DIOXINS AND PCBs IN CHINESE MITTEN CRABS FROM DUTCH RIVERS AND LAKES

Hoogenboom LAP[1]*, Kotterman MJJ[2], Hoek-Van Nieuwenhuizen M[2], Lee Van MK [1], Leeuwen Van SPJ[1]

[1] RIKILT Wageningen UR, Akkermaalsbos 2, Wageningen, The Netherlands; [2] Imares Wageningen UR, Haringkade 1, IJmuiden, The Netherlands

Introduction

Dioxins and PCBs are an important threat to the health of consumers with fish being an important source of these compounds. Especially bottom-dwelling fish, like eel (*Anguila Anguila*) living in contaminated rivers and lakes may contain rather high levels. In the Netherlands commercial eel fishery was prohibited in many of these waters in 2011. Not surprisingly perhaps, Clark et al. (2009) reported rather high dioxin and dl-PCB levels in another species commercially fished in freshwater, being the Chinese mitten crab (*Eriocheir Sinensis*). This invasive species in many European waters is considered a delicacy among Chinese consumers. The legs and claws (appendages) containing white meat (muscle meat), but especially the meat in the body, being a mixture of brown and white meat is eaten. It was shown that particularly the brown meat (including the hepatopancreas and gonads) contains the higher contaminant levels. In the EU-legislation, the brown meat was exempted from the limits, based on a previous discussion about cadmium and more specifically the fact that brown meat of crabs is normally not consumed. In the case of mitten crabs this seems not to be correct. Since Clark et al. (2009) did not only examine crabs from the UK (Thames) but actually saw the highest levels in crabs from two Dutch rivers, it was decided to start further investigations in 2010. Based on the results, crab fishing was prohibited from the same waters that are also closed for eel fishery. In addition studies were started in the less polluted lakes but also in individual crabs, since like eel, this species migrates back to the sea in the autumn. As such, crabs caught during this season may derive from both contaminated and less polluted areas. The present paper describes the results from these investigations.

Materials and methods

Mitten crabs were collected from various locations (see Figure 1), both open and closed for fishing. Whenever possible, 25 crabs were collected. With the exception of 2010, meat from the legs and claws (white meat) and body (brown and white meat) were collected. For each pooled sample, the crab size, crab weight, and crab sexe of the individual crabs were recorded. The meat of the individual crabs was pooled, so that a composed sample was obtained per sample point. In 2011 however, the meat from the body of crabs from several locations was analysed individually to examine the variation in the levels in the brown meat. Levels in white meat from these crabs were measured in pooled samples.

Samples were analysed by GC/HRMS for dioxins and PCBs by routine methods applied at RIKILT. The meat was extracted by the method of Smedes[2]. In short 10 grams of homogenized meat was spiked with ^{13}C-labeled standards, then mixed with 10 gram hydromatrix and transfered to an ASE sample tube, which was 3 times extracted with 20 ml hexane:acetone (1:1) at 100°C and 1500 PSI. The extract was filtered over a funnel with anhydrous Na_2SO_4 and the solvent evaporated in a rotorvapor. After drying overnight at 40ºC, the fat was weight and extracted using a Powerprep system. The two obtained fractions were analysed for respectively dioxins and non-ortho dl-PCBs, and for the mono-ortho dl-PCBs and non-dioxin-like PCBs[3,4]. The performance of the methods is regularly checked by participation in PT-tests.

Results and discussion

Mitten crabs had fresh weights between 100 and 200 grams, of which around 12% was meat in the appendages and about 20% meat in the body. No attempt was made to separate the white and brown meat in the body. The fat content in the white meat from the legs was in general less than 1% (Table 1). Levels of dioxins and PCBs in crabs from the closed areas were in general lower than in those from closed areas, with the highest levels in the

Figure 1. Sampling locations of mitten crab in the Netherlands, showing the locations from 2012 (light blue), 2011 (dark blue) and 2010 (yellow). Locations include the Maas coming from the south and running towards Rotterdam, the Rijn/Waal running from east to west (Arnhem-Rotterdam, including Hollands Diep), the IJssel spliiting off from the Rijn in Arhem and running North to the Ketelmeer and then IJssel lake, and locations in the North like IJsselmeer Medemblik, Lauwersmeer and Margrietkanaal.

Table 1. Levels of dioxins, dl-PCBs (pg TEQ/g fw) and ndl-PCBs (ng/g fw) in white meat from the legs of mitten crabs from different locations and collection dates.

