# Caribbean Coastal Pollution Project (CCPP)

## Monitoring Persistent Organic Pollutants (POPs) in White Grunt from the Wider Caribbean Region: A Preliminary Analysis

## Interim Report

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## **Introduction**:

Most Caribbean nations are signatories to the Stockholm Convention, which aims to reduce and mitigate contamination from selected persistent organic pollutants (POPs). However, there is little capacity within the Caribbean to analyze and monitor POPs in humans, fish and wildlife and the abiotic environment. Studies of POPs contamination in the Caribbean coastal environment have been limited to a few projects that have detected localized sources of contamination (Coat et al., 2006; Norena-Barroso et al., 2004). However, the Caribbean basin may be influenced by inputs of POPs at a regional scale from large continental rivers, such as the Orinoco River to the southeast and the three major rivers that enter the Gulf of Honduras to the southwest. Finally, atmospheric deposition of POPs to the Caribbean may be changing over time as a result of climate change (Semeena et al., 2006). This project was initiated to develop capacity within the Caribbean for monitoring POPs in the coastal environment and to gather data on the distribution of POPs in marine resources throughout the wider Caribbean region.

Through discussions at the first and second planning meetings for the Caribbean Coastal Pollution Project, the partner countries agreed to collect white grunt (*Haemulon plumieri*) for an initial survey to monitor the levels of POPs in fish tissues from the Wider Caribbean Region. It was agreed that each country would collect at least 3 fish (where available) at an average of 6 sites per country. Ideally at each site, the fish sampled would be 300 – 500 g in weight. If no white grunt were present, another benthic-feeding, non-pelagic fish could be substituted. The rationale for selecting the white grunt for the monitoring study was that this species: i) is widely distributed across the Caribbean, ii) is a reef fish that is relatively philopatric, and so reflects contamination at a discrete site and, iii) has been monitored previously for POPs in the western Caribbean through the MBRS program. It was decided that muscle tissue should be analyzed because of the relative ease in collecting dorsal muscle (as opposed to liver tissue), and because analysis of muscle can be related to risk analysis for the consumption of POPs in fish. It was acknowledged that there are drawbacks to using white grunt for a monitoring study of POPs. This species of fish is not high in trophic position, and therefore, is expected to show little effect of biomagnifications through food webs. It also has low lipid content in its tissue, and therefore, is not likely to accumulate lipophilic contaminants (i.e. POPs) to high concentrations.

Following the inter-laboratory comparison exercise in the summer of 2009, the two regional laboratories began to prepare white grunt tissues for analysis. This report provides an overview of the results generated from the analysis of a relatively small number of white grunt that were collected from coastal waters off of Belize (n=26), Jamaica (n=7), Trinidad and Tobago (n=6) and St. Lucia (n=5).

**Figure 1:** Sites in the wider Caribbean region where white grunt were sampled for analysis by the regional laboratories at UWI Mona (Jamaica) and CINVESTAV (Mexico).

## Methods:

White grunt were collected by the 8 partner countries from several sites in the wider Caribbean region (Figure 1) and were shipped to the regional laboratories at UWI Mona in Jamaica (i.e. fish from Jamaica, Trinidad and Tobago, St. Lucia), and at CINVESTAV in Mexico (i.e. fish from Belize, Mexico, Guatemala, Honduras and the Dominican Republic). Dorsal muscle tissues of white grunt (4-5 g) were spiked with an internal standard (PCB 30) and extracted using cold column extraction at UWI Mona, and by another solvent extraction method at CINVESTAV. Because of the low lipid content of the white grunt tissues (i.e. <0.5%), it was not necessary to remove lipid using gel permeation chromatography (GPC), so tissues were cleaned up directly using florisil column chromatography. Three fractions were generated by florisil chromatography: i) Fraction 1 containing primarily PCBs, and ii) Fractions II and III containing organochlorine compounds.

**Table 1:** List of target compounds analyzed in samples of white grunt dorsal muscle.

**Organochlorine compounds**

- ∑ chlordanes: *cis*-chlordane, *trans*-chlordane, *oxy*-chlordane
- ∑ DDTs: o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE, o,p'-DDT, p,p'-DDT
- ∑ HCHs : α-HCH, ß-HCH, γ-HCH
- Aldrin
- Dieldrin
- Endrin
- Heptachlor
- *cis*-heptachlor epoxide
- *trans*-heptachlor epoxide
- Mirex
- HCB

**PCBs:**

Congener numbers 17/18, 28/31, 33, 44, 49, 52, 70, 74, 82/151, 87, 66/95, 99, 101, 105/132, 110, 118, 128, 138,149,153, 156/171, 158, 170, 177, 180, 183, 187,191, 194,195/208,199/201, 205, 206, 209

