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Editorial

Could the Ukrainian sunflower oil contaminated with mineral oil wake up sleeping dogs?

During winter/spring 2007/2008, in the Ukraine around 100,000 tonnes of sunflower oil were contaminated with mineral oil at concentrations often above 1000 mg/kg. The paraffins of this mineral oil ranged from about C_{18} to C_{40} (centered at about C_{28}), were almost free of n-alkanes (a deparaffinated product), and thus corresponded to the composition of base oil for manufacturing lubricating or hydraulic oils. It is assumed that it was added as a fraud, since in the Ukraine such oil was cheaper than sunflower oil. Much of the contaminated oil was withdrawn, but there are products on the market which were produced before this contamination was detected; and in autumn 2008 there are still several 10,000 tonnes of contaminated oil in the Ukraine and in other parts of the world.

To protect consumers, a broad analytical campaign was initiated throughout Europe. The European Commission decided to apply a legal limit of 50 mg/kg to the mineral paraffins in Ukrainian sunflower oil and in September 2008 it organized a workshop together with the Official Food Control Authority of Zurich, Switzerland.

Mineral oil contamination is common

Such an analytical campaign is likely to wake up sleeping dogs. It will bring to our attention that more foods are sometimes or even constantly contaminated with mineral oil materials at concentrations above 50 mg/kg. Jute and sisal bags used for transportation and storage of hazelnuts, coffee, cocoa beans, rice, linseeds and many other products were produced using fibers "batched" with a brownish mineral oil consisting of some 25% (poly)aromatics and these bags constantly contaminated foods at concentrations of 50–300 mg/kg [1, 2]. For the European market this should have changed some 10 years ago, but did not for the markets in other parts of the world. Up to the 1990s, weekly truckloads of release agent consisting of paraffin oil were delivered to industrial bakeries and left these with the bread and other products at concentrations of 700–3000 mg/kg. At least in Switzerland such practices were stopped, but paraffin oil is included in the draft of the Codex General Standard for Food Additives (GSFA) for numerous food categories, with maximum use levels of 200–3,000 mg/kg [3], *e.g.* as dust binder for wheat and rice to prevent dust explosions. Numerous other foods, including edible oils of many types, were found to be contaminated with mineral oil – sometimes reaching 1000 mg/kg; and usually the source could not be identified [4]. Grape seed oils are commonly contaminated by mineral oil material at 30–150 mg/kg; presumably the pesticide formulations are the source [5]. In 2001, peanut oils contained up to 85 mg/kg mineral oil paraffins (mean of 35 mg/kg; $n = 52$) and seemingly all Argentinean oils were affected. Olive pomace oils are contaminated at levels of 100–350 mg/kg [6]. Canned oily products often contain more than 100 mg/kg paraffin oil used for shaping the can, but also fish is commonly contaminated with mineral oil components at levels of 50–1000 mg/kg referring to the fat – making the identification of the source in canned fish difficult. Finally all foods are contaminated by environmental pollution, above all from soot and lubricating oil from Diesel engines [7]. The 6 Swiss wheat germ oils analyzed in 2001 contained 20–180 mg/kg mineral oil (average 60 mg/kg), also thought to be of environmental origin.

It will be difficult to convince producers to withdraw sunflower oils containing somewhat more than 50 mg/kg mineral oil material from the market when many other products have exceeded this level for a long time and authorities have not taken any action.

Not always white, food-grade paraffin oils!

More questions will be asked about the relevance of this contamination and the qualities of the mineral oil material involved. It will be difficult to argue that the mineral oil in the Ukrainian sunflower oil is more dangerous than others. The range of molecular masses resembles that of

the other most common contaminants. First results in our laboratory indicated that it contained aromatics at substantial concentrations, *i.e.* that it was not a food grade white oil. However, this also applies to other foods contaminated with mineral oil [8].

The low priority so far given to mineral oil contamination of foods is due to the assumed low toxicity. The scientific proof for this is not unambiguous however. In 1989, the European Scientific Committee on Food (SCF) set a tolerable daily intake (TDI) of 0.005 mg/kg body weight (bw) for oleum-treated mineral oils (such as those usually used for lubricating and hydraulic oils) and of 0.05 mg/kg bw for hydrogenated oils (food grade white oils). For most of the oils found in foods this would result in legal limits below 1 mg/kg. Environmental contamination of oil seeds alone usually exceeds this level, bearing in mind that soot and lubricating oil from the exhaust of engines are by no means of "food grade" quality.

In 1995, the SCF expressed the opinion that a far higher exposure can be tolerated (TDI of 4 mg/kg bw) provided the average molecular mass of a white paraffin oil is at least 480 Da (corresponding approximately to the alkanes C_{34}) and less than 5% of the paraffins are below C_{25}. It was based on an assumed low resorption of high molecular mass paraffins by the human organism. This increase of the TDI by a factor of more than 100 was surprising since paraffin oils are broad mixtures and the oil specified for the higher TDI will contain more than 1% of the oil previously taxed more critically.

