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Mineral oil paraffins in human body fat and milk

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Abstract

Paraffins of mineral oil origin (mineral paraffins) were analyzed in tissue fat collected from 144 volunteers with Caesarean sections as well as in milk fat from days 4 and 20 after birth of the same women living in Austria. In the tissue samples, the composition of the mineral paraffins was largely identical and consisted of an unresolved mixture of iso- and cycloalkanes, in gas chromatographic retention times ranging from n-C_{17} to n-C_{32} and centered at n-C_{23}/C_{24}. Since the mineral oil products we are exposed to range from much smaller to much higher molecular mass and may contain prominent n-alkanes, the contaminants in the tissue fat must be a residue from selective uptake, elimination by evaporation and metabolic degradation. Concentrations varied between 15 and 360 mg/kg fat, with an average of 60.7 mg/kg and a median of 52.5 mg/kg. Mineral paraffins might be the largest contaminant of our body, widely amounting to 1 g per person and reaching 10 g in extreme cases. If food were the main source, exposure data would suggest the mineral paraffins being accumulated over many years or even lifetime.

The milk samples of day 4 contained virtually the same mixture of mineral paraffins as the tissue fat at concentrations between 10 and 355 mg/kg (average, 44.6 mg/kg; median, 30 mg/kg). The fats from the day 20 milks contained <5–285 mg/kg mineral paraffins (average, 21.7; median, 10 mg/kg), whereby almost all elevated concentrations were linked with a modified composition, suggesting a new source, such as the use of breast salves. The contamination of the milk fat with mineral paraffins seems to decrease more rapidly than for other organic contaminants, and the transfer of mineral paraffins to the baby amounts to only around 1% of that in the body of the mother.

Keywords: Mineral oil paraffins; Human tissue fat; Human milk; Caesarean section

1. Introduction

In the nineteen eighties, during routine control at the Official Food Control Authority of Zurich, a biscuit (Madeleine) was found which contained 1.5% paraffins of mineral oil origin (mineral paraffins) used as release agent, i.e. to facilitate the detachment of the finished piece from the baking dish. Rice from a second refining (after long-term storage) was turned shiny again by spraying mineral paraffins onto it, resulting in a concentration of 0.1–0.3% (Grob, unpublished work). This finding of occasionally massive food contamination with mineral paraffins initiated a broader investigation, with a first summary by Grob et al. (1992a).

Jute and sisal fibers were treated with batching oil to improve their processing properties. Brownish mineral oil fractions containing 20–25% aromatic hydrocarbons were used (Grob et al., 1991a; Moret et al., 1997).

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Concentrations of the mineral paraffins in foods transported and stored in jute, such as hazelnuts, cocoa beans (chocolate), linseeds and rice were typically in the range of 10–100 mg/kg (Grob et al., 1991b, 1992b, 1993). Food packaging materials released mineral waxes and oils at concentrations reaching several 100 mg/kg (Castle, 1991; Grob et al., 1991c, 1997; Jickells et al., 1994). Lubricating oils and release agents used in food industry often consisted of mineral paraffins and concentrations, e.g., in bread and bakery ware frequently exceeded 1000 mg/kg (Grob et al., 1991d; 1994). Printing inks often contained mineral paraffins as a solvent which reached 10–100 mg/kg in the foods packed in cardboard boxes (Droz and Grob, 1997). Some animal feeds contained used edible oils and fats (e.g. frying oils) from public waste collection sites not properly separating them from used motor oil and other technical products. They resulted in contaminated meat and eggs (Grob et al., 2001). Animal feeds may also contain mineral paraffins as a binder for minor components like minerals and vitamins in powder form. A large proportion of the edible oils were found to be contaminated with more than 10 mg/kg mineral paraffins (Wagner et al., 2001), with maximum concentrations of around 400 mg/kg (Moret et al., 2003). The broad contamination is thought to be from the atmosphere, i.e. lubricating oil emitted from diesel engines and other soot (Neukom et al., 2002), more specific and higher contamination from tractors moving around raw materials (olive pomace, grape seeds) before oil extraction. Fish often contains mineral paraffins and aromatics in the order of 100–1000 mg/kg referring to the fat (Moret et al., 1997). The source has not been identified.

