DIOXINS IN DUTCH VEGETABLES

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Introduction

In the past decade there has been much attention for the presence of organic micropollutants such as polychlorobiphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in the diet in The Netherlands. This interest has started in the eighties of the previous century with the contamination of cow's milk with PCDD/Fs originating from a municipal waste incinerator. Concentrations of these substances in the diet have declined since, but are presently strictly monitored. In a recent study the median dietary intake of PCDD/Fs and dioxin-like PCBs in the Netherlands during a human life was calculated to be 1.2 pg WHO-TEQ/kg bw/day[1] while the TDI derived by the Scientific Committee on Food is 2 pg WHO-TEQ/kg bw/day[2]. The intake of dioxins due to the consumption of vegetables was estimated by using a composite sample that contained a proportion of the vegetables as consumed in the Netherlands. Mainly because of low levels of dioxins in vegetables the determination of the average level in this composite sample was difficult which resulted in an estimate with substantial uncertainty. Therefore the present study was conducted which is not based on a single composite sample but on composite samples for all relevant type of vegetables.

Methods and Materials

Based on the consumption pattern of vegetables in The Netherlands the 18 most important vegetables were selected using the results of the Dutch National Food Consumption Survey 97/98 (DNFCS 3). This survey describes the consumption of the Dutch population and includes information on the daily consumption over two consecutive days of 6250 individuals[3].

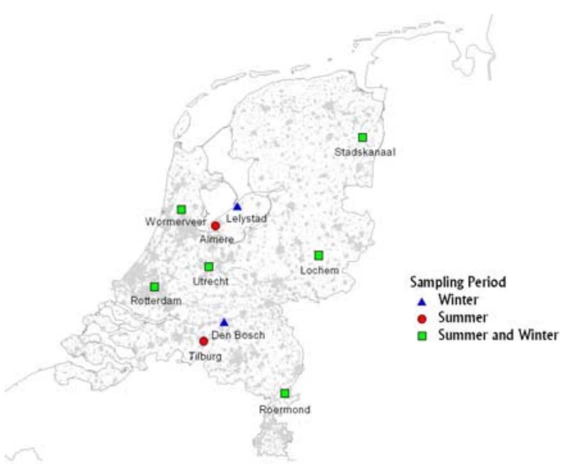

Figure 1. Location of the stores

For some other vegetables the characteristic properties (leaf surface to weight ratio, growing period, position of the edible parts etc) were assumed to be sufficiently comparable to estimate the concentrations by it's look a like. Examples are broccoli estimated by cauliflower and red cabbage by white cabbage. For each type of vegetable 8 volunteers bought sufficient material in shops at locations situated all over The Netherlands. The vegetables were divided into two categories summer vegetables and winter vegetables. The summer vegetables were bought in July 2001 and the winter vegetables in Jan 2002. The stores were selected to be representative for the stores where most of the vegetables are usually bought. The large majority of the vegetables were grown in The Netherlands.

Visual soil and other dirt were removed from the vegetables. The non-edible parts were removed. From each sample 30 g. was taken as representatively as possible. These parts were combined to make a pooled sample out of the eight individual samples. To the test portions, a solution of toluene containing 13C12-labeled internal quantification standards (Cambridge Isotope Laboratories, Woburn, MA, USA) of the 2,3,7,8-chlorine substituted PCDDs and PCDFs, and non-ortho PCBs 77, 81, 126 and 169 was added at levels between 0.7 and 3 pg/g vegetable. After freeze drying and refluxing with dichloromethane, extracts were brought onto the top of a Carbosphere column. Then an Al_2O_3 clean up, evaporation to dryness and redissolvation in 50 µl of toluene took place. 4-6 µl of the final extract was injected on a non-polar column (60 m DB-5MS ; J&W Scientific, Folsom, USA; 0.25 mm ID, 0.10 µm film thickness). Followed by a mass spectrometer operated at resolution 5000 and ionisation with 31 eV electrons.

To control blank levels also blank samples (peeled cucumber) were analysed. For some congeners low levels of dioxins in these blank samples could be detected. Results were not corrected for these levels in the blanks. The levels of TEQ have been calculated assuming non-detects equal to zero (lower bound estimates) and non-detects equal to LOD (upper bound estimates). In addition the available pattern information is used to estimate a most likely TEQ with its uncertainty by multiple imputation. This method applied on an artificially censored data set of dioxins in cow's milk appeared to have both a small error of prediction and an adequate estimate for the uncertainty[4].