Location	Date	part	Fat (%)	PCDD/Fs	dl-PCBs	Sum-TEQ	Ndl-PCBs
Closed							
Ketelmeer	2011 aut	Legs	0.8	0.3	0.3	0.6	7
	2012 aut	Legs	0.4	0.4	0.3	0.8	9
	2012 aut	Legs	0.5	0.5	0.4	0.8	12
Hollands Diep	2011 aut	Legs	0.5	0.3	0.2	0.5	7
	2012 aut	Legs	0.4	0.5	0.4	0.8	13
IJssel, Deventer	2011 aut	Legs	0.4	0.3	0.5	0.8	14
Noordzeekanaal	2011 aut	Legs	0.5	0.8	0.3	1.2	8
	2012 aut	Legs	0.5	0.6	0.3	0.8	7
Rijn Lobith	2011 aut	Legs	0.4	0.3	0.4	0.7	9
Waal, Tiel	2011 aut	Legs	3.0	0.2	0.3	0.5	6
Maas-Pernis	2011 aut	Legs	0.6	0.8	0.6	1.5	19
	2012 sum	Legs	0.3	1.2	1.5	2.7	62
	2012 sum,pur	Legs	0.2	1.2	1.5	2.7	49
Open							
Lauwersmeer	2012 aut	Legs	0.4	0.2	0.1	0.3	2
Margrietkanaal	2011 aut	Legs	0.7	0.3	0.3	0.6	9
IJsselmeer (Med)	2011 aut	Legs	0.5	0.2	0.1	0.3	3
IJsselmeer (Oev)	2012 aut	Legs	0.3	0.2	0.2	0.3	1

Pur : kept in a net for several days ; Med : Medemblik, Oev : sluizen Den Oever ; aut : autumn, sum : summer

Table 2. Levels of dioxins, dl-PCBs (pg TEQ/g fw) and ndl-PCBs (ng/g fw) in meat (white and brown) from the body of mitten crabs from different open and closed locations and collection dates.

Location	Date	part	Fat (%)	PCDD/Fs	dl-PCBs	Sum-TEQ	Ndl-PCBs
Closed							
Ketelmeer	2011aut (25)*	Body	12.7	16.4	25.0	41.4	674
	2012 aut	Body	13.0	20.3	24.2	44.5	758
	2012 aut	Body	15.9	18.7	34.0	52.6	987
Hollands Diep	2011aut (25)*	Body	11.6	17.2	25.5	42.8	924
	2012 aut	Body	13.5	19.2	23.4	42.6	826
IJssel, Deventer	2011 aut	Body	18.2	22.6	58.7	81.4	1271
Noordzeekanaal	2011 aut (15)*	Body	6.1	26.8	12.2	39.1	267
	2012 aut	Body	8.2	21.8	13.5	35.4	341
Merwede	2010 sum	Body ♀	3.8	33.6	36.9	70.5	1147
	2010 aut	Body ♀	13.5	5.9	6.0	11.9	134
	2010 aut	Body♂	10.5	6.3	6.9	13.3	159
Rijn Arnhem	2010 sum	Body♂	12.7	12.2	19.0	31.2	594
Rijn Lobith	2011 aut (14)	Body	7.0	8.2	7.8	16.0	233
Waal, Tiel	2011 aut (3)*	Body	8.1	18.4	41.4	59.8	858
Maas Kessel	2010 sum	Body ♀	1.4	14.9	15.8	30.7	395
	2010 sum	Body♂	1.9	22.9	25.7	48.6	734
Maas-Pernis	2011 aut (25)*	Body	7.0	32.4	35.1	67.4	1151
	2012 sum	Body	3.6	19.0	26.2	45.2	934
	2012 sum, pur	Body	3.6	21.8	30.3	52.0	924
Open							
Lauwersmeer	2010 aut	Body ♀	18.6	5.6	4.1	9.7	60
	2010 aut	Body♂	14.1	4.6	3.6	8.2	52
	2012 aut	Body	8.2	5.7	4.1	9.8	79
Margrietkanaal	2011 aut	Body	10.1	3.9	5.2	9.1	107
IJsselmeer (Med)	2011 aut	Body	17.1	9.5	11.1	20.5	287
IJsselmeer (Oev)	2012 aut	Body	15.1	7.1	6.1	13.3	117

Pur : kept in a net for several days ; Med : Medemblik, Oev : sluizen Den Oever ; aut : autumn, sum : summer
* mean of individual results from 3-25 crabs (n)

Maas near Rotterdam (Pernis). None of the samples exceeded the MLs for dioxins (3.5 pg TEQ/g), dioxins plus dl-PCBs (6.5 pg TEQ/g), or ndl-PCBs (75 ng/g).

