in mg/dm² over a period of 6 hours (summarization of 3-fold consecutive migration for 2 hours respectively) made of PA6.6 or PA 6T/6I, averaged results of a double determination; numbers on right side represent the migration into the 3rd migrate (2 h) in mg/dm²

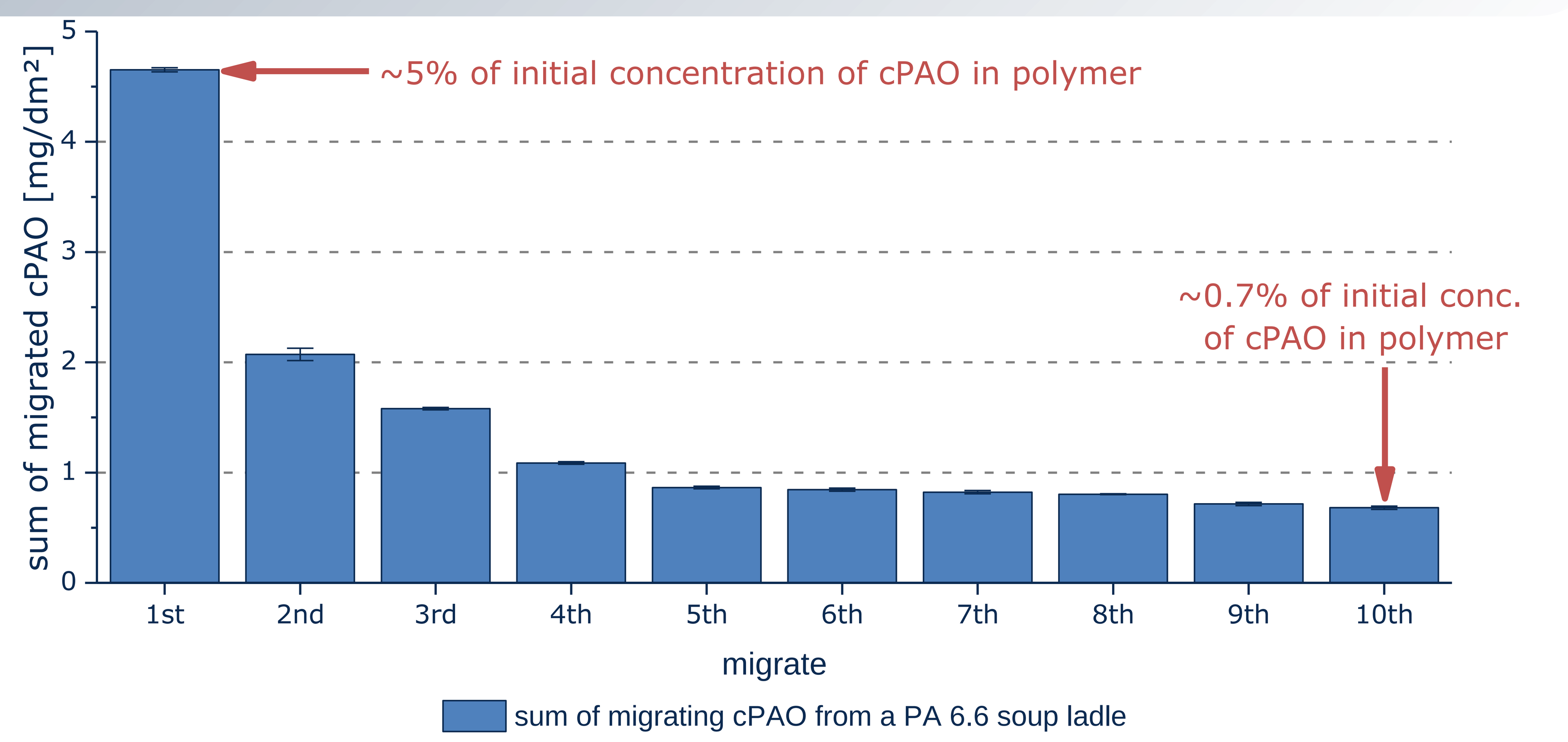

Fig. 3 – amount of migrating cyclic oligomers into water in mg/dm² from a soup ladle made of PA 6.6 at 100°C into the 1st – 10th migrate with a migration time of 2 hours respectively; averaged results of a double determination incl. standard deviation

matrix-dependent migration

Migration of cPAO from PA 6.6 kitchen utensils into 20%-ethanol shows an elevated migration level by a factor of 1,7 compared to water and a factor of 200 compared to the migration into sunflower oil under same conditions **(Fig. 4).** Therefore, it should not be used as simulant for foods which contain a relevant amount of lipophilic ingredients but could be applicable as simulant for the use of kitchen utensils in contact with alcoholic beverages at elevated temperatures, e.g. mulled wine. The 3rd migrate into sunflower oil at 200°C for 30 minutes points to the same dimension as the 3rd migrate into water at 100°C and can be a good estimation for the migration level when using PA kitchen utensils for frying applications.