**PBDEs:**

Congener numbers 3, 7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 123, 138, 153, 154, 183, 184, 196, 197

These florisil fractions were analyzed for the PCB congeners and organochlorine compounds listed in Table 1 by gas chromatography using an Agilent 7890 gas chromatograph with an electron capture detector (i.e. GC-ECD). Sample blanks and a standard reference material (SRM) were extracted with each batch of 3-6 white grunt samples. In addition, a limited number of samples of white grunt collected from Belize (n=5) were analyzed for concentrations of selected congeners of polybrominated diphenyl ethers (PBDEs). Fraction II from the florisil cleanup step was analyzed by gas chromatography using an Agilent 7890 gas chromatograph with a mass selective detector (i.e. GC-MSD). Analysis of the PBDE congeners listed in Table 1 was conducted at the Great Lakes Institute for Environmental Research (GLIER) at the University of Windsor.

## Results and Discussion:

### PCBs:

Several PCB congeners were detected in the extracts from white grunt muscle tissue. As illustrated in Figure 2 for fish collected at four locations in the Caribbean, the congener patterns were dominated by PCBs with a low degree of chlorination (i.e. tri- and tetra-chlorobiphenyl ethers). This contrasts with the distribution of more highly chlorinated PCBs that dominate the congener pattern in fish from the Great Lakes (Figure 3a), and from fish in other regions of the world where there have historically been direct inputs of PCBs into the environment. The pattern of PCB congeners seen in white grunt form the greater Caribbean region indicates that the source of contamination is atmospheric deposition, since the less chlorinated PCB compounds are subject to transport in the atmosphere. Similar congener profiles were noted in the tissues of elephant seals from the Antarctic region, where atmospheric transport is the only possible source of contamination (Miranda Filho et al., 2007).

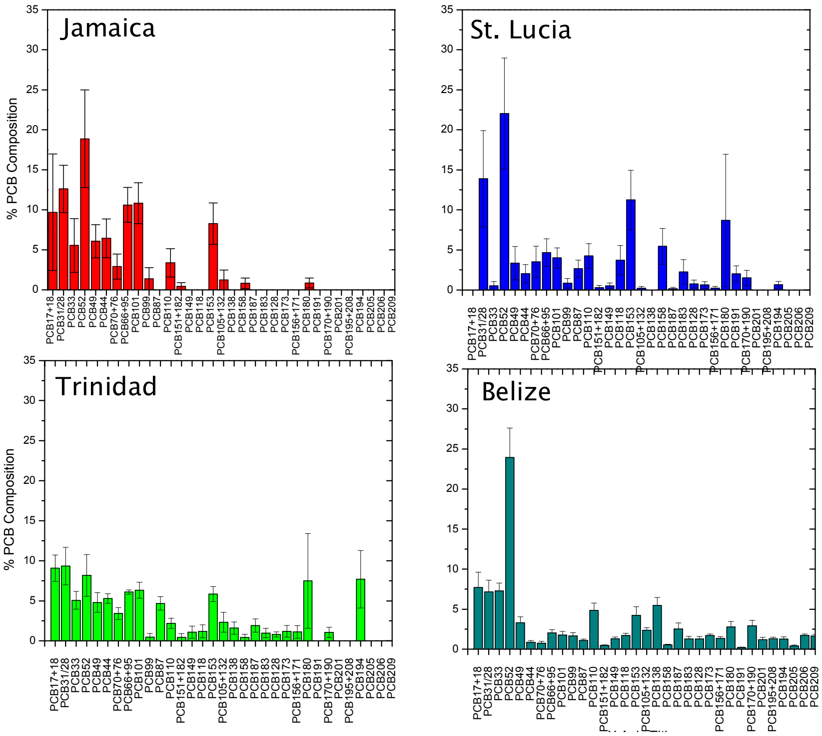

**Figure 2:** Congener patterns (% of total) for PCBs detected in samples of white grunt collected in 2009 from coastal waters in Jamaica, St. Lucia, Trinidad and Tobago, and Belize.

