

**PCDD/Fs and PCBs in Aquatic Organisms from the Venice Lagoon: Spatial  
and Species Variations**

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**Introduction**

The Venice Lagoon supports a large fishing industry, harvesting shellfish, fin fish and crustacea. The immediate vicinity of the Lagoon is also home to almost half a million people, as well as a major chemical industrial zone, oil refineries, incinerators, power stations, a large shipping port and an international airport. The potential impact on the fishing of these activities is of considerable concern. A survey was commissioned to assess the PCDD/F and PCB contamination in sediments and organisms from the Lagoon, which would additionally allow an estimation to be made of the contribution fish make to the dietary exposure of the local population to these contaminants. This paper presents the results for the organisms. Other elements of this survey are reported elsewhere in these volumes<sup>(1-3)</sup>.

**Materials**

49 samples were taken from across the Lagoon, excluding the Marghera Industrial Zone and the city of Venice. Two shellfish species; *Tapes philippinarum* (n=22) and *Mytilus galloprovincialis* (n=6), two fin fish species; *Zosterisessor ophiocephalus* (n=8) and *Chelon labrosus* (n=4), and one crustacean; *Carcinus mediterraneus* (n=9) were sampled. A shellfish sample was also collected from outside the Lagoon, in the Adriatic Sea, and another from a depuration plant.

*C. labrosus* were taken from fish ponds and filleted before freezing. Six of the *C. mediterraneus* samples were shelled before freezing, the other three were not as they were in the moult phase at the time of sampling. This did not appear to have any effect on the results. *T. philippinarum* samples were shelled by dropping them in liquid nitrogen after standing for several hours in oxygenated water from their sampling site to allow expulsion of coarse sediment. *M. galloprovincialis* were opened manually. Samples were frozen to -20°C after processing, for storage and transport.

**Methods**

A portion of the thawed sample was spiked with 20 <sup>13</sup>C<sub>12</sub>-labeled PCDD/Fs and 9 <sup>13</sup>C<sub>12</sub>-labeled PCBs 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<sub>2</sub>SO<sub>4</sub>, adsorption chromatography with acid treated and base treated silica gel and GPC. Fractionation of PCDD/Fs, nonortho-PCBs and orthochlorinated PCBs were fractionated using Alumina B Super-1 (ICN Biomedicals, Eschwege, Germany).

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PCDD/Fs were quantified by HRGC/HRMS (HP 6890/Micromass Autospec Ultima) using HP5-ms and SP2331 capillary columns. Non-ortho PCBs were quantified by HRGC/HRMS using a HP5-ms column, orthochlorinated PCBs were quantified by HRGC/LRMS (Fisons GC8000/Fisons MD800) using an Ultra 2 column.

### Results and Discussion

Table 1 summarises the results for each of the five species analysed. The information provides a slightly clouded view of the interspecies variability of contamination because some species were only sampled from less polluted areas of the Lagoon, as described from analysis of sediment samples<sup>(1)</sup>, whereas samples of other species were more representatively dispersed.

**Table 1**

Summary of results for five species, reported on a wet weight basis.

TEQ Ratios are % contribution of PCDD/Fs : non-orthoPCBs : orthochloroPCBs to the I-TEQ

Species	<b>M. gall.</b> mean range	<b>T. phill.</b> mean range	<b>C. labrosus</b> mean range	<b>Z. ophio.</b> mean range	<b>C. medit.</b> mean range
ΣPCDD/F pg/g	<b>5.9</b> 2-11	<b>16</b> 1-89	<b>2.3</b> 1-4	<b>2.5</b> 1-10	<b>33</b> 7-80
ΣPCB ng/g	<b>4.7</b> 2-7	<b>5.2</b> 1-13	<b>13</b> 10-16	<b>59</b> 16-133	<b>133</b> 14-719
I-TEQ pg/g	<b>0.3</b> 0.2-0.5	<b>0.6</b> 0.1-1.8	<b>1.3</b> 0.8-1.7	<b>3.3</b> 1.3-6.3	<b>7</b> 1-28
TEQ Ratio	40:40:20	50:35:15	35:45:20	15:45:40	25:45:30