risk assessment - exposition

Risk assessment of cPAO shall be carried out by usage of the TTC-concept due to a lack of toxicological data. All cPAO are classified into Cramer Class III which leads to a maximum exposure of 90 µg/60 kg person/day. To calculate the exposition of the consumer an area-to-food-ratio needs to be applied, which can range from 0,5 dm²/kg (a soup ladle in 5 kg food) to 4,5 dm²/kg (a soup ladle in 600 g food). The concept of envelope volume, which originates from the CoE Resolution on metals and alloys, may be suitable to estimate a realistic surface-to-volume-ratio. Assuming the daily consumption of a 60 kg person of 0,1-1 kg food prepared with PA 6.6 kitchen utensils, the exposition ranges from 0,03 to 10,6 mg/person/day **(Fig. 5)**.

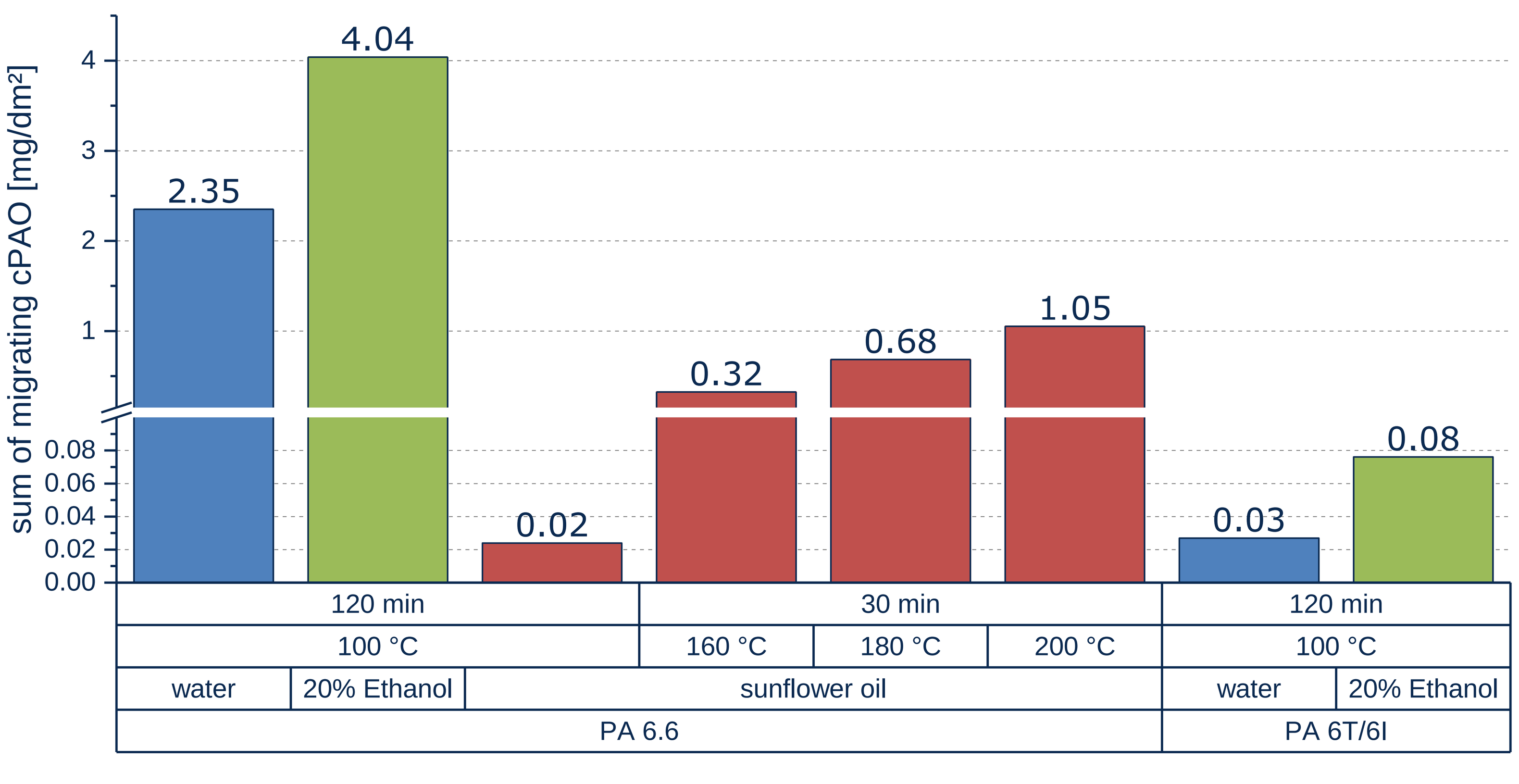

Fig. 4 – migration of the sum of cPAO in mg/dm² into the 3rd migrate from a set of skimmer made of PA 6.6 or PA 6T/6I under variation of time, temperature and simulant; migration in: blue: water, red: sunflower oil, green: 20% Ethanol