Based on food consumption data and estimated concentrations in these items, Heimbach et al. (2002) estimated the mean dietary exposure to mineral paraffins in the US as 0.875 mg/kg body weight (bw). Half of this exposure was from white paraffin oils used as release agents in baking, for de-dusting of stored grain, in confectionaries and for coatings of fruits and vegetables. In Europe, most of these applications are illegal (de-dusting of grain, coating of fruits and vegetables) or were voluntarily stopped (use as release agents for bakery ware). Tennant (2004) estimated the mean and 97.5 percentile exposure in Europe as 0.39 and 0.91 mg/kg bw, respectively, for adults and as 0.75 and 1.77 mg/kg bw, respectively, for children. This would correspond to an average concentration in food of 25–60 mg/kg (1 kg food/d). Surveillance data by the Official Food Control of Zurich might have agreed with this in the early nineteen nineties, but since the major uses were stopped, exposure decreased substantially. More recent targeted analyses detected some foods containing around 50 mg/kg mineral paraffins, but the average was probably below 5 mg/kg and environmental contamination could well have become the predominant source (i.e. paraffins accompanied by aromatics and other materials).

Mineral paraffins are also used in many cosmetics and pharmaceutical products. Corresponding chromatograms were shown in Noti et al. (2003). In the extreme cases, these products virtually exclusively consist of mineral paraffins (paraffin oils, vaselines). No review on the exposure from this source was found in the scientific literature.

A summary of the toxicological findings regarding mineral paraffins was given by Noti et al. (2003). In 1989, the EU-Scientific Committee on Food concluded that "there was no toxicological justification for the continued use of mineral hydrocarbons as food additives". A temporary tolerable daily intake (TDI) of 0–0.005 mg/kg bw was set for oleum-treated mineral paraffins and of 0–0.05 mg/kg bw for hydrogenated products (SCF, 1989). Resulting limits in foods would have been in the range of 0.3–3 mg/kg, but were not imposed by legislation.

Perhaps in view of the broad use of mineral paraffins resulting in higher concentrations, the SCF revised its opinion and considered higher exposure safe provided the paraffins have a sufficiently high molecular mass not to be absorbed to a relevant extent (SCF, 1995). For mineral paraffin waxes, a group acceptable daily intake (ADI) of 0–20 mg/kg bw was allocated to highly refined products characterized by a minimum viscosity, a maximum of 5% components with a boiling point below that of the *n*-alkane C_{25} and an average molecular mass of no less than 500 Da. Regarding mineral paraffin oils, a temporary group ADI of 0–4 mg/kg bw was set for products specified by a minimum viscosity, a maximum of 5% components below the n-C_{25} and an average molecular mass of no less than 480 Da (C_{34}-paraffins, 478 Da).

In 2001, the SCF evaluated hydrogenated poly-1-decene as food additive, a synthetic substitute also called poly-alpha-olefines (PAO) containing 1.5% components with less than 30 carbon atoms (SCF, 2001). The material is poorly absorbed from the gastrointestinal tract (<1%) and an ADI of 0–6 mg/kg bw was established. In 2006, the European Food Safety Authority (EFSA) evaluated "waxes, paraffinic, refined, derived from petroleum based or synthetic hydrocarbon feedstocks", with an average molecular weight no less than 350 Da (about C_{32}), a minimum viscosity and a "content of hydrocarbons with carbon number less than 25, not more than 40% (w/w)". Owing to lack of toxicity data, a restriction of 0.05 mg/kg food was specified (EFSA, 2006).

The toxicological evaluation strongly differentiated by the molecular mass distribution. This corresponds to observations concerning uptake by animals. On the one hand, hens transferred 1.5–3% of the mineral paraffins centered at C_{21}–C_{24} alkanes added to the commercial feed into the eggs (Grob et al., 2001). On the other, cow milk or beef body fat usually contains no mineral oil material (detection limit, 3 mg/kg) of types used for lubrication, centered at C_{27}–C_{29} alkanes, although their feed is contaminated with it by the air (Neukom et al., 2002).

The sometimes apparently rather careless use of mineral paraffins raised the question about the relevance for humans, particularly regarding uptake from food, cosmetics, pharmaceutical products and possibly other sources. To this end, 33 samples of human milk were analyzed (Noti