Measuring and monitoring persistent organic pollutants in the context of risk assessment

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ABSTRACT

Due to growing concerns regarding persistent organic pollutants (POPs) in the environment, extensive studies and monitoring programs have been carried out in the last two decades to determine their concentrations in water, sediment, and more recently, in biota. An extensive review and analysis of the existing literature shows that whilst the vast majority of these efforts either attempt to compare (a) spatial changes (to identify "hot spots"), or (b) temporal changes to detect deterioration/improvement occurring in the environment, most studies could not provide sufficient statistical power to estimate concentrations of POPs in the environment and detect spatial and temporal changes. Despite various national POPs standards having been established, there has been a surprising paucity of emphasis in establishing accurate threshold concentrations that indicate potential significant threats to ecosystems and public health. Although most monitoring programs attempt to check compliance through reference to certain "environmental quality objectives", it should be pointed out that many of these established standards are typically associated with a large degree of uncertainty and rely on a large number of assumptions, some of which may be arbitrary. Non-compliance should trigger concern, so that the problem can be tracked down and rectified, but non-compliance must not be interpreted in a simplistic and mechanical way. Contaminants occurring in the physical environment may not necessarily be biologically available, and even when they are bioavailable, they may not necessarily elicit adverse biological effects at the individual or population levels. As such, we here argue that routine monitoring and reporting of abiotic and biotic POPs concentrations could be of limited use, unless such data can be related directly to the assessment of public health and ecological risks. Risk can be inferred from the ratio of predicted environmental concentration (PEC) and the predicted no effect concentration (PNEC). Currently, the paucity of data does not allow accurate estimation of PNEC, and future endeavors should therefore, be devoted to determine the threshold concentrations of POPs that can cause undesirable biological effects on sensitive receivers and important biological components in the receiving environment (e.g. keystone species, populations with high energy flow values, etc.), to enable derivation of PNECs based on solid scientific evidence and reduce uncertainty. Using the threshold body burden of POPs required to elicit damages of lysosomal integrity in the green mussel (*Perna virvidis*) as an example, we illustrate how measurement of POPs in body tissue could be used in predicting environmental risk in a meaningful way.

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1. Introduction

Since the publication of the book *Silent Spring* (Carson, 1962), an enormous number of surveys have been conducted in which local and regional contamination by a wide variety of xenobiotic substances has been elucidated. Larger-scale surveys have also provided a global and regional distribution picture for major contaminants (including metals, pesticides, industrial and consumer compounds) and, at least in some cases, attempts have also been made to correlate distribution patterns revealed with effects on living organisms (including humans).

In recent years, particular attention has been paid to the occurrence and role of various persistent organic pollutants (POPs) in marine environmental contamination. POPs include a wide variety of chemicals, from petroleum compounds and their derivatives (including the polycyclic aromatic hydrocarbons, PAHs) to organohalogenated compounds, such as the chlorinated pesticides DDT,

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aldrin and dieldrin; the polyhalogenated biphenyls (e.g. PCBs and PBBs); fire retardants such as the polybrominated diphenyl ethers (PBDEs); and most recently, the per- and poly-fluorinated compounds which have been widely used in surface applications on a variety of household and consumer items.

Interest in the local, regional and global distribution of POPs in marine environments is exemplified by the ever-increasing number of environmental surveys and monitoring programmes which have been undertaken, especially since the 1970s when analytical techniques were sufficiently developed to permit detection of environmental concentrations of these compounds (see Fig. 1). Such studies have revealed the ubiquity of POPs in many environments, not only in sediments, air and water, but also in living organisms. POPs have been shown to be globally distributed throughout the marine world, from Antarctica to the Arctic, and from inter-tidal to abyssal marine systems. Indeed, their distribution, residence and importance within polar biota *via* such processes as the "grasshopper effect" (Wania and Mackay, 1996) have been the subject of debate for some time.

The persistence of many POPs in environmental media, combined with an increasing knowledge of their toxicity, has inevitably led to grave concerns for ecosystem and public health. Correspondingly, numerous studies have been carried out to assess POPs in marine environments, increasingly with a focus on "possible biological effects". Although this is undoubtedly a soundly-based premise, it remains a fact that the majority of environmental surveys still primarily focus on the chemical aspects of monitoring, and almost inevitably result in the translation of these data into what could be viewed as "artificial" forms of pollution assessment, based more often than not on "pseudo-comparisons" with "comparable" species or other, "similar" environments (e.g. see Richardson, 2007).

The primary objectives of most monitoring surveys can be summarized as follows:

1. Comparisons of spatial changes to identify sources and so-called "hot spots" containing great contaminant concentrations.
2. Comparisons of temporal changes to detect deterioration or improvement of contaminant concentrations in the environment.
3. Checks on compliance (with reference, for instance, to governmental standards and established guidelines).
4. Assessment of possible adverse effects (e.g. ecological and public health risks).
5. Provision of exposure data for more detailed risk assessments.