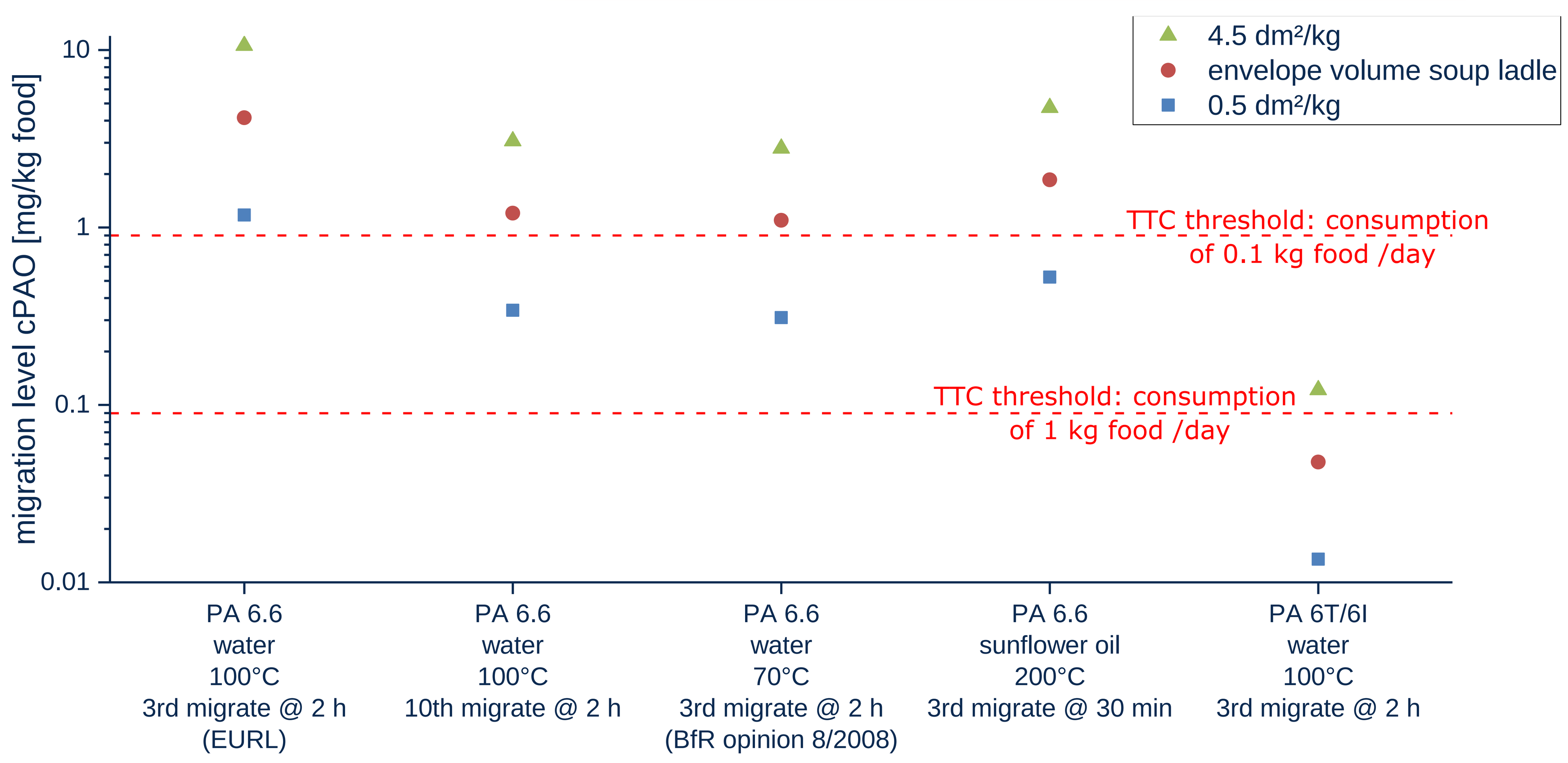

Fig. 5 – translation of selected migration per surface values into migration per kg food (**logarithmic scale**) using: blue: small surface to volume-ratio of 0,5 dm²/kg food; red: envelope volume for a soup ladle which was used for migration testing (2,7dm²/1,5kg food); green: a large surface-to-volume-ratio of 4,5dm²/kg food