PCDD/Fs in Venetian foods and a quantitative assessment of dietary intake.

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INTRODUCTION

The main route by which humans are exposed to PCDD/Fs is through the ingestion of food particularly from animal-based fats which contribute over 90% of the total exposure to PCDD/Fs. Fish has been isolated as an important source of organic contaminant exposure in Nordic countries constituting >40% of total PCDD/F exposure. The region around the Venice Lagoon has a higher than average consumption of fish within Europe and represents an area in which fish could also dominate PCDD/F exposure for some members of the population. The area has a long history of industrial activity, with oil refining and chemical production plants around Porto Marghera, where some areas are known to have elevated PCDD/Fs and a range of other persistent organic compounds in the sediments. Very little information is available on PCDD/F concentrations in foods in this area, in particular on the range of concentrations in locally caught species of fish, shellfish and crustaceans. This study was designed to provide information about these concerns and place PCDD/F dietary intake of the Venetian population within the context of typical levels around Europe.

This paper incorporates a survey of PCDD/F concentrations in a range of basic animal-based food components bought in Venice, a detailed survey of fish and shellfish PCDD/F concentrations in the Lagoon and local food intake statistics, so that an indication of Venetian PCDD/F exposure can be estimated. These are then compared with recent estimates from other European countries. It is assumed that plant products are not a major source of direct PCDD/F contamination in the human diet and therefore have been excluded from this survey.

MATERIALS AND METHODS

The food survey. Between the 15th and 16th July 1997 popular brands of butter (n=3), milk (n=6), cheese (n=15), beef (n=3), chicken (n=3) and pork (n=3) were collected from a range of food retailers around Venice. Butter was collected in 250g packs and meats in 200-300 g samples. The produce was sourced from a range of European counties and is more representative of a European food basket rather than one which is purely Venetian. They were bought in their original packaging then wrapped in hexane rinsed aluminium foil for storage. Samples were immediately frozen and stored at the Public Health Department ASL 12 at -20^{o}C awaiting shipping.

Food consumption surveys

ISTAT 1994-96 data used for food consumption statistics in the Veneto region. To allow for deficiencies in the direct consumption data for fish/shellfish for the inhabitants of Venice a survey was commissioned to update existing data. A survey for estimating butter and fat consumption was given by AC Nielson.

Fish/shell fish surveys. Between January 1997 and July 1997 fish/shellfish were collected from the Lagoon of Venice by ASL 12. Samples were collected from different areas of the Lagoon (north, middle and south) excluding the industrial canals. Samples were coded and their position recorded using GPS so that locations could be matched to individual grid square positions used by Consorzio Venezia Nuova for sediment sampling. All samples were carefully prepared at the ARPAV-PMP Venice Laboratory, placed in hexane rinsed glass jars and frozen at -20^{o}C. The samples were air freighted under dry ice to Lancaster University for analysis. *Chelon labrosus* was collected in three samples composed of 6/7 fish of standard dimensions. These were ONLY collected from managed fish farms. Six samples of *Zosterissor ophiocephalus* were collected with 30 individuals making up each sample. The whole fish was homogenized to represent local eating habits. Twenty three samples of *Tapes philippinarum* and seven samples of *Mytilus galloprovincialis* were collected from around the Lagoon, each sample weighing ~2 kg. Tapes p. were kept for several hours in water tanks containing Lagoon water to ensure they were clean of sediment. Six samples (30 individuals in each sample) of *Carcinus mediterraneus* were also collected.

Analysis- A portion of the thawed samples was spiked with 20 $^{13}C_{12}$-labelled PCDD/Fs (and 9 $^{13}C_{12}$-labelled PCBs in the case of the fish and shellfish) and extracted either by blending with acetone/hexane or by grinding with sodium sulphate followed by soxhlet extraction with DCM. Lipid contents were determined gravimetrically on a small aliquot of the extract. Extracts were cleaned by digestion with CH_2SO_4, adsorption chromatography with acid treated and base treated silica gel and GPC. PCDD/Fs were quantified by HRGC/HRMS (HP 6890/Micromass Autospec Ultima) using HP5-ms and SP2331 capillary columns.

PCDD/Fs in foods

In general the levels of PCDD/Fs found in the food samples were very low and for several congeners at the limits of quantitation. On a whole weight basis, ΣTEQ ranged from 0.001 - 0.07 pg/g for the meat samples, 0.04-1.05 for the cheeses, 1.5 - 9 pg/l for the milk and 0.42 to 5.3 pg/g for the butter. Of all the cheese samples analysed the 3 mozzarella cheese samples displayed the greatest range in concentrations. One sample was over an order of magnitude higher in TEQ (1.05 pg/g whole weight) than the other two samples (0.05 and 0.07 pg/g). This increase is almost entirely due to increased concentrations of a single congener (2,3,7,8-PeCDF). The 3 samples of butter analyzed also showed a wide variation in concentrations with a single butter sample containing 5.46 pg/g TEQ on a whole weight basis. Re-analysis of this sample confirmed this. Investigations into the elevated concentrations in this sample are ongoing.