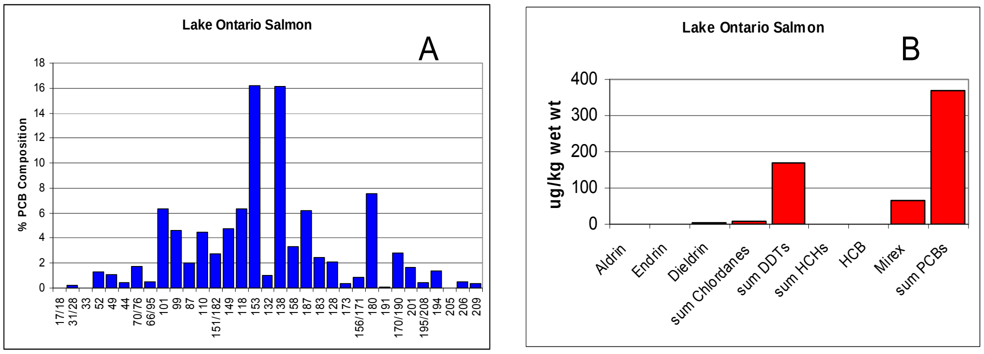

**Figure 3:** PCB congener patterns (A) and concentrations of organochlorine compounds (B) in adult female Chinook salmon (introduced) collected from Lake Ontario in 2001. Data are from O'Toole et al. (2006).

The total PCB concentrations (i.e. sum of all congeners) in the muscle of white grunt were all less than 10 µg/kg wet weight, and these concentrations were relatively consistent across all four countries included in this preliminary analysis (Figure 4). For comparison, the average total PCB concentration reported by O"Toole et al. (2006) for female Chinook salmon from Lake Ontario (data illustrated in Figure 3) was 387 µg/kg wet weight. Note that these concentrations are below the most restrictive fish consumption advisory for PCBs reported in the USA of 50 µg/kg wet weight. The Health Canada fish consumption advisory for PCBs is 2,000 µg/kg wet weight. Overall, these data indicate that PCB contamination in white grunt is not likely to be a health risk to fish consumers in these four Caribbean countries. The very low lipid content of the muscle tissues for this fish species contributed to the low concentrations of these lipophilic compounds. Also, it appears that there are no appreciable point sources in the four countries and that PCBs are being transported to the region by atmospheric deposition. However, it must be emphasized that these are only preliminary data from a small number of fish collected from four of the eight partner countries.

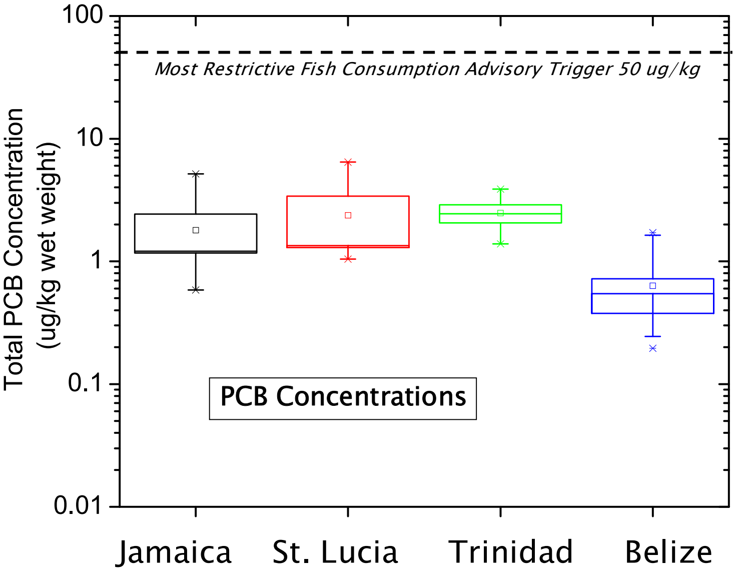

**Figure 4:** Mean and range of concentrations of total PCBs detected in white grunt collected from four partner countries in 2009. The line at the top of the figure shows the most restrictive fish consumption advisory for PCBs in the USA.

**Organochlorine compounds:**

Several of the organochlorine target compounds were detected at concentrations <10 μg/kg wet weight in samples of muscle from white grunt collected in Jamaica, Trinidad and Tobago, Belize and St. Lucia. As illustrated in Figure 5, the relative patterns of contamination in white grunt appeared to vary between the countries, with chlordane and HCH compounds dominating in fish from Jamaica, Trinidad and Tobago and St. Lucia, and dieldrin and DDT compounds being more important in samples from Belize. However, because of the high variability in the distribution of dieldrin in white grunt collected off the coast of Belize (Figure 5), these analyses should be confirmed by GC-MS. The differences between countries may reflect geographical differences in the use or the atmospheric deposition of POPs between the western and eastern Caribbean, but a more complete data set is required to evaluate these trends.

