



## Evaluation of hydrocarbon contaminants in olives and virgin olive oils from Tunisia



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### ABSTRACT

The present paper investigated on the presence of some hydrocarbon contaminants, namely polycyclic aromatic hydrocarbons (PAHs), mineral oil hydrocarbons (MOH) comprising saturated (MOSH) and aromatic (MOAH) compounds, and polyolefin oligomeric saturated hydrocarbons (POSH) in olives and extra virgin olive oils from Tunisia. Olive fruits were collected in sites exposed to different environmental contamination, and the oil extracted both by physical mean (using an Abencor extractor) and with solvent (using microwave assisted extraction, MAE). Analytical determination was performed by SPE cleanup on silica cartridge followed by spectrofluorometric detection, for PAH, and on-line HPLC-GC-FID for MOH and POSH. Oils extracted from olives by physical mean, as well as extra virgin olive oils from the market, had PAH levels never exceeding the EU legal limits. All olive samples showed similar MOSH profiles, but not clear correlation between the variable contamination levels and considered sources of contamination, was evidenced. The average MOSH content in oil extracted from olives by solvent (11.1 mg/kg) was about four time higher than in oil extracted by physical mean (2.6 mg/kg). MOSH in extra virgin oil from the market ranged from 10.3 to 38.0 mg/kg, while MOAH were not detected. The higher MOSH levels found in oils from the market evidenced an important contribution due to oil processing and/or packaging. Two of the samples were clearly contaminated with polyolefin oligomeric hydrocarbons (POSH) migrated from the plastic cap.

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## 1. Introduction

Extra virgin olive oil is a staple food largely consumed in the Mediterranean Countries. Its benefits to health have prompted an increased demand worldwide (Luchetti, 2002). In Tunisia, olive oil production plays an important role in the agronomy and economy (Gharbi et al., 2015). Accounting for more than 4% of the world olive oil production, Tunisia is holding an important position in the olive oil market; it exports about 75% of its production and is ranked as the second largest exporter after the European Union with an average of 115,000 tons per year over the last five years (ONH, 2015).

Edible oils can be contaminated with polycyclic aromatic hydrocarbons (PAHs) and mineral oil hydrocarbons (MOH) which are

both environmental and processing contaminants (EFSA, 2008; EFSA, 2012). Due to their similarity to MOH, some concerns also derive by possible migration of polyolefin oligomeric saturated hydrocarbons (POSH) (Biedermann-Brem, Kasprick, Simat, & Grob, 2012) from polyolefin materials (PE and PP) in contact with oils.

PAHs are a class of organic compounds with 2–6 fused aromatic rings, produced at high temperature during incomplete combustion of organic matter, mainly combustion of fossil fuels, motor vehicle exhausts and industrial emission. Forest fires, volcanoes or hydrothermal processes are natural sources of PAHs (Poster, Schantz, Sander, & Wise, 2006). Only heavy PAHs (4–6 benzene rings) are genotoxics and carcinogenic, while light PAHs (2–4 benzene rings) may act as synergists (EFSA, 2008). The necessity for a legislation arose in 2001 after the finding of a highly contaminated batch of olive pomace oil in the Czech Republic (Purcaro, Barp & Moret, 2016). Regulation 1881/2006 (European Commission, 2006) harmonized the PAH legislation among EU Member States

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and fixed a limit for the presence of benzo[*a*]pyrene (BaP) only, used as a marker of the presence of genotoxic and carcinogenic PAHs. Later, EFSA (2008) recognized that BaP alone is not a suitable marker, and suggested to use PAH8, sum of benz[*a*]anthracene (BaA), chrysene (Ch), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), BaP, dibenz[*a,h*]anthracene (DBaA), benzo[*g,h,i*]perylene (BghiP) and indeno [1, 2, 3-*cd*] pyrene (IP), or PAH4 (sum of BaA, Ch, BbF, and BaP). Regulation 835/2011 (European Commission, 2011) fixed a limit of 2 mg/kg for BaP and 10 mg/kg for PAH4 in vegetable oils and fats. No legal limit has been established for total PAHs, even though the German Society of Fat Science considered a maximum acceptable level of 25 µg/kg for the sum of 16 PAHs (PAH8 plus 8 light PAHs) indicated as priority by the Environmental Protection Agency (EPA).

MOH are complex mixtures of saturated (MOSH) and aromatic (MOAH) hydrocarbons generated by geochemical processes, giving gas chromatographic (GC) traces characterized by “humps” of unresolved peaks. MOSH consist of linear and branched alkanes (paraffins), and alkyl-substituted cyclo-alkanes (naphthenes), whilst MOAH include 1–3-ring alkyl-substituted PAHs (parent PAHs represent less than 1–5% of total hydrocarbons). Neukom, Grob, Biedermann, & Noti (2002), observed that plant materials and edible oils are contaminated with mineral oil hydrocarbons from the air (primarily from particulate matter), mostly originating from incomplete combustion of heating and diesel oils, engine lubricating oils, and road tar debris.