Of the fish and shellfish analyzed, *Carcinus* contained the highest concentrations of PCDD/Fs with ΣTEQ ranging from 0.9 to 3.2 pg TEQ g-1 with an average of 1.7 pg TEQ g^{-1}. Congeners 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF contributed the greatest amount to the ΣTEQ in this species. The fin fish (*Zosterisessor* and *Chelon*) contained similar concentrations of PCDD/Fs in all samples ranging between 0.23 and 0.82 pg TEQ g^{-1}. Again, 2,3,4,7,8-PeCDF dominated in all samples. Fin fish collected in the Venice Lagoon have similar PCDD/F TEQ concentrations in a

recent survey of brown trout in fish farms in the UK (MAFF 1998) which had a mean of 0.24 (range 0.06-0.67) pg TEQ g^{-1}. Concentrations of PCDD/Fs in samples of molluscs (*Tapes* and *Mytilus*) ranged from 0.06 to 1.98 pg TEQ g^{-1} with a mean of 0.29 pg TEQ g^{-1}.

Table 1: Mean whole weight TEQ results (fg TEQ/g) for individual species Mytilus, Tapes, Zosterisessor, Chelon and Carcinus

TEQ (fg/g)	*Chelon (n=3)*	*Mytilus (n=7)*	*Tapes (n=23)*	*Zoster (n=6)*	*Carcinus (n=6)*
2,3,7,8-TCDF	110	48	87	10	401
1,2,3,7,8-PeCDF	10	4.2	19	2.5	80
2,3,4,7,8-PeCDF	205	43	123	284	658
1,2,3,4,7,8-HxCDF	4.6	12	65	40	130
1,2,3,6,7,8-HxCDF	3.3	7.3	34	25	84
1,2,3,7,8,9-HxCDF	1.3	1.3	7.4	1.6	6.2
2,3,4,6,7,8-HxCDF	5.0	5.1	24	14	52
1,2,3,4,6,7,8-HpCDF	0.2	5.0	22	2.1	14
1,2,3,4,7,8,9-HpCDF	0.1	0.2	2.6	0.3	2.0
OCDF	0.04	0.7	3.1	0.2	0.9
2,3,7,8-TCDD	80	10	21	56	114
1,2,3,7,8-PeCDD	38	4.8	16	48	106
1,2,3,4,7,8-HxCDD	1.0	1.1	3.4	2.6	10
1,2,3,6,7,8-HxCDD	1.7	1.4	4.4	8.9	16
1,2,3,7,8,9-HxCDD	0.8	1.0	3.0	4.0	2.8
1,2,3,4,6,7,8-HpCDD	0.2	1.5	3.6	1.1	3.4
OCDD	0.1	0.6	1.4	0.3	1.3
PCDD/F TEQ (fg/g)	**461**	**147**	**440**	**502**	**1682**

Estimation of PCDD/F dietary intake. The results of the chemical analyses were used as the basis for the intake calculations. Values below the detection limit were assumed to be half the detection limit. Calculations were carried out for adult consumers only. Concentrations of PCDD/Fs in products not selected for analysis e.g. eggs were estimated using recent published data. A summary of the results is presented in Table 2. Average PCDD/F-TEQ intake for the Venetian population was estimated to be 42 pg/TEQ/day (median 30) with a range of between 15 and 128 pg TEQ/day. Venetian dietary exposure to PCDD/Fs is at the lower end of the range of values recently reported around Europe (between about 25 to 140 pg TEQ/day). For example, PCDD/F dietary exposure to PCDD/Fs in Norway averaged between 51 to 85 pg TEQ/day, depending on the use of non-detect concentrations as 0 or set at the limit of detection (Becher et al., 1998). In this region where fish makes up a high proportion of the diet, fish contributed

between 25 and 40% of average PCDD/F intake. For comparison, dietary exposure to PCDD/Fs in New Zealand, where environmental levels of PCDD/Fs are generally much lower than in Europe, has recently been estimated to be about 15 pg/TEQ/day for adult males (Buckland et al., 1998). For the Venetian population, average fish and shellfish consumption make up ~45% of the ΣTEQ, with dairy produce contributing most of the rest of the dietary exposure to PCDD/Fs.

Table 2: PCDD/F-TEQ dietary intake around the Venice Lagoon

Food Group		*PCDD/F Concentrations (fg/g)*				PCDD/F Intake (pg TEQ/day)			
	g/day	Min	Max	Mean	Median	Min	Max	Mean	Median
Beef (n=3)	48	17	28	21	19	0.82	1.4	1.0	0.9
Poultry (n=3)	32	20	74	38	21	0.64	2.4	1.2	0.7
Other meat (n=3)	28	8	28	18	18	0.23	0.8	0.5	0.5
Seafood (1016g/month)									
Molluscs (n=27)	15	56	1983	294	160	0.8	30	4.4	2.4
Crustacans (n=6)	3	904	3211	1682	1555	3.1	11	5.7	5.3
Fin fish (n=11)	16	232	816	482	455	3.6	13	7.5	7.1
Milk (n=6)	230ml	1.5	9			0.35	2.1		
Cheese (n=15)	38	48	1049	239	198	1.8	40	9.1	7.5
Butter (n=3)	5	497	5663	2252	796	2.3	26	10	3.6
Eggs[1]	10.0	160	220	190	190	1.6	2.2	1.9	1.9
TOTAL (pg TEQ/day)						**15**	**128**	**42**	**30**

[1] UK Total Diet Study egg concentration data used from MAFF (1997) in the absence of measured Venetian egg data

It must be remembered that the intake estimations are based on average consumption data. High level intakes of foods with elevated PCDD/F concentrations could have a large impact on the total TEQ intake. Continued declines in dietary intake are not surprising given the evidence of recent declines in PCDD/F concentrations reported throughout Europe in a range of environmental media.

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