ORGANOHALOGEN COMPOUNDS IN HISTORIC AND PRESENT DAY MIDDLE EASTERN VEGETABLE OILS

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Introduction

Organohalogen chemicals such as those classified as Persistent Organic Pollutant (POPs), and also hexachlorohexanes (HCHs) 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 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 oil samples are generally far less contaminated than animal fats. There have been serious poisoning episodes with vegetable oil contamination incidents, such as Yusho, in Japan in 1969 where rice oils where contaminated with polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxin and furan (PCDD/F) mixtures, and also Yu Cheng in Taiwan (1979). Apart from these incidents, to date there is relatively little information in the public domain on historic and present day levels of pollutants in vegetable oils. Here we report the PCDD/F, dioxin like PCBs, PCBs, organochlorine pesticides and PBDE levels detected in four vegetable oils from the Middle East, two of which were produced in the 1940's and two present day samples.

Methods

One can each of olive oil and peanut oil, manufactured and canned in Palestine prior to 1940 by 'Shemen' oil canning company, were obtained from a private home, where they were kept at room temperature, for over 50 years. Both samples were stored in tin-coated steel that had remained sealed since manufacture. Two present day samples of olive oil and peanut oil were obtained from Egypt, to provide a comparison. All the samples can be considered 'samples of opportunity'. It was not possible to obtain samples from present day Palestine. The company 'Shemen' is no longer in business and it is extremely difficult to produce and obtain similar vegetable oils from the Palestinian areas due to the present political climate in the Middle East.

To access the oils, 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 refrigerated until further use. For analysis an aliquot of each oil sample was sent to ERGO-Forschungsgesellschaft, Germany for analysis of dioxin-like chemicals. A second sample was send to the Toxicological Center at the University of Antwerp, Belgium for analysis of organochlorine pesticides, PCBs (non-dioxin like PCBs) and PBDEs.

At ERGO sub-samples equivalent to about 10 g of lipid were homogenised in a water bath (40 °C) and the lipophilic phase was separated then filtered through anhydrous Na_2SO_4 after which the lipid content was determined gravimetrically. Then samples were spiked with ^{13}C-labelled

PCDD/F and PCB standards, purified on an automated system using activated carbon followed by addition of H_2SO_4/SiO_2. Following several hours' reaction time samples were filtered and concentrated and further purified using an acid/base activated silica gel column. The purified samples were concentrated to near dryness, transferred to vials and ^{13}C-labelled 1,2,3,4-TCDD recovery standard was added to the PCDD/F and co-planar PCBs fraction. Analysis of tetra- to octa-CDD/Fs, co-planar and mono-ortho PCBs was performed on a GC/MS (VG Autospec).[2]

For analysis of PCBs, organochlorine pesticides and PBDEs at the Toxicology Center, 1.0 - 1.5 g of sample was homogenized with anhydrous Na_2SO_4, spiked with known quantities of internal standard (PCB 46 & PCB 143, ε-HCH, BB 103 & BB 155) and Soxhlet extracted using hexane:acetone (3:1). A small aliquot was used to quantify the lipid content whereas the reminder was subjected to clean-up on a cartridge containing ~8g silica impregnated with concentrated sulphuric acid (1/1, w/w). PCBs, pesticides and PBDEs were eluted with 15 ml hexane followed by 10 ml dichloromethane. The final eluate was concentrated to near dryness then taken up in 80µl iso-octane. PCBs and DDTs were analysed on a GC equipped with a µ–ECD, while PBDEs and other organochlorine pesticides were analysed using GC/MS operated in NCI mode (SIM).[3]
Both laboratories use a range of standard QC/QA procedures with clearly defined techniques that assure appropriate recognition of peaks, laboratory blanks, QC samples, detection limits and participation in interlaboratory calibration studies.

Results and Discussion

The results for the PCDD/Fs, mono-ortho and non-ortho PCBs and WHO-TEQ values[4] are presented in Table 1. PBDE (IUPAC) no's 28, 47, 49, 99, 100, 153, 154, 183 were not detected in any of the oil samples, the sum of 8 PBDEs was <0.05ng/g lipid. PBDEs are newer environmental contaminants, particularly in industrialized countries, and this is reflected in the PBDE data for the historic oils and butters[5].