Depending on their composition and molecular range, mineral oil fractions may have different bioaccumulation potential and toxicity. MOSH from *n*-C16 to *n*-C35 accumulate in several tissues (lymph nodes, spleen and liver) and cause microgranulomas in Fisher 344 rats. Exposure to MOAH through food is considered of great concern due to the carcinogenic risk associated with this class of hydrocarbons (Barp et al., 2014). No legal limit are actually in force for mineral oil content in vegetable oils or other foodstuffs. Nevertheless, a draft ordinance of the German Federal Ministry for Food and Agriculture (BMEL) on the presence of MOSH and MOAH in food, as consequence of migration from recycled paperboard, established a limit of 2 mg/kg for MOSH *n*-C20–35 and 0.5 mg/kg for MOAH *n*-C10–35, and, recently, very restrictive limits have been requested in extra virgin olive oil by large scale distribution in German.

Virgin olive oil is extracted from the olive fruit exclusively by mechanical processes. Environmental contamination generally proceeds via atmospheric deposition on growing crops. Thus, oil extracted from olive fruits is expected to contain a background contamination reflecting the contamination of the environment where the olive grows. High PAH concentrations were occasionally reported in oil obtained from olive collected in an olive-grove in a rural area with piles of old railways ties (Moret, Purcaro, & Conte, 2007).

With the exception of some refining steps (decoloration and deodorization), which lead to a decrease of the contamination (Cejpek, Hajslova, Kocourek, Tomaniová, & Cmolík, 1998; Moret, Populin, & Conte, 2010; Teixeira, Casal, & Oliveira, 2007), edible oil processing generally contribute to increase the contamination with both PAHs and MOH. Direct contact with combustion gases during the drying process of grapeseeds (or the pomace) before oil extraction can lead to very high PAH load (Moret, Dudine, & Conte, 2000). Storage of pomace under inadequate conditions contributes to increase the MOH load (Moret, Populin, Conte, Grob, & Neukom, 2003). Use of mineral oil based pesticide, mechanical harvesting, contact with lubricatings used for maintenance of extraction plant, transport in jute bags, are some of the possible sources of contamination for MOH (Brühl, 2016; Moret & Conte, 2000).

In conclusion, both MOH and PAHs can enter the oil product

through different routes, along the production chain. Rapid alerts (RASSF) succeeded in the last years on the presence of warning amounts of these contaminants in vegetable oils, confirm the importance to maintain under control their presence.

The aim of the present work was to investigate, for the first time, the presence and origin of PAH and MOH in olives and virgin olive oil from Tunisia. To these purpose the background contamination already present in olive fruits differently exposed to some potential environmental contamination was evaluated and compared to the contamination found in bottled extra virgin olive oil from the market.

## 2. Material and methods

### 2.1. Reagents and standards

All solvents used (Sigma-Aldrich, Milan, Italy) were of HPLC grade. Ultra pure water was obtained with a MilliQ filter system (Millipore, Bedford, MA, USA). To avoid contamination during sample preparation, all the glassware was carefully washed and rinsed with clean solvents (acetone and hexane) before use.

The 610 PAH mixture in 1 mL of methanol/dichloromethane (Supelco, Bellefonte, PA, USA) consisted of: acenaphthene (Ac) (1000 µg/mL), fluoranthene (Fl) (200 µg/mL), naphthalene (Na) (1000 µg/mL), BaA (100 µg/mL), BbF (200 µg/mL), BaP (100 µg/mL), BkF (100 µg/mL), Ch (100 µg/mL), acenaphthylene (Ap) (2000 µg/mL), anthracene (A) (100 µg/mL), BghiP (200 µg/mL), fluorene (F) (200 µg/mL), phenanthrene (Pa) (100 µg/mL), DBaA (200 µg/mL), IP (100 µg/mL) and pyrene (P) (100 µg/mL).

Internal standards for MOH analysis were purchased from Supelco (Milan, Italy) and the standard solution was prepared by mixing 5- $\alpha$ -cholestane (Cho, 0.6 mg/mL), *n*-C11 (0.3 mg/mL), *n*-C13 (0.15 mg/mL), cyclohexylcyclohexane, (CyCy, 0.3 mg/mL), *n*-pentylbenzene (5B, 0.30 mg/mL), 1-methylnaphthalene (1-MN, 0.30 mg/mL), 2-methylnaphthalene (2-MN, 0.30 mg/mL), tritert-butylbenzene (TBB, 0.3 mg/mL), and perylene (Per, 0.6 mg/mL) in toluene.

The C10–C40 *n*-alkane standard mixture (50 mg/L each) used to check the performance of the system, was purchased by Sigma-Aldrich.

### 2.2. Sampling

Five extra virgin olive oil samples (different brands) were randomly purchased from the retail market. Despite the low number of samples, they covered about 50% of commercial extra virgin olive oils brands marketed in Tunisia. Such oils are produced by mills which export most of their products and sell only small quantities in the local market. On the other hand, Tunisian people mostly consumes oil produced from olives grown in their family olive groves. Olive samples (11) were collected by hand in different sites during the crop season 2014/2015. They were all from the olive variety Chemlali, which is the most diffused in Tunisia, covering more than 60% of the total Tunisian olive tree growing area.

Table 1 resumes some characteristics of the sampling sites (information on the area, number of inhabitants, distance from the main road and level of vehicular traffic). To facilitate a rough estimation of exposure to urban emission, the sites were classified as urban, semi-urban and rural, depending on dimension and density of the populated area. Based on these data and type of road (main or secondary road), roads were classified into three groups (with low, medium and high vehicular traffic). All sites, except that corresponding to sample OF1, which was very close to an industrial area (production of stones for house construction), were far from sources of industrial emission (>2 km). Use of pesticides was also

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