Results and Discussion

The results of the analytical chemical analysis are summarised in Table 1 for each of the food categories. In the analyses of the summer vegetables extremely low detection limits are obtained (< 1 pg/kg vegetable). Due to this low detection limit it is obvious that all summer vegetables have a TEQ that is lower than 10 pg TEQ/kg vegetable. The results show that differences between the various vegetables exist which generally follow the assumption that vegetables with high surface to content ratio are high (endive and spinach) and that vegetables with low surface to content ratios (tomato and cucumber) are low. Another observation from the data is that in general for all components observed a strong consistency between the congener patterns seems to be present.

The analysis of the winter vegetables showed higher limits of detection. Therefor the difference between the upper and lower bound results are relatively large. Presumable this higher detection limit is partly due to the difference in consistency between summer and winter vegetables. The latter are known to have higher contents of interfering components like a waxy surface layer. From the results one observation is very clear: curly kale shows much higher levels that any other vegetable analysed. This has been predicted and observed before since curly kale is famous for its large surface/ content ratio, for a thick wax surface layer that perfectly absorbs hydrophobic contaminants, and for it's extremely long presence on the field (9 months)[5].

Table 1 shows a large difference between the lower and upper bound estimates of the winter vegetables. The congener data show a large similarity in the dioxin patterns of the summer vegetables and of the curly kale. This indicates that this pattern similarity probably exists through out our whole data set and can be used for a more precise estimate of the TEQ using the multiple imputation algorithm. The results, shown in table 1, indicate that the most likely estimate is, especially for the winter vegetables, much closer to the lower bound estimate than to the upper bound estimate. The explanation probably is the fact that for most winter vegetables the observed levels of OCDD and PCB 77 are low compared to the level in curly kale (<< 10 %) and to the leafy summer vegetables (< 30 %) and that also some of the detection limits observed are lower than these levels.

Table 1 shows the average intake of the various vegetables per capita. After multiplying and summation of these numbers with the dioxin concentrations the average intake of dioxins can be estimated. This is also shown in Table 1.
In Dutch curly kale samples analysed previously levels in background locations of around 1000 pg TEQ/ g kale were found. This indicates that levels in kale have decreased considerably which coincides with the decrease in the emission of the major sources emitting to the Dutch air.
Recent data of dioxins (PCDDs/PCDFs only) in vegetables from Japan and Korea shows levels from 100-170 pg TEQ /kg spinage[6]. That is much higher than the level found in this study. Levels found in other vegetables are much lower, unfortunately in the lower bound presentation of the data the presumably large influence of the non-detects is not quantitatively indicated. A study on British vegetables[7] showed upperbound levels varying between 100-900 pg i-TEQ/kg for several vegetables and fruit. The low range of this data is determined by the values of the detection limit. In general these data seem to be considerably higher than the values reported in our study. In an American vegetable composite sample all toxic PCDDs/PCDFs are below their limit of detection of 10-60 pg/g[8] . The only comparison that can be made is that analysis of a mixture of our samples presumably would have given the same result.

Conclusions

Dioxin levels in summer vegetables are measured extremely sensitive. Upper bound levels vary between 3 and 10 pg TEQ/kg vegetable. Winter vegetables are measured less sensitive (LOD approx. 10 pg/kg per congener). Upper bound levels (with exception of curly kale) vary between 30 and 70 pg TEQ/ kg vegetable. The average level in Curly kale is estimated as 100-200 pg TEQ/ kg. Using upper bound levels the average intake of PCDDs/PCDFs and no PCB's is estimated as 0.12 pg TEQ/kg bw /day. When a consistency of patterns between detected and non-detected levels is assumed the most likely estimate is 0.014 pg TEQ/kg bw /day. The latter is less than 2 % of the mean total daily intake.

Acknowledgements

George Groenemeijer, Bertwin Stoffelsen, Rob Zwartjes, Dennis Mooibroek, Rick van Poll, Jan Freijer, Harrie Bremmer and Jan ten Hove are acknowledged for buying and handling the vegetables

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Table 1: Concentrations of PCDDs, PCDFs and PCBs in Dutch consumer vegetables with several TEQ estimates and intake estimates

