Interdisciplinary Studies on Environmental Chemistry—Biological Responses to Chemical Pollutants, Eds., Y. Murakami, K. Nakayama, S.-I. Kitamura, H. Iwata and S. Tanabe, pp. 1–6.

Measuring and Monitoring POPs: A Critique

Rudolf S. S. WU[1], Alice K. Y. CHAN[1], Bruce RICHARDSON[1], Doris W. T. AU[1], James K. H. FONG[1], Paul K. S. LAM[1] and John P. GIESY[1,2,3]

[1]*Department of Biology and Chemistry, Research Centre for Coastal Pollution and Conservation, City University of Hong Kong, Hong Kong*
[2]*Department of Veterinary Biomedical Sciences and Toxicology Center, University of Saskatchewan, Canada*
[3]*Zoology Department, Center for Integrative Toxicology, National Food Safety and Toxicology Center, Michigan State University, East Lansing, MI 48824, U.S.A.*

(Received 3 June 2008; accepted 29 July 2008)

INTRODUCTION

In recent years, the occurrence and role of various persistent organic pollutants (POPs) in the marine environment have received much attention, as exemplified by the increasing number of environmental surveys and monitoring programs. POPs are now widely distributed from Antarctica to the Arctic, and from intertidal to abyssal marine systems. At the same time, numerous studies have been carried out to assess the effects of POPs on marine environments. Nevertheless, the majority of environmental surveys still primarily focus on determining the concentrations, and based on which, the possible environmental effects are extrapolated.

The objectives of POPs monitoring normally fall within one or more of the following five categories:

1. Comparisons of spatial changes to identify sources and "hot spots";
2. Comparisons of temporal changes to detect deterioration or improvement;
3. Checks on compliance with reference to established standards or guidelines;
4. Assessment of possible adverse effects;
5. Provision of exposure data for more detailed risk assessments.

The ability of a program to achieve the above goal(s), however, relies on a sampling design which is statistically valid, and standards and guidelines which are scientifically sound. However, an extensive review and analyses on literature carried out by us show that the vast majority of existing studies may fall short in these two important criteria.

A CRITIQUE ON SAMPLING DESIGN

Of 661 SCI papers reporting concentrations of POPs, PAHs and PCBs in the environmental media we analyzed, 46% reported concentrations only at a single

Table 1. Range and variations in concentration of different types of POPs in sediment, soil, fish and mussel samples.

Sample	Chemical	N	Mean ± SD	CV	Reference
Sediment	PAHs	12	593 ± 284 ng/g	0.48	Bouloubassi *et al.* (2006)
		5	1670 ± 875 ng/g	0.52	Motelay-Massei *et al.* (2004)
Soil	DDT	5	0.32 ± 0.47 mg/kg	1.47	Gaw *et al.* (2006)
		?	9.82 ± 10.91 ug/kg	1.11	Tieyu *et al.* (2005)
Fish	PCB	3	110 ± 95 ng/g ww	0.86	Sethajintanin *et al.* (2004)
		3	290 ± 78 ng/g ww	0.27	Streets *et al.* (2006)
Fish	HCH	5	0.06 ± 0.06 ng/g	1.00	O'Toole *et al.* (2006)
Mussel	PCB	4	289 ± 253 ng/g	0.44	Cheung *et al.* (2002)
		3	5430 ± 2438 pg/g	0.45	Danis *et al.* (2006)

Table 2. The probability of detecting a 20% difference in POPs concentration in sediment, water, fish and mussel samples, given n = 2, 5 and 10.