A major question is of course, whether the observed levels in the crab from the closed areas present a potential risk, considering the reported rather low consumption of mitten crab. In practice meat from the body and potentially the legs are consumed. Based on one location (Ketelmeer, 2011), where 25 individual crabs were dissected and meat in legs and body collected as accurate as possible, an average for contribution of meat from body and legs to the total weight was calculated, being respectively 15.1 and 6.6% and an average ratio between the two of 2.8. A portion size of 100 grams per meal seems a reasonable amount (3-4 crabs). The average sum-TEQ level in the body meat is 43 pg TEQ/g, the average in the legs 1.1 pg TEQ/g, corresponding to an absolute amount of 3.2 ng TEQ based on the ratio of 2.8. The legs contribute for less than 1% to this intake. Based on a body weight of 65 kg this corresponds with an additional exposure of 49 pg TEQ/kg bw which is 3.5 times the TWI of 14 pg TEQ/kg bw used within the EU or 0.7 times the TMI established by JECFA. For consumers with already a high exposure, this intake could certainly be significant. However, the overall effect on the body burden might be relatively small, especially when mitten crab is consumed only a few times a year. A remaining issue is whether such an incidental intake could actually result in a temporary increase in the blood levels, and as such an increased exposure during a critical phase in the development. This is still an unresolved issue with respect to the risk assessment of dioxins and dl-PCBs.

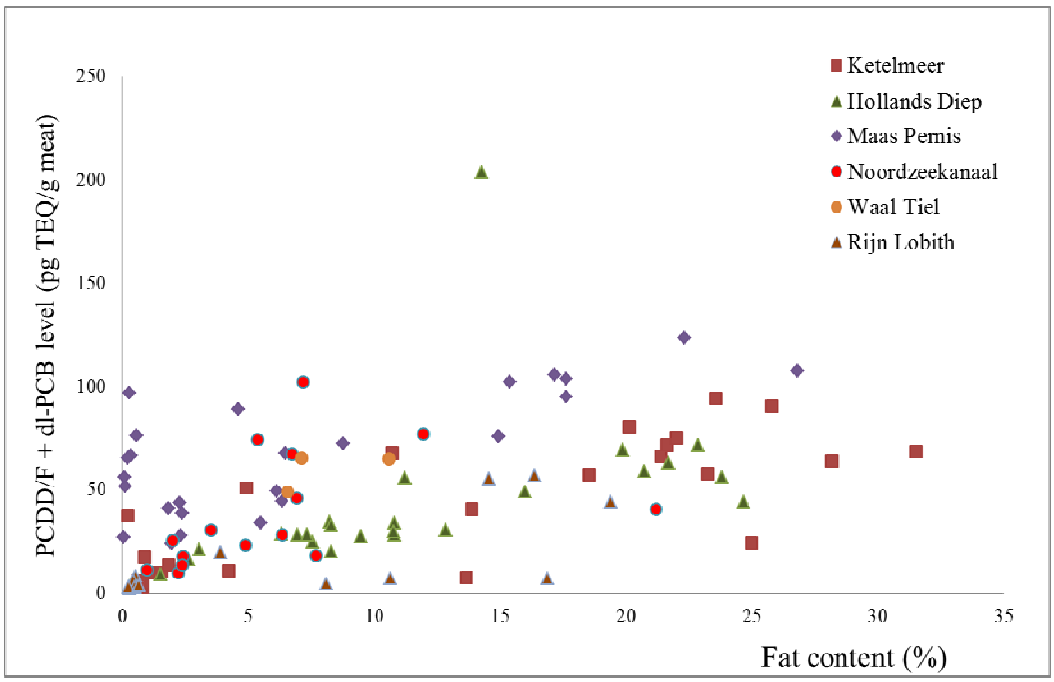

Figure 2. Levels of PCDD/Fs and dl-PCBs in 107 individually analyzed mitten crabs from 6 locations in the closed fishing areas, as compared to the fat content.

Conclusions

Mitten crabs caught in large rivers and connecting canals in the Netherlands contain rather high levels of dioxins and PCBs in the meat from the body. These levels comprise a potential risk to the consumer, especially when consumed frequently. Crabs caught in the lakes in the North of the Netherland contain in general much lower levels.

Acknowledgements

The study was financed by the Dutch Ministry of Economics. The authors would like to acknowledge the help of the people collecting and dissecting the crabs at IMARES and the technicians at RIKILT.

References

1. Clark PF, Mortimer DN, Law RJ, Averns JM, Cohen BA , Wood D, Rose MD, Fernandes AR, Rainbow P. (2009) *Environ. Sci. Technol.* 43: 1624–29
2. Smedes F (1999) *Analyst* 124, 1711-18.
3. Tuinstra LGMTh, Traag WA, Van Rhijn JA, Van de Spreng PF (1994) *Chemosphere* 29, 1859-75.
4. Hoogenboom LAP, Van Eijkeren JCH, Zeilmaker MJ, Mengelers MJB, Herbes R, Immerzeel J, Traag WA (2007) *Chemosphere*, 68, 814-23.