

Organohalogen compounds in present day vegetable oils sourced from the Middle East

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Introduction

Organohalogen chemicals such as hexachlorohexanes (HCHs), hexachlorobenzene (HCBs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are persistent, hydrophobic and thus accumulate in the food chain.

The relevance of fish and dairy products as source for human contamination with these pollutants is widely recognized and as a result, routine monitoring programs of fish and dairy products are used to monitor exposure.

Monitoring of vegetable oils for organohalogen contaminants is more on an ad hoc basis as vegetable oils are generally far less contaminated than animal fats. Where monitoring is undertaken, samples originating from or entering the European and US market are generally analysed and data are available in the published literature¹⁻³. However, little data is available in the public domain for other major producers, particularly the Middle East.

Olive oil is integral to Middle Eastern cooking and is widely consumed in relatively large quantities. Rich in monounsaturated fatty acids, nutritionally olive oil is considered to impart important health benefits as observed in southern Mediterranean diet studies^{4,5}.

Here we report the levels of PCBs, organochlorine pesticides (OCPs) and PBDEs in eight olive oil and three vegetable oil samples from the Middle East obtained in 2003 and in three additional olive oil samples from the Mediterranean countries (Turkey, Greece and Egypt). The present study provides an extension of our previous study on organohalogen contaminant data in historic olive and ground nut oil from Palestine⁶ and gives a preliminary indication of dietary exposure to organohalogen contaminants from vegetable oils.

Methods

Sample Collection

Eight present-day samples of olive oil and three samples of vegetable oils were sourced from Jordan and Syria in November 2003. The sources included supermarkets in Amman, Jordan, a nature reserve shop, a supermarket in Damascus and a community olive oil press in Northern Syria. Three additional olive oil samples, originating from Turkey, Greece and Egypt, but obtained from supermarkets in London, UK, were included for comparison. All the samples can be considered

'samples of opportunity'. The samples were packaged predominantly in glass bottles, but plastic bottles and cans were also packaging materials, particularly for larger quantities.

To access the oils, bottles were opened or the cans of oil were punctured with two small holes. Then each oil sample was aliquoted into a solvent free washed glass jar, mixed, and sent to the Toxicological Center at the University of Antwerp for analysis of OCPs, non-dioxin like PCBs and PBDEs.

Sample Analysis

For analysis of PCBs, OCPs and PBDEs, approximately 0.5 g oil was solubilized in 3 ml hexane and spiked with known quantities of internal standards (PCB 46 & PCB 143, α -HCH, BB 103 & BB 155). The obtained solution was subjected to clean-up on a cartridge containing ~8g silica impregnated with concentrated sulphuric acid (1/1, w/w). Analytes were eluted with 15 ml hexane followed by 10 ml dichloromethane. The final eluate was concentrated to near dryness and taken up in 80 μ l iso-octane. PCBs were analysed on a GC equipped with a ^{63}Ni -ECD, while PBDEs and OCPs were analysed using GC/MS operated in NCI mode.⁷

A range of standard QC/QA procedures with clearly defined techniques, including laboratory blanks, QC samples, and regular participation in interlaboratory calibration studies, were used to assure adequate quality of data. Detection limits for individual compounds were between 0.05 and 0.1 ng/g lipid.

Results and Discussion

PCBs

As expected, the concentrations of PCBs (IUPAC no. 28, 31, 74, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 153, 156, 163, 170, 180, 183, 187, 194, 199), were below the limit of detection (< 1 ng/g lipid for the sum of 22 congeners) for all the vegetable oils.

PBDEs

PBDE (IUPAC no. 28, 47, 49, 99, 100, 153, 154, 183) were not detected in any of the oil samples, the sum of 8 PBDEs was < 0.1 ng/g lipid. PBDEs are newer environmental contaminants, particularly in industrialized countries. This is reflected in this study and in the PBDE data for the historic vegetable oils⁶ and butters⁸.

Organohalogen pesticides

The results for the measured organochlorine pesticides are presented in Table 1.

HCHs

Organochlorine pesticides were detectable in all the olive oil samples, but not in the sunflower oil samples. HCHs were detectable in all but one of the olive oil samples ranging from ND to 2.3 ng/g lipid, but were not detected in the sunflower and corn oil samples. α -HCH was the dominant HCH isomer for the Jordanian, Syrian and Egyptian olive oil samples. Similar levels of α -HCH and γ -HCH were measured in the Turkish sample, while the Greek sample was dominated by the γ -HCH isomer.

We have previously found the γ -HCH isomer to dominate the HCHs detected in present day vegetable oils obtained from UK⁵. Where detected, the HCH levels were much lower than

levels observed in animal fat matrices such as butter⁷ and fish oils^{7,9} but were comparable with the levels detected for organically produced omega-3 rich unsaturated vegetable fatty acids⁹.