DDTs and HCHs

Organochlorine pesticides were detectable in all the oil samples. HCHs were detectable in all samples ranging from 0.4 ng/g lipid in olive oil from the 1940s to 3 ng/g lipid in olive oil from 2003, and were several magnitudes less than the detections observed in animal fat matrices such as butter[5] and fish oils[1]. Similarly the concentrations of DDTs ranged from about 3.4 ng/g lipid in the most recent samples to 25ng/g lipid in the historic peanut oil sample, which was dominated by the parent compound pp-DDT, widely in use at the time, and was a magnitude greater than that observed in the 1940's olive oil. The high ratio of pp-DDT to pp-DDE indicates that this sample had not been subject to more extended metabolic activities, as observed in a butter sample canned during a similar period in time.[5] For both DDTs and HCHs, the ratios of individual isomers (HCHs) or metabolites (DDTs) revealed an interesting pattern. β-HCH, the most stable isomer of HCHs was not detected at all, and p'p-DDE, a key stable metabolite of DDT, did not dominate the samples, as generally reported from current day samples of dietary fats. α-HCH was detected in all the samples (0.1-0.6 ng/g lipid). In contrast to the older samples, γ-HCH was the dominant HCH isomer detected in the present day vegetable oil sample. For DDTs there was a shift towards pp-DDE in the present day olive oil sample, compared to pp-DDT, but this was not the case with the vegetable oil reported here or with other present day vegetable oils.[1] An increase in pp-DDE to pp-DDT ratios is frequently observed in present day animal fat matrices, as a probable

consequence of the (almost global) ban on DDT use. Higher pp-DDT ratios may indicate continued exposure as a consequence of continued use of the pesticide.

Dioxins

Dioxins were detectable in all samples from the 1940s to the present day, but were greatest in the peanut oil from the 1940s. DDT levels were also greatest in this sample. As reported previously for butter, in relative terms, the greatest contributor was OCDD, a key contributor to the sum of PCDDs. OCDD levels were highest in the 1940 samples, particularly the peanut oil, compared to present day samples. The sum WHO-TEQ levels incorporate the non-detected congeners at the limit of detection. Due to the high number of non-detections, it is likely that the TEQ values given in Table 1 overestimate the total.

PCBs

PCBs were analysed in two laboratories. The concentrations for PCBs (IUPAC no's) 28, 31, 74, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 153, 156, 163, 170, 180, 183, 187, 194, 199 for all the vegetable oils, were below the limit of detection (< 1 ng/g lipid for the sum of 22 congeners), while PCBs 81, 77, 126, 105, 118, 169, were detected on HRMS with a limit of detection ranging between 9-62 pg/g lipid. PCB 77 detection levels were comparable in both the 1940's olive oil and the present day olive oil, but on the whole, the PCB levels were greatest in the present day olive oil sample compared with the 1940's samples.

Conclusions

This study reports the results for a very small sample number, it therefore provides a snapshot indication, and cannot be considered to be representative of the organohalogen pollutants in Middle Eastern vegetable oils in the 1940's, or of current vegetable oil products. However analysis of sealed vegetable oil samples can provide a good indication for historic contamination of regional environments and diets, with persistent organohalogen compounds. The data presented here, together with data from other fat matrices from the same time period[5] indicate that for organochlorine pesticides, levels increased rapidly following their introduction. The data can add to that provided for animal fat matrices to give a likely indication of the potential cumulative pollutant exposure of human populations via dietary sources.

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Table 1. PCDDs/PCDFs, PCBs and organochlorine pesticides in historic and present day vegetable oil samples from the Middle East.

PCDD/PCDF and PCB values in pg/g (ppt) lipid, pesticide values in ng/g (ppb) lipid.