### Shellfish

Both shellfish species appeared to behave similarly in their contaminant uptake and storage. All *M. galloprovincialis* samples were from sites of low PCDD/F and PCB sediment burden and their concentrations were congruent with those found in *T. philipinarum* samples from similar locations. Furthermore, the homologue profiles of the two species were similar (Figure 1), as were their congener patterns (not shown). The relative concentrations of all the shellfish samples follow the contamination map observed for sediments<sup>(1)</sup>, with higher levels encountered in samples from near Porto Marghera, Fusina, the Marghera-Malamocco Canal and around an outflow of the river Brenta. The remainder of the Lagoon being broadly clean.

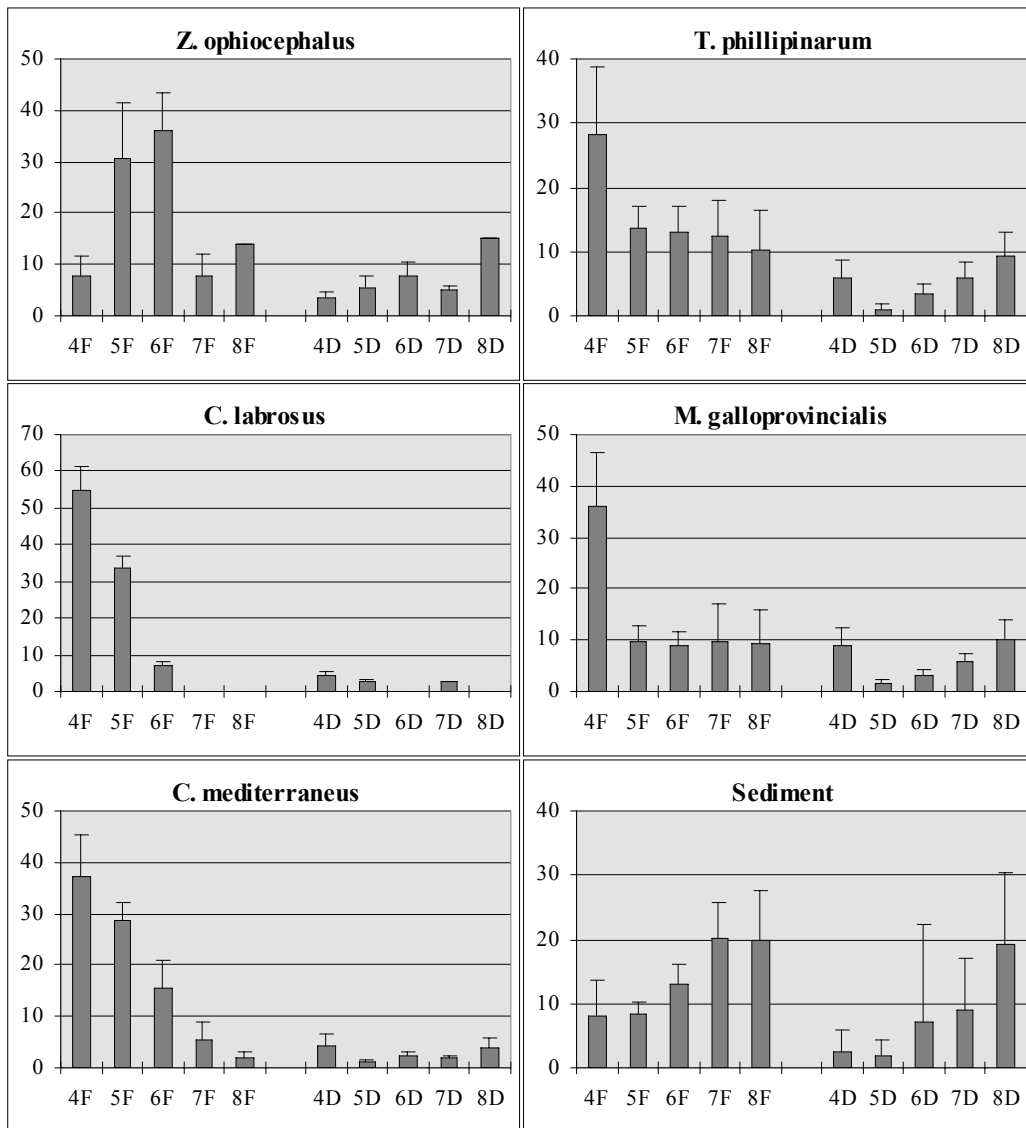
Interestingly, a single *M. galloprovincialis* sample taken from the Adriatic Sea gave higher values of both PCDD/Fs and PCBs (14pg/g and 20 ng/g respectively) than any of this species from within the Lagoon. A sample of *T. philipinarum* taken from a depuration plant contained the highest concentrations of both PCDD/Fs and PCBs (140pg/g and 35ng/g respectively) found for this species.