Whether these aims are, in most instances, achievable or even realistic is open to debate – a key issue which we wish to pursue in this paper. Certainly, the scientific complexity of the aims increases (from 1 to 5 above); concomitantly, the number of papers published addressing each of these aims decreases.

To add to the proliferation of data, many national & international monitoring programs have been developed to assess POPs in the marine environment. Such programmes include, for example, the National Status & Trends assessments in the United States (US), undertaken by the National Oceanographic and Atmospheric Administration (NOAA) (since 1984); various Mussel Watch monitoring activities, especially in the US (e.g. the California Mussel Watch, since 1986); the US FDA Pesticide Residue Monitoring Program (since 1987); the US EPA Environmental Measurement and Assessment Program (since 1988); the Dioxin Monitoring Program by the US State of Maine (since 2001); and the Global POPs Monitoring Program (GMP), established to evaluate the effectiveness of the Stockholm Convention. These studies have contributed valuable information to global monitoring, but the key question which we wish to address concerns their effectiveness in producing definitive results which reliably identify spatial and temporal differences in contaminants, let alone providing data which may be used to assess environmental risks or to set reference standards and guidelines.

As a basis for this paper, we have reviewed literature reporting POPs concentrations in the marine environment, with a view to providing a critique on the deficiencies, limitations and problems of (a) sampling design and effort, and (b) current standards and guidelines. We will also argue that measuring and monitoring POPs *per se* would be of limited merit, unless such measurements are performed in the context of risk assessment.

2. Literature review

We searched the ISI database for papers published during the period 1970–2006, using the following keywords and acronyms: persistent organic pollutants; POPs; polycyclic aromatic hydrocarbons; PAHs; polychlorinated biphenyls; PCBs; DDT. A total of 9088 papers were found (see database lodged at the website: http://www.cityu.edu.hk/bch/merit/message/message.html.). Notably, the number of papers reporting trace organic contaminants has risen since the 1980s (Fig. 1).

3. A critique on sampling design

Out of the 9088 papers mentioned above, detailed analyses were conducted on data from 661 papers published since 1990, in which the number of replicates as well as environmental levels of persistent organic pollutants in water, sediment or biota were reported.

Of the 661 papers examining concentrations of POPs, PAHs and PCBs in environmental media, 304 reported concentrations only at a single time point at a single location, or samples that were pooled for analysis. Of the remaining 346 papers, 290 (60.4% of the 511 "concentrations-based papers") reported spatial distributions of POPs, 29 reported temporal changes in concentrations, and 27 both spatial and temporal changes. Very few papers 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 (if not most) marine monitoring programmes. However, both spatial heterogeneity and temporal variability in POPs concentrations can be considerable. A number of factors can contribute to error in measurements, which will ultimately affect the ability to discriminate the differences between sites and/or times of sampling. The ability to discriminate differences between measurements depends upon the following three factors:

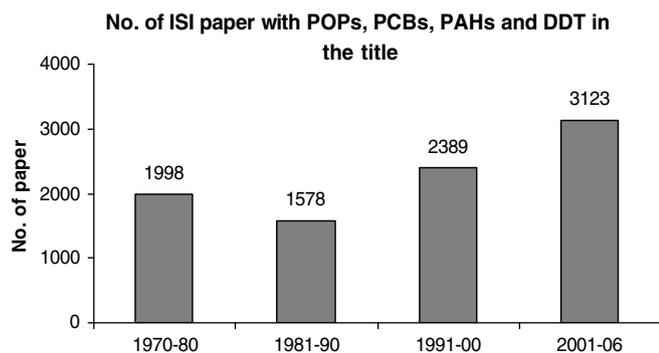**No. of ISI paper with POPs, PCBs, PAHs and DDT in the title**

Fig. 1. Number of papers published in ISI journals since the 1970s with POPs, PCBs, PAHs and DDT in their titles.

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/	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)

- Variance among treatments (SS among; i.e. the "signal");
- Variance within treatments (SS within; i.e. the "noise"); and
- The number of replicates involved in the sampling.

The "within" variance of POPs concentrations was extracted from nine typical marine monitoring studies, which measured DDT, HCH, PCBs and PAHs with varying sample replication in sediments, soils, fish and mussels (Table 1) as examples. The data indicated 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 mussels, 0.44–0.45 (n = 3–4; Cheung et al., 2002; Danis et al., 2006); for HCH in fish, 1.0 (O'Toole et al., 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 replicates would be correspondingly required to provide a reliable estimate of field concentrations and to discriminate differences in monitoring programmes.

Clearly, sufficient replicates must be taken in order to (a) provide reliable, statistically valid estimates of field concentrations 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, 511 concerned themselves with reporting concentrations of POPs in various sample types (sediment, fish, mussels, birds, seal and waters), 134 (21%) did not take any replicates at all, and 165 (25%) did not report replication or take any replicate samples, or samples were pooled as a composite sample prior to chemical analyses (Fig. 2), the latter practice appearing common in surveys examining bivalves or fish. Indeed, it is the usual practice in Mussel Watch surveys that individually