Congener	OO 1940	WHO-TEQ	PO 1940	WHO-TEQ	OOE 2003	WHO-TEQ	VO 2003	WHO-TEQ	BLANK	WHO-TEQ
2,3,7,8-TCDD	n.d.	0.030	n.d.	0.039	n.d.	0.043	n.d.	0.030	n.d.	0.048
1,2,3,7,8-PCDD	n.d.	0.030	n.d.	0.030	0.06	0.058	n.d.	0.030	n.d.	0.030
1,2,3,4,7,8-HCDD	n.d.	0.003	n.d.	0.004	n.d.	0.004	n.d.	0.003	n.d.	0.003
1,2,3,6,7,8-HCDD	n.d.	0.004	0.07	0.007	0.05	0.005	n.d.	0.003	n.d.	0.003
1,2,3,7,8,9-HCDD	n.d.	0.003	0.05	0.005	n.d.	0.003	n.d.	0.003	n.d.	0.003
2,3,7,8-HCDD	n.d.	0.010	0.12	0.016	0.05	0.012	n.d.	0.009	n.d.	0.009
1,2,3,4,6,7,8-HCDD	0.48	0.005	0.56	0.006	0.09	0.001	0.21	0.002	0.04	< 0.001
OCDD	2.26	< 0.001	4.89	< 0.001	n.d.	< 0.001	1.30	< 0.001	0.45	< 0.001
2,3,7,8-TCDF	0.15	0.015	0.29	0.029	2.38	0.238	0.73	0.073	0.10	0.010
1,2,3,7,8-PCDF	n.d.	0.002	0.10	0.005	0.24	0.012	n.d.	0.002	n.d.	0.002
2,3,4,7,8-PCDF	0.05	0.023	0.09	0.043	0.22	0.112	n.d.	0.015	n.d.	0.015
2,3,7,8-PCDF	0.05	0.024	0.19	0.048	0.47	0.124	n.d.	-	n.d.	-
1,2,3,4,7,8-HCDF	0.11	0.011	0.15	0.015	0.14	0.014	n.d.	0.003	n.d.	0.003
1,2,3,6,7,8-HCDF	0.05	0.005	0.08	0.008	0.15	0.015	n.d.	0.003	n.d.	0.003
1,2,3,7,8,9-HCDF	n.d.	0.003	n.d.	0.003	n.d.	0.003	n.d.	0.003	n.d.	0.003
2,3,4,6,7,8-HCDF	n.d.	0.007	n.d.	0.007	n.d.	0.007	n.d.	0.007	0.07	0.007
2,3,7,8-HCDF	0.15	0.025	0.23	0.033	0.29	0.039	n.d.	0.016	0.07	0.016
1,2,3,4,6,7,8-HCDF	0.21	0.002	1.86	0.019	0.12	0.001	0.10	0.001	n.d.	< 0.001
1,2,3,4,7,8,9-HCDF	n.d.	< 0.001	0.08	0.001	n.d.	< 0.001	n.d.	< 0.001	n.d.	< 0.001
2,3,7,8-HCDF	0.21	0.003	1.94	0.019	0.12	0.002	0.10	0.001	n.d.	0.001
OCDF	0.12	< 0.001	1.26	< 0.001	n.d.	< 0.001	0.07	< 0.001	0.06	< 0.001
Total 2,3,7,8-PCDD	2.74	0.075	5.58	0.092	0.20	0.114	1.52	0.071	0.49	0.088
Total 2,3,7,8-PCDF	0.68	0.067	3.91	0.129	3.24	0.402	0.91	0.107	0.23	0.043
Total 2,3,7,8-PCDD/F	3.42	0.142	9.48	0.221	3.44	0.515	2.42	0.178	0.73	0.131
3,4,4',5-TCB 81	0.3	< 0.001	0.2	< 0.001	1.3	< 0.001	0.2	< 0.001	0.1	< 0.001
3,3',4,4'-TCB 77	5.3	0.001	3.9	< 0.001	7.2	0.001	2.4	< 0.001	1.9	< 0.001
3,3',4,4',5-PCB 126	n.d.	0.057	n.d.	0.056	2.0	0.200	0.8	0.084	0.6	0.057
3,3',4,4',5,5'-HCB 169	n.d.	0.003	n.d.	0.003	n.d.	0.003	n.d.	0.003	0.3	0.003
Total non-ortho PCB	5.7	0.060	4.2	0.060	10.5	0.203	3.5	0.087	2.8	0.060
2,3,3',4,4'-PCB 105	n.d.	0.002	n.d.	0.002	30	0.003	n.d.	0.002	n.d.	0.001
2,3,4,4',5-PCB 114	n.d.	0.005	n.d.	0.007	n.d.	0.012	n.d.	0.011	n.d.	0.005
2,3',4,4',5-PCB 118	n.d.	0.006	n.d.	0.006	111	0.011	n.d.	0.006	62	0.006
2',3,4,4',5-PCB 123	n.d.	0.001	n.d.	0.002	n.d.	0.003	n.d.	0.003	n.d.	< 0.001
2,3,3',4,4',5,-HCB 156	n.d.	0.005	n.d.	0.008	n.d.	0.013	n.d.	0.010	n.d.	0.005
2,3,3',4,4',5'-HCB 157	n.d.	0.005	n.d.	0.005	n.d.	0.011	n.d.	0.010	n.d.	0.006
2,3',4,4',5,5'-HCB 167	n.d.	< 0.001	n.d.	< 0.001	n.d.	< 0.001	n.d.	< 0.001	n.d.	< 0.001
2,3,3',4,4',5,5'-HCB 189	n.d.	0.001	n.d.	0.002	n.d.	0.004	n.d.	0.003	n.d.	0.002
Total mono-ortho PCB	n.d.	0.026	n.d.	0.032	141	0.056	n.d.	0.044	62	0.024
PCDD/PCDF TEQ(WHO)*		0.142		0.221		0.515		0.178		0.131
PCDD/PCDF/dioxin-like PCBs TEQ		0.228		0.313		0.774		0.309		0.215
a-HCH	0.1		0.6		0.4		0.5			
g-HCH	0.3		0.4		0.2		2.5			
b-HCH	n.d.		n.d.		n.d.		n.d.			
TOTAL HCHs	0.4		1.0		0.7		3.0			
HCB	0.1		0.1		0.5		n.d.			
pp-DDE	0.2		1.0		1.6		0.2			
pp-DDD	2.7		3.0		1.0		1.6			
pp-DDT	1.5		20.8		1.8		1.7			
DDTs	4.4		24.8		4.4		3.4			

Key: OO=Olive Oil from Palestine; OOE=Olive oil from Egypt; PO=Peanut Oil from Palestine; VO=Vegetable oil; n.d.=not detected; LOD=Limits of detection ranged from 0.03 to 0.07 pg/g lipid for the PCDD/Fs, for the non-ortho PCBs from 0.3-0.6 pg/g lipid, and for the mono-ortho PCBs from 9-62 pg/g lipid. *=100% LOD used for WHO-TEQ summations.