Because of their recent or ongoing use for the control of insect pests, high concentration of HCHs and chlordane compounds have been detected in marine biota from tropical and subtropical countries in both the western and eastern hemispheres (Imo et al., 2008; Minh et al., 2006; Bayen et al., 2005; Norena-Barroso et al., 2004). Dieldrin has been detected in marine biota from other developing countries in the western hemisphere, such as Argentina (Menone et al., 2001), but the origin of this compound could be from the widespread use of the related insecticide, aldrin, which is rapidly transformed in the environment to dieldrin. Rainwater et al (2007) detected dieldrin, as well as DDE, DDT, endrin and methoxychlor in the caudal scutes of crocodiles sampled off the coast of Belize. Total DDT was not present at high concentrations in the white grunt samples (Figure 5), and p,p'-DDE was the predominant compound detected from this class, which reflects transformation from DDT that was used at some time in the past and not contamination from recent use of this insecticide. In contrast, Figure 3b shows the relative concentrations of organochlorine pesticides in salmon from Lake Ontario, illustrating the high concentrations of total DDT in fish from this region, where there were historically high direct inputs of the insecticide.

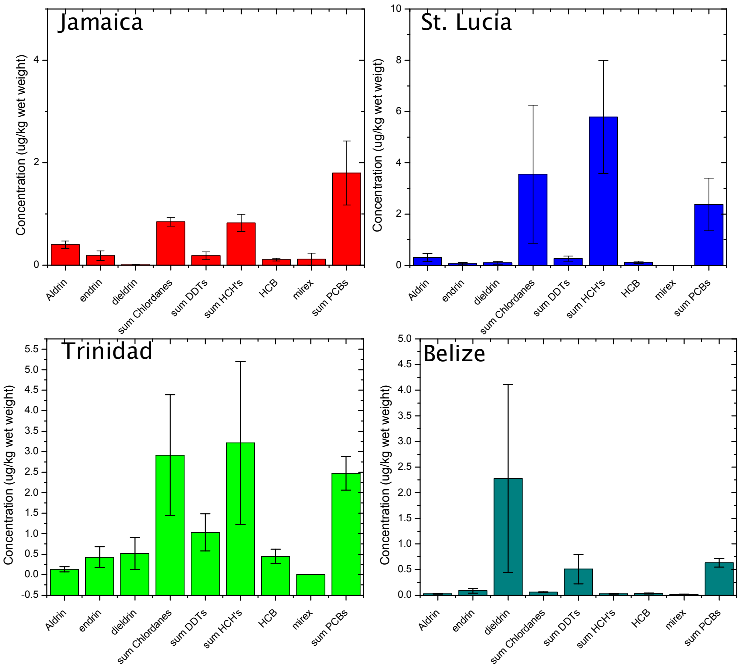

**Figure 5:** Mean and standard deviation of concentrations of organochlorine compounds (µg/kg wet weight) detected in muscle tissue of white grunt collected in 2009 from coastal waters in Jamaica, St. Lucia, Trinidad and Tobago, and Belize.

**Table 2:** Mean and maximum concentrations and fish consumption advisory values (µg/kg wet weight) for the organochlorine compounds and total PCBs detected in white grunt muscle. The advisory levels reported are for the most stringent values from the USA, and where applicable, for higher values from Health Canada.

| Chemical | Jamaica | St. Lucia | Trinidad | Belize | **Advisory Trigger** |
|---|---|---|---|---|---|
| Aldrin | 0.4±0.1<br>0.7 max | 0.3±0.2<br>0.9 max | 0.1±0.06<br>0.4 max | 0.03±0.01<br>0.1 max | **300** |
| Endrin | 0.2±0.1<br>0.6 max | 0.06±0.04<br>0.2 max | 0.4±0.3<br>1.4 max | 0.1±0.05<br>1.2 max | **300** |
| Dieldrin | <0.01<br>0.02 max | 0.1±0.05<br>0.3 max | 0.5±0.4<br>2.1 max | 2.7±1.8<br>**49 max** | **300** |
| ∑Chlordanes + heptachlor | 0.8±0.1<br>1.2 max | 3.6±2.7<br>14.3 max | 2.9±1.5<br>8.7 max | 0.06±0.01<br>0.1 max | **300, 5620** |
| ∑ DDTs | 0.2±0.08<br>0.6 max | 0.3±0.1<br>0.6 max | 1.0±0.5<br>2.6 max | 0.5±0.3<br>7.9 max | **5000** |
| ∑ HCHs | 0.8±0.2<br>1.4 max | 5.8±2.2<br>12.7 max | 3.2±2.0<br>11.1 max | 0.03±0.01<br>0.2 max | **100, 300** |
| HCB | 0.1±0.03<br>0.2 max | 0.1±0.04<br>0.2 max | 0.4±0.2<br>1.1 max | 0.03±0.01<br>0.3 max | **10*, 100** |
| ∑PCBs | 1.8±0.6<br>5.1 max | 2.4±1.0<br>6.4 max | 2.5±0.4<br>3.9 max | 0.6±0.1<br>1.7 max | **50, 2000** |

The summary data shown in Table 2 shows that none of the concentrations of these compounds approach the most stringent fish consumption advisory levels from the USA, or in some cases, the higher advisories from Health Canada. Therefore, there are not likely to be any health impacts from the consumption of white grunt from these four regions of the Caribbean.