Comparison of the PCDD/F homologue profiles of the shellfish with those observed in Venice Lagoon sediments (Figure 1) indicate a general uptake with a gradual bias towards lower chlorinated compounds. A spatially defined variation of the OCDF/OCDD ratio observed in sediments<sup>(1)</sup> was preserved, although less marked, in the shellfish.

### Figure 1

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Mean PCDD/F homologue profiles for five species and sediment samples from the Venice Lagoon, with error bars representing one standard deviation.



*Fin Fish*

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Only four *C. labrosus* samples were analysed, all from unpolluted sites of the Lagoon. Even so the I-TEQ values were higher than for the shellfish. This is equally due to increased PCB concentrations (ca 5 times the  $\Sigma$ PCB in shellfish from similar sites) and the fact that the entire PCDD/F burden is made up of 2,3,7,8-substituted congeners.

Eight *Z. ophiocephalus* samples from a variety of locations were analysed. The concentrations of both PCDD/Fs and PCBs are similar to those found in *C. labrosus* from proximate locations. Samples from around Porto Marghera, the Brenta river outflow and Chioggia contained higher levels relative to samples from other parts of the Lagoon. Whereas the total concentrations of the two fin fish species are similar, there are marked differences in their patterns of PCDD/F homologues (Figure 1) and congeners (not shown). In addition the influence of orthochlorinated PCBs on the I-TEQ for *Z. ophiocephalus* is considerably larger than was observed for *C. labrosus*. This could be due to differences in dietary exposure, age, metabolism and contaminant exchange with the surrounding water.

### Crabs

Nine *C. mediterraneus* samples from a variety of locations were analysed. Again, the relative concentrations of the samples reflected their location, although their contamination was high relative to other species even in the less polluted parts of the Lagoon. *C. mediterraneus* matched *Z. ophiocephalus* for PCB concentrations and exceeded all species in PCDD/F concentrations. One sample from around an outflow of the river Brenta contained abnormally high PCB concentrations ( $\Sigma$ PCB=719ng/g) giving rise to an I-TEQ of 28pg/g. Excluding this one sample, the mean values of PCBs (and with them the I-TEQs) for the remaining eight samples halved.

### General

There is a complex relationship between the concentrations of PCB/DD/DFs in organisms and the local sediment, which is highly species dependent. Samples of different species from the same location have distinct congener patterns, homologue patterns and ratios of  $\Sigma$ PCB: $\Sigma$ PCDD/F. The spatial variation of PCDD/F and PCB contamination for each species reflected the sediment concentrations, showing specific areas of elevated contamination while large parts of the Lagoon are seen to be clean.

### Acknowledgments

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