PERSISTENT ORGANIC POLLUTANTS IN OCEANIA: ANALYTICAL CAPACITY FOR TESTING BASIC POP CHEMICALS IN PACIFIC ISLANDS

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Introduction
Persistent organic pollutants (POPs) are a group of toxic chemical compounds that are ubiquitous and found in the environment and humans worldwide. POPs have long half-lives in soil, sediments, air or biota. The Stockholm Convention is a legal treaty that aims to rid the world of such toxic chemicals and a number of countries are signatories and accept to either ban or reduce production and release of POPs. Each county has its own National Implementation Plan (NIP) that determines how the country will attempt to meet its commitments under the Stockholm Convention. Monitoring of POPs in the country’s population and environment is an important part of the Stockholm Convention. A Global Monitoring Plan (GMP) has been developed to monitor POPs in ambient air and humans. In the Pacific Island Region (PIR) a number of countries are signatories to the Stockholm Convention, however, there has been very little scientific research on POPs. It is noteworthy that there has been no manufacture of POP chemicals in the PIR, although many of them are known to have been used in the region. Most of the concentration data on POPs from the PIR is on abiotic samples, including ambient air, surface water, soil and sediments and few on biota like fish. There is very little information on POPs levels in humans and the only recent studies on populations were from the World Health Organisation (WHO). The WHO has an ongoing program on monitoring contaminant levels in human breast milk. Fiji first took part in this program in the 2002 round and the study reported the presence of a range of POPs, including organochlorine pesticides as well as the unintentionally produced dioxin-like POPs. With the signing of the Stockholm Convention on POPs and the development of global monitoring programs, there is an increased need for developing countries to determine polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). The knowledge gaps on POPs in the PIR can also be attributed to a lack of a specialized analytical facility in the region that is able to generate reliable data on POPs. In this paper we give a brief overview on the development of analytical capacity to test basic POPs in a regional laboratory and investigate concentration data for human breast milk samples from the PIR.

Materials and methods
Approximately 5 – 6 g of composite human breast milk samples (n=5) were soxhlet extracted for a minimum of 16 hours using 175 mL of hexane: acetone (3:1 v/v). For each gram of wet sample, 3 g of anhydrous sodium sulphate was added to dry the sample. Clean-up for samples was done on an alumina column, while fractionation was done over silica column. Analysis for organochlorine pesticides and PCBs was carried out at the Institute of Applied Sciences (IAS), an ISO17025 accredited laboratory using methods adopted from the Institute for Environmental Studies (IVM) analytical methods for UNEP Chemicals POPs Training Project (i.e Internal standard technique and quantification using a high resolution gas chromatograph with a micro-ECD). Analytes of interest targeted in this study included the organochlorine pesticides (including DDTs, HCHs and Drins) and the only recent studies on populations were from the World Health Organisation (WHO). The WHO has an ongoing program on monitoring contaminant levels in human breast milk. Fiji first took part in this program in the 2002 round and the study reported the presence of a range of POPs, including organochlorine pesticides as well as the unintentionally produced dioxin-like POPs. With the signing of the Stockholm Convention on POPs and the development of global monitoring programs, there is an increased need for developing countries to determine polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). The knowledge gaps on POPs in the PIR can also be attributed to a lack of a specialized analytical facility in the region that is able to generate reliable data on POPs. In this paper we give a brief overview on the development of analytical capacity to test basic POPs in a regional laboratory and investigate concentration data for human breast milk samples from the PIR.

Results and discussion
Analytical capacity for trace level testing of POPs in human milk requires specific skills and instrumentation. The Institute of Applied Sciences laboratory of the University of the South Pacific took part in a UNEP POPs Analytical Capacity Building project under which specific training was provided by IVM, a UNEP expert laboratory for POPs. Training of staff at IAS laboratory in Fiji included alumina clean-up for fat removal and
fractionation of samples on silica column. Furthermore, to attain lower detection limits a Gas Chromatograph (GC) with a micro–electron capture detector (µ-ECD) was purchased from Agilent Technologies. To avoid contamination the new GC was dedicated exclusively to POP analysis. It must be stressed that getting reliable concentration data on basic POPs was also possible through QA/QC measures such as the use of internal standards.