DDTs

While p,p'-DDD was not detected in any of the samples sourced from Jordan and Syria, it was present in the Turkish, Egyptian and Greek samples at levels of 0.8, 1.0 and 1.3 ng/g lipid respectively. p,p'-DDE and p,p'-DDT were not detected in the sunflower and corn oil samples, but detected in all the olive oil samples. p,p'-DDE ranged from ND to 6.7 ng/g lipid, this latter Syrian sample from a supermarket in Damascus, was similar to that from a Greek sample, 7.0 ng/g lipid, sourced from a supermarket in London, UK. Excluding the Syrian supermarket sample, the Middle Eastern oils analysed here presented very low levels of total DDTs, ranging from ND to 1.3 ng/g lipid. In contrast, samples from Turkey, Egypt and Greece were 2.6, 4.4 and 12.7 ng/g lipid, respectively. However, the total DDT levels in the samples presented in this study were lower than historic oil samples previously reported⁶.

For DDTs, the ratios of individual metabolites revealed an interesting pattern. Apart from two samples (from the Syrian supermarket and Turkey), p,p'-DDE, a key stable metabolite of DDT, did not dominate the samples, as frequently found with current day samples of dietary fats. An increase in p,p'-DDE to p,p'-DDT ratios is frequently observed in present day animal fat matrices, as a probable consequence of the (almost global) ban on DDT use. Higher p,p'-DDT ratios may indicate continued exposure as a consequence of continued use of the pesticide.

HCB

Levels of HCB were very low and ranged from ND to 0.5 ng/g lipid. HCB was not detected in sunflower oils, while for the olive oils obtained from Syria and Jordan, the HCB levels ranged from ND to 0.2 ng/g lipid, compared to 0.4 - 0.5 ng/g lipid for the olive oils from Turkey, Greece and Egypt.

Conclusions

On the basis of this limited data set it would appear that the organohalogenated residues in vegetable oils from Syria and Jordan, are extremely low and, apart from one sample, they are comparable with the levels observed in organically produced omega-3 rich unsaturated vegetable fatty acids, reported previously⁹.

References

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Table 1. Organochlorine pesticides in present day olive oil and vegetable oil samples from the Middle East, Turkey and Greece. All values in ng/g (ppb) lipid.

Sample ID	Mass (g)	Country of origin	Source	Oil type	α -HCH	γ -HCH	β -HCH	Sum HCHs	HCB	p,p'-DDE	p,p'-DDD	p,p'-DDT	Sum DDTs
ME-01	0.481	Jordan	Dana nature reserve	OO	0.6	0.4	0.2	1.2	ND	0.4	ND	0.2	0.6
ME-02	0.492	Syria	supermarket, Damascus	OO	0.8	0.3	ND	1.0	0.1	6.7	ND	1.0	7.7
ME-03	0.501	Jordan	supermarket, Amman	OO	0.8	0.2	0.2	1.1	0.1	0.3	ND	0.3	0.6
ME-04	0.491	Jordan	supermarket, Amman	OO	1.6	0.3	0.3	2.3	0.2	0.3	ND	0.2	0.5
ME-05	0.502	Jordan	supermarket, Amman	OO	0.8	0.3	0.1	1.2	ND	0.6	ND	0.7	1.3
ME-06	0.496	Jordan	supermarket, Amman	OO	1.3	0.4	0.3	2.0	0.1	0.6	ND	0.5	1.1
ME-07	0.507	N. Syria	village oil press	OO	ND	ND	ND	ND	ND	ND	ND	0.3	0.3
ME-08	0.511	Lebanon	supermarket, Amman	SO	ND	ND	ND	ND	ND	ND	ND	ND	ND
ME-09	0.502	UAE	supermarket, Amman	SO	ND	ND	ND	ND	ND	ND	ND	ND	ND
ME-10	0.500	Jordan	supermarket, Amman	CO	ND	ND	ND	ND	0.2	ND	ND	ND	ND
ME-11	0.496	Jordan	supermarket, Amman	OO	1.2	0.3	0.3	1.8	ND	0.5	ND	0.4	0.9
MJ4-O	0.583	Turkey	supermarket, London, UK	OO	0.1	0.1	ND	0.2	0.4	0.8	0.8	1.1	2.6
MJ5-O	0.630	Egypt	supermarket, Sharm el Sheikh, Egypt	OO	0.4	0.2	ND	0.6	0.5	1.6	1.0	1.8	4.4
MJ7-O	0.638	Greece	supermarket, London, UK	OO	0.4	1.9	ND	2.3	0.4	7.0	1.3	4.5	12.7

Key: OO = Olive Oil; CO = Corn oil; SO = sunflower oil; N.D = not detected (<0.1 ng/g lipid).