Samples	Countries/Regions	∑POPs	Average CV	Probability of detecting a 20% difference		
				n = 2	n = 5	n = 10
Sediment	France	PAHs	0.44	6%	12%	22%
	New Zealand	DDTs	1.07	3%	4%	5%
Water	Spain	HCBs	0.39	7%	15%	28%
Fish	Salton Sea, U.S.A.	PCBs	0.23	17%	40%	71%
	Salton Sea, U.S.A.	HCHs	0.25	14%	34%	63%
	Oregon, U.S.A.	PCBs	0.56	5%	8%	14%
	Antarctica	HCHs	0.16	33%	72%	96%
	Antarctica	DDEs	0.24	15%	37%	67%
Mussel	Hong Kong	PCBs	0.69	4%	6%	10%

time point at a single location, or samples were pooled for analysis. Of the remaining papers reporting spatial distributions of POPs, very few related the observed concentrations to environmental consequences. The measurement of spatial and temporal concentrations of POPs in environmental samples is fundamental to the objectives of many marine monitoring programmes. However, both spatial heterogeneity and temporal variability in POPs concentrations can be considerable. The ability to discriminate differences between measurements depends upon (a) variance among treatments (the "signal"); (b) variance within treatments (the "noise"); and (c) the number of replicates involved in the sampling. Using information on the "within" variance of POPs concentrations from nine typical marine monitoring studies, which measured DDT, HCH, PCBs and PAHs with varying sample replication in sediments, soils, fish and mussels, we show that the coefficients of variation (CV) for PAHs in sediment were 0.48–0.52 (n = 5–12; Motelay-Massei *et al.*, 2004; Bouloubassi *et al.*, 2006); for DDT in soil, 1.11–1.47 (n = 5; Tieyu *et al.*, 2005; Gaw *et al.*, 2006); for PCBs in

Table 3. The probability of detecting a difference in POPs concentration with 80% probability in sediment, water, fish and mussel samples, given n = 2, 5 and 10.

Samples	Countries/Regions	∑POPs	Average CV	% difference (δ) detectable with 80% probability		
				n = 2	n = 5	n = 10
Sediment	France	PAHs	0.44	448%	74%	44%
	New Zealand	DDTs	1.07	1089%	181%	108%
Water	Spain	HCBs	0.39	397%	66%	39%
Fish	Salton Sea, US	PCBs	0.23	234%	39%	23%
	Salton Sea, US	HCHs	0.25	255%	42%	25%
	Oregon, US	PCBs	0.56	570%	95%	57%
	Antarctica	HCHs	0.16	163%	27%	16%
	Antarctica	DDEs	0.24	244%	41%	24%
Mussel	Hong Kong	PCBs	0.69	703%	117%	70%

mussels, 0.44–0.45 (n = 3–4; Cheung *et al*., 2002; Danis *et al*., 2006); for HCH in fish, 1.0 (O'Toole, 2006), and for PCBs in fish, 0.27–0.86 (n = 3; Sethajintanin *et al*., 2004; Streets *et al*., 2006). The great variability suggests that a large number of replication would be correspondingly required to provide a reliable estimate on field concentration and to discriminate differences in monitoring programmes.

Sufficient replicates must therefore, be taken in order to (a) provide reliable, statistically valid estimates of field concentration at a particular site or particular time; and/or (b) discriminate differences between sampling sites and/or times, in order to prevent erroneous conclusions. Amongst the 661 papers on POPs from 1996 to 2006 we analyzed, 134 of which (21%) did not take any replicate at all, and 165 of which (25%) did not report replication or take any replicate samples, or pooled their samples prior to chemical analyses. Of the remaining papers, 30% of studies took between 2 and 4 replicate samples, and only 24% of the studies took >5 replicate samples.

Using the variance within treatment from 9 reported field data sets on various types of POPs from a variety of regions in sediments, waters, fish and mussel samples (Table 1), we performed power analysis to calculate the probability of detecting a 20% difference between site and/or time (the minimal difference we considered useful in discerning temporal/spatial changes in field studies and monitoring) using 2, 5 and 10 replicates (Table 2).

The results of our analysis showed that:

- for n = 2 replicates, the probability of detecting a 20% difference ranged from 3–33%;
- for n = 5 replicates, the probability of detecting a 20% difference ranged from 4–40% in 8 cases, and only in one out of 9 cases was the detection power >50%;
- for n = 10 replicates, the probability of detecting a 20% difference ranged from 5–28% in 5 cases, and in 4 out of 9 cases the detection power was >50% (67–96%).

Table 4. Guideline for various types of POPs in seafood (in μg/kg wet wt., except where specified).