Vegetable	potato	onion	carrot	chicory	leek	Brussels sprouts	curly kale	white cabbage	beetroot	cucumber	French bean	tomato	lettuce	endive	lettuce Iceberg	spinach	mushrooms	cauliflower	Intake [pg TEQ/ kg bw/day]
intake vegetable g/ kg bw/day	1.91	0.15	0.14	0.11	0.07	0.07	0.04	0.14	0.05	0.13	0.31	0.2	0.05	0.07	0.05	0.09	0.04	0.2	
TEQ lower bound (pg/kg)	0.26	0.01	0.02	0.01	0.02	1.16	98.0	0.01	0.01	1.64	2.91	1.32	2.20	6.72	1.85	4.47	1.32	0.42	0.008
TEQ upper bound (pg/kg)	36.0	73.4	53.4	55.9	61.9	62.9	122.1	51.5	36.2	4.4	5.4	4.6	4.6	9.3	4.2	6.9	4.1	3.8	0.127
most likely TEQ (pg/kg)	2.5	1.1	1.4	0.9	1.7	2.6	100.2	0.8	1.5	1.9	3.2	2.1	2.5	7.1	2.3	4.7	1.7	1.0	0.014
uncertainty most likely TEQ (pg/kg)	1.7	1.4	0.8	1.3	0.6	0.8	5.1	0.5	1.3	0.1	0.5	0.7	0.4	0.7	0.4	0.7	0.4	0.9	0.003
	Winter									Summer									
dioxins (pg/kg)																			
2,3,7,8-TCDD	<10	<30	<10	<20	<10	<20	<10	<10	<10	<1	<1	<1	<1	<1	<1	<1	<1	<1	
1,2,3,7,8-PeCDD	<10	<20	<20	<20	<20	<20	<10	<20	<10	<1	<1	<1	<1	<1	<1	<1	<1	<1	
1,2,3,4,7,8-HxCDD	<10	<10	<10	<10	<10	<20	21	<10	<10	<1	<1	<1	<1	2	<1	<1	<1	<1	
1,2,3,6,7,8-HxCDD	<10	<10	<10	<10	<10	<20	34	<10	<10	<1	<1	<1	2	4	1	2	3	<1	
1,2,3,7,8,9-HxCDD	<10	<10	<10	<10	<10	<20	46	<10	<10	<1	<1	<1	<1	3	1	<1	<1	<1	
1,2,3,4,6,7,8-HpCDD	<10	<10	<10	<10	<10	14	<50	<20	<40	13	14	20	27	51	23	33	17	6	
OCDD	51	64	75	51	88	85	1536	54	59	85	114	146	240	305	162	247	73	67	
furans (pg/kg)																			
2,3,7,8-TCDF	<10	<30	<30	<10	<20	<20	27	<10	<10	<1	<1	<1	<1	<1	<1	<1	<1	<1	
1,2,3,7,8-PeCDF	<10	<20	<20	<10	<30	<10	<10	<20	<10	<1	1	<1	1	2	1	2	<1	<1	
2,3,4,7,8-PeCDF	<10	<20	<20	<10	<30	<10	46	<20	<10	1	1	<1	1	4	1	2	1	<1	
1,2,3,4,7,8-HxCDF	<10	<10	<10	<10	<20	<20	<10	<10	<10	<1	1	<1	1	<4	1	2	<1	<1	
1,2,3,6,7,8-HxCDF	<10	<10	<10	<10	<20	<20	<10	<10	<10	<1	1	<1	1	4	1	2	<1	<1	
1,2,3,7,8,9-HxCDF	<10	<10	<10	<10	<20	<20	<10	<10	<10	<1	<1	<1	<1	<1	<1	<1	<1	<1	
2,3,4,6,7,8-HxCDF	<10	<10	<10	<10	<20	<20	37	<10	<10	3	3	3	3	6	3	3	<1	<1	
1,2,3,4,6,7,8-HpCDF	24	<10	<10	<10	<10	<10	140	<10	<10	8	6	8	14	30	13	22	4	4	
1,2,3,4,7,8,9-HpCDF	<10	<10	<10	<10	<10	<10	<10	<10	<10	1	1	<1	1	2	2	2	<1	<1	
OCDF	63	<10	12	<10	13	12	109	<10	<100	9	10	13	20	39	18	37	5	<1	
PCB's																			
3,3',4,4'-PCB(77)	70	70	70	60	80	140	3130	50	80	92	315	221	79	222	47	372	55	76	
3,4,4',5-PCB(81)	<20	<20	<20	<20	<20	<20	240	<20	<20	15	21	23	8	9	8	25	11	9	
3,3',4,4',5-PCB(126)	<20	<20	<20	<20	<20	10	560	<20	<20	6	16	7	5	18	2	18	3	3	
3,3',4,4',5,5'-PCB(169)	<5	<5	<5	<5	<5	<5	60	<5	<5	<0.8	<0.8	<0.8	<0.8	3	<0.8	3	<0.8	<0.8	