Largest contaminant of our body

In the mean time it was discovered that the human body fat probably contains mineral paraffins in the order of 1 g (extrapolated from abdominal fat sampled during Caesarean sections of Austrian women) [9]. It was remarkable that the mineral paraffins in all 144 samples had quite exactly the same composition (ranging from about n-C_{17} to n-C_{32}, centered at n-C_{24} – which means iso-C_{25} and iso-C_{26}). This questions the specification of the SCF: the limit of molecular mass would have to be above n-C_{30} to ensure negligible resorption.

The composition of the paraffins in the human body fat does not resemble the mineral oil products we are exposed to. Experiments with labeled paraffins showed that merely 0.3% of the paraffins remained in the body after 2 days and 0.1% after 21 days [10]. Our metabolism is continuously burdened with large amounts of paraffins from plant origin (largely n-alkanes C_{23}-C_{33}) and constantly eliminates these, but there seem to be certain mineral isoalkanes it is unable to cope with. Toxicity testing should focus on these, since they accumulate to high concentrations. If these were the components causing the toxic effects observed in animal tests and if they were present in the mineral oils used for testing at a concentration of 0.1%, the paraffins in our body could be 1000 times more toxic than the mixture used for testing. However, we do not know the composition of the accumulated hydrocarbons.

Some foods contain more than 10 mg/kg mineral aromatics [8]. A substantial proportion consists of alkylated benzenes and naphthalenes, but there may still be aromatics with 3 and more rings at the mg/kg level. In contrast to the polyaromatics from combustion processes, nearly all are alkylated. For this reason toxicity is not directly comparable, but concentrations are some three orders of magnitude higher than those considered of concern for the non-alkylated polyaromatics.

The Ukrainian sunflower oil has not exposed us to mineral oil for the first time. If 0.1% of the paraffins are picked up perhaps permanently by our body, the consumption of 1 L sunflower oil contaminated at 1000 mg/kg would contribute 1 mg to our body burden, *i.e.* 0.1% of what we carry already.

The time has come for broader investigations

Such arguments should not be taken to play down the probable scandal that people adulterated food with mineral oil, but it should make us aware of a problem which might have been underestimated (or neglected because of analytical problems). Mineral oil is probably the quantitatively largest contaminant of our body, and the proof that this contaminant can be tolerated

without health concerns is not convincing. Either this proof can be substantiated or we should reduce our exposure – from all sources, including cosmetics, pharmaceuticals and the environmental contamination.

Hopefully the contamination of the Ukrainian sunflower oil, the inconsistencies coming to light when imposing a 50 mg/kg limit and further insights into the accumulation of certain mineral hydrocarbons in the human body will wake up sleeping dogs.

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References

[1] K. Grob, M. Lanfranchi, J. Egli, A. Artho: Determination of food contamination by mineral oil from jute bags using coupled LC-GC. *J Assoc Off Agric Chem.* 1991, **74**, 506–512.

[2] K. Grob, M. Biedermann, A. Caramaschi, B. Pacciarelli: LC-GC analysis of the aromatics in a mineral oil: batching oil for jute bags. *J High Resol Chromatogr.* 1991, **14**, 33–39.

[3] Codex Alimentarius, food additive details (FAO and WHO 2008). ahttp://www.codexalimentarius.net/gsfaonline/additives/details.html?id=292

[4] Ch. Wagner, H.-P. Neukom, K. Grob, S. Moret, T. Populin, L. S. Conte: Mineral paraffins in vegetable oils and refinery by-products for animal feeds. *Mitt. Lebensm. Hyg.* 2001, **92**, 499–514.

[5] D. Fiorini, K. Fiselier, M. Biedermann, R. Ballini, E. Coni, K. Grob: Contamination of grape seed oil with mineral oil paraffins. *J. Agric. Food Chem.* 2008, in press.

[6] S. Moret, T. Populin, L. S. Conte, K. Grob, H.-P. Neukom: Occurrence of C15-C45 mineral paraffins in olives and olive oils. *Food Addit Contam.* 2003, **20**, 417–426.

[7] H.-P. Neukom, K. Grob, M. Biedermann, A. Noti: Food contamination by C20-C50 mineral paraffins from the atmosphere. *Atmos. Environ.* 2002, **36**, 4839–4847.

[8] S. Moret, K. Grob, L.S. Conte: Mineral oil polyaromatic hydrocarbons in foods, e.g. from jute bags, by on-line LC-solvent evaporation (SE)-LC-GC-FID. *Z Lebensm Unters Forsch.* 1997, **204**, 241–246.

[9] N. Concin, G. Hofstetter, B. Plattner, C. Tomovski, K. Fiselier, K. Gerritzen, S. Fessler, G. Windbichler, A. Zeimet, H. Ulmer, H. Siegl, K. Rieger, H. Concin, K. Grob: Mineral oil paraffins in human body fat and milk. *Food Chem Toxicol.* 2008, **46**, 544–552.

[10] A.G. Ebert, C.R. Schleifer, S.M. Hess: Absorption, disposition, and excretion of tritium-mineral oil in rats. *J Pharm Sci.* 1966, **9**, 923–929.