Human milk samples from five Pacific Island Countries (PICs) were analysed for basic POP chemicals. It is noteworthy that concentration data are reported on a wet weight (ww) basis for testing done at IAS laboratory. A number of contaminants including DDTs (total of o,p’-DDT, p,p’-DDT, o,p’-DDD, p,p’-DDE, p,p’-DDE), HCHs (total for a-HCH, β-HCH, γ-HCH, δ-HCH), Drins (aldrin, endrin and dieldrin) and indicator PCBs (congeners 28, 52, 101, 118,153, 138, 180) were detected. The recoveries for internal standards were in a range of 73-119%. The concentrations of ∑DDTs (total of o,p’-DDT, p,p’-DDT, o,p’-DDD, p,p’-DDD, o,p’-DDE, p,p’-DDE) found in human breast milk samples from PICs are summarized in Table 1. The concentration range for ∑DDTs detected in human milk samples from PICs was 4.2 to 28.5 ng g⁻¹ ww (SD=10.1; median=14.5). The current study on human milk from PICs indicates that p,p’-DDE is found as the dominant contributor to ∑DDTs.

The concentrations for ∑HCHs (total for α-HCH, β-HCH, γ-HCH, δ-HCH) found in human milk samples from PICs are also summarized in Table 1. The concentration range for ∑HCHs detected in human milk samples from PICs was 0.2 to 2.1 ng g⁻¹ ww (SD = 0.8; median = 0.8).

<table>
<thead>
<tr>
<th>POPs</th>
<th>Solomon Islands</th>
<th>Fiji</th>
<th>Tuvalu</th>
<th>Kiribati</th>
<th>Samoa</th>
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</thead>
<tbody>
<tr>
<td>∑DDTs</td>
<td>28.5</td>
<td>4.2</td>
<td>5.3</td>
<td>10.7</td>
<td>18.3</td>
</tr>
<tr>
<td>∑HCHs</td>
<td>2.1</td>
<td>0.6</td>
<td>0.9</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>∑Drins</td>
<td>9.6</td>
<td>2.3</td>
<td>3.4</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>∑PCB₇s</td>
<td>0.2</td>
<td>3.5</td>
<td>0.7</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 1 also gives the concentration range for ∑Drins (total of aldrin, dieldrin, and endrin) in the human milk samples. The concentration range for ∑Drins was 0.2 to 9.6 ng g⁻¹ ww (SD = 3.9; median = 2.9). The results indicate that dieldrin is most widely detected of the Drins in human milk samples from the PICs. The concentrations for ∑PCB₇s (total of PCBs 28, 52,101,118,153,138,180) found in human milk from PICs are summarized in Table 1. The concentration range for ∑PCB₇s was 0.1 to 3.5 ng g⁻¹ ww (SD = 1.5; median = 0.5).

It is also noteworthy that a number of newly added POP chemicals added during the 4th meeting of the Conference of the Parties (COP4) in 2009 were also detected but in low concentrations in composite human milk samples tested at the IAS laboratory. This included β-HCH, α-Endosulfan, pentachlorobiphenyl (PentaCB), cis-heptachloropoxide (cis-HeptEpox) and trans-heptachloropoxide (trans-HeptEpox) (Table 2). From the five new POPs tested, β-HCH and α-Endosulfan concentrations were found in a range of 0.5 to 0.7 ng g⁻¹ ww while PentaCB, cis-HeptEpox and trans-HeptEpox were detected in a lower concentration range of 0.01 to 0.03 ng g⁻¹ ww.

<table>
<thead>
<tr>
<th>Sum basic POPs</th>
<th>CompM1</th>
<th>CompM2</th>
<th>CompM3</th>
<th>Blank</th>
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</thead>
<tbody>
<tr>
<td>β-HCH</td>
<td>0.5</td>
<td>0.7</td>
<td>0.5</td>
<td>0.01</td>
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<tr>
<td>α-Endosulfan</td>
<td>0.7</td>
<td>0.5</td>
<td>0.7</td>
<td>0.01</td>
</tr>
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<td>PentaCB</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
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<tr>
<td>cis-HeptEpox</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>trans-HeptEpox</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Overall, it can be seen that ∑DDTs are still the dominant POP chemical found in human breast milk samples from the PICs with a high contribution from p,p' -DDE towards ∑DDTs. Furthermore, it is significant that POP concentrations in human milk from PICs (except those from the Solomon Islands) are low in comparison to human milk data from many other countries in the world. The comparatively higher concentration for ∑DDTs in the Solomon Islands is attributed to continued use of the pesticide DDT for control of malaria. Furthermore, there is a need for more national studies on exposure of local populations to the newly added POPs to the Stockholm Convention during the 4th meeting of the Conference of the Parties (COP4) in 2009 as this will provide important information for guidance on risk management actions and analytical capacity building requirements for POPs testing in PICs.

Acknowledgements
The authors gratefully acknowledges UNEP Chemicals Division and Global Environment Facility (GEF) for funding the Global Monitoring Programme (GMP) in the Pacific and for providing technical support in terms of training staff at the Institute of Applied Sciences laboratory in Fiji. We also thank the University of the South Pacific and UNEP for purchase of a new GC. Special thanks to all mothers in the PICs who gave human breast milk samples for testing of POPs.

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