**PBDEs:**

Analysis of samples prepared from five white grunt that were collected off the coast of Belize for PBDEs revealed that several congeners were present at detectable concentrations in the muscle tissue, including congeners 47, 77, 99, 85, 126, 153 and 184 (Figure 6). The mean and maximum total PBDE concentrations were 0.84 and 1.4 µg/kg wet weight, respectively, or 284 and 452 µg/g lipid weight, respectively. The concentrations on a lipid normalized basis are similar to fish from other regions of the world, and the congener pattern is the same as has been reported for marine fish from regions in the Pacific, North America and Europe ( (Minh et al., 2006; Brown et al., 2006; Ueno et al., 2004; Boon et al., 2002; Dodder et al., 2002).

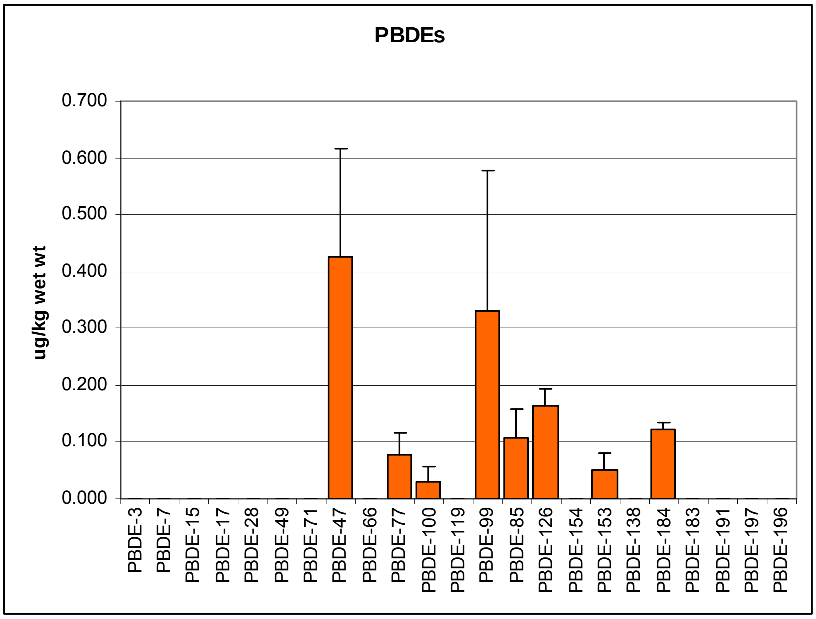

**Figure 6:** Mean concentrations of PBDE congeners in white grunt (n=5) collected off the coast of Belize.

## Conclusions:

Overall, these data indicate that contamination by POPs in white grunt is not likely to be a health risk to fish consumers in the four Caribbean countries from which the samples were collected. However, it must be emphasized that these are only preliminary data from a small number of fish collected from four of the eight partner countries. These preliminary data do indicate that atmospheric sources of contamination may be responsible for contamination by some compounds (e.g. PCBs), but point sources may contribute to contamination by some pesticides (e.g. dieldrin in fish from Belize). More data are required to determine whether there are geographic trends in the distribution of POPs contamination in these fish.

It would be useful to determine the distribution of POPs in biota from the entire food web in the Caribbean, including fish species that have a higher trophic status and/or have a high lipid content in their tissues (Ueno et al., 2004). Other food web studies have shown that marine crustaceans can accumulate relatively high concentrations of POPs, including crabs (Bayen et al., 2005; Menone et al., 2001) and spiny lobster (Coat et al., 2006). Future work should also focus on determining whether there is contamination of white grunt and other marine biota from the wider Caribbean region by persistent organic pollutants that were recently added to the Stockholm Convention list (e.g. PBDEs, PFOS, chlordecone), and persistent and toxic substances of emerging interest (e.g. mercury, synthetic musks, “new” brominated flame retardants). However, it must be pointed out that this report contains the only data that are currently available on POPs contamination in fish distributed across the wider Caribbean region, and therefore, are a valuable contribution to the literature on contamination of marine resources.

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