	USFDA[1]	EU[2]/OSPAR	China[3]	Canada[4]	Japan[1]
∑DDT	5000	Finland: 500	10	5000	
PAHs		Fish: 2 C: 5 B: 10			
PCBs	2000			2000	Offshore: 500 Coastal: 3000
Dioxin		EU: 4–12 pg/g		20 pg TCDD/g	

[1]Food and Drug Administration (2005); [2]FAO Fisheries Technical Paper 473 (2005); [3]GB18421-2001; [4]Canadian Food Inspection Agency (2007).

Using the same set of field data, power analysis was further performed to determine the percent difference could be detected with an 80% probability (the discriminating power commonly expected in field studies and monitoring) using 2, 5 and 10 replicates. The results (Table 3) indicated:

- for $n = 2$ replicates, a concentration difference of 163–1,089% between sites and/or times could be detected with an 80% probability;
- for $n = 5$ replicates, only in one out of 9 cases could a concentration difference of <30% between sites and/or times be detected with an 80% probability;
- for $n = 10$ replicates, only 4 out of 9 cases could detect a concentration difference of <30% between sites and/or times with an 80% probability.

The above analyses showed that concentrations of POPs in the vast majority of existing studies were measured without sufficient replication. This defeats the purpose of the study and monitoring since it does not allow us to detect spatial differences or temporal changes. Even worse, this may lead to erroneous conclusions (both false positive and false negative).

A CRITIQUE OF CURRENT STANDARDS AND GUIDELINES

The presence of a chemical in the environment (contamination) does not necessarily mean that it is biologically available, as contaminants may exist in different chemical forms, and whilst some forms may be bioavailable while others may not. Further, even if contaminants enter biological systems, they may not necessary elicit any adverse biological effects. Thus, concentrations of contaminants below thresholds of adverse effects are of little environmental concern.

This strongly suggests that establishing a reliable threshold of concern is of utmost importance, since it underpins the primary objective of all field monitoring activities. We further argue that, unless there are clear objectives regarding the environmental concentrations that trigger concern, or the course of action that should be taken with respect to a given concentration, there is little merit in measuring these chemicals in the environment. The paucity of chronic toxicity

data on POPs calls for an urgent need to accumulate accurate chronic toxicity data for POPs, so that reliable estimates of the thresholds of environmental concern can be made.

Our review showed that the present standards and guidelines for POPs vary considerably between different countries (see Table 4 for an example). They tend to have been based on a combination of experimental data, assumptions as well as political and economic factors. Thus, non-compliance should trigger concern, so that problems can be tracked down and rectified. Nonetheless, noting the very great degree of uncertainty associated, the standards and guidelines should not be viewed and interpreted in a simple and mechanistic manner.

MEASURING POPS IN THE CONTEXT OF RISK ASSESSMENT

We would strongly argue that an ecological risk assessment approach should be adopted for measuring POPs in the environment. We further argue that routine monitoring and reporting of abiotic and biotic concentrations are of limited use, unless such data can be related directly to the assessment of public health risk and ecological risk.

The underlying principle of ecological risk assessment involves a comparison between environmental concentrations (either predicted, PEC, or measured, MEC) with predicted no effect concentrations (PNEC). As such, the reliability of both values is of paramount importance in ecological risk assessment, and effort must be devoted to reduce uncertainties in both estimates. In the ecological risk assessment approach, field measurements are performed to estimate MEC for comparison with PNEC values, and PNEC is estimated in most cases from LC_{50} or EC_{50} data. Most of the existing data are based on acute toxicity, while concentrations leading to acute toxicity would seldom occur in the natural environment. Chronic toxicity of POPs are much more relevant to setting standards and guidelines, but there is a paucity in chronic toxicity data, especially for long term chronic exposure. As such, future research should endeavor to fill this important gap.

Finally, chemical measurements of POPs in the marine environment *per se* may be of limited use unless these data can be clearly related to biological effects via a risk assessment-based approach. The determination of threshold effects concentrations of POPs using sensitive receivers (especially keystone and commercial species, and populations with great energy flow value) urgently needs to be undertaken in order to derive PNEC values, based on solid scientific evidence, with a greater level of certainty.

Acknowledgments—This study is wholly supported by an "Area of Excellence" Grant (AoE P-04/04) from the University Grants Committee. We thank Mr. Michael Chiang for preparing the figures and tables. This paper is based on our work published in Wu *et al.* (2008): *Mar. Pollut. Bull.*, **57**, 236–244.

REFERENCES

Bouloubassi, I., L. Méjanelle, R. Pete, J. Fillaux, A. Lorre and V. Point (2006): PAH transport by

sinking particles in the open Mediterranean Sea: A 1 year sediment trap study. *Mar. Pollut. Bull.*, **52**, 560–571.

Canadian Food Inspection Agency (2007): Fish Products Standards and Methods Manual. Appendix 3 Canadian Guidelines for Chemical Contaminants and Toxins in Fish and Fish Products. http://www.inspection.gc.ca/english/anima/fispoi/manman/samnem/app3e.shtml

Cheung, C. C. C., G. J. Zheng, P. K. S. Lam and B. J. Richardson (2002): Relationships between tissue concentrations of chlorinated hydrocarbons (polychlorinated biphenyls and chlorinated pesticides) and antioxidative responses of marine mussels *Perna viridis*. *Mar. Pollut. Bull.*, **45**, 181–191.

Danis, B., V. Debacker, C. T. Miranda and Ph. Dubois (2006): Levels and effects of PCDD/Fs and co-PCBs in sediments, mussels, and sea stars of the intertidal zone in the southern North Sea and the English Channel. *Ecotoxicol. Environ. Saf.*, **65**, 188–200.

FAO Fisheries Technical Paper 473 (2005): Causes of detentions and rejections in international fish trade: Annexes Relevant regulations, procedures, guidance or standards used by the European Union. http://www.fao.org/docrep/008/y5924e/y5924e00.htm

Food and Drug Administration (2005): National Shellfish Sanitation Program Guide for the Control of Molluscan Shellfish. http://www.cfsan.fda.gov/~ear/nss3-42d.html

Gaw, S. K., A. L. Wilkins, N. D. Kim, G. T. Palmer and P. Robinson (2006): Trace element and ∑DDT concentrations in horticultural soils from the Tasman, Waikato and Auckland regions of New Zealand. *Sci. Total Environ.*, **355**, 31–47.

GB18421-2001 (2001):Marine Biological Quality. China. http://www.zjepb.gov.cn/hbbj/hb/i4210.pdf

Motelay-Massei, A., D. Ollivon, B. Garban, M. J. Teil, M. Blanchard and M. Chevreuil (2004): Distribution and spatial trends of PAHs and PCBs in soils in the Seine River basin, France. *Chemosphere*, **55**, 555–565.

O'Toole, S., C. Metcalfe, I. Craine and M. Gross (2006): Release of persistent organic contaminants from carcasses of Lake Ontario Chinook salmon (*Oncorhynchus tshawytscha*). *Environ. Pollut.*, **140**, 102–113.

Sethajintanin, D., E. R. Johnson, B. R. Loper and K. A. Anderson (2004): Bioaccumulation profiles of chemical contaminations in fish from the Lower Willamette river, Portland harbor, Oregon. *Arch. Environ. Cont. Toxicol.*, **46**, 114–123.

Streets, S. S., S. A. Henderson, A. D. Stoner, D. L. Carlson, M. F. Simcik and D. L. Swackhamer (2006): Partitioning and Bioaccumulation of PBDEs and PCBs in Lake Michigan. *Environ. Sci. Technol.*, **40**, 7263–7269.

Tieyu, W., L. Yonlong, S. Yajuan and Z. Hong (2005): Spatial distribution of organochlorine pesticide residues in soils surrounding Guanting reservoir, People's Republic of China. *Bull. Environ. Cont. Toxicol.* **74**, 623–630.

R. S. S. Wu (e-mail: bhrswu@cityu.edu.hk), A. K. Y. Chan, B. Richardson, D. W. T. Au, J. K. H. Fong, P. K. S. Lam and J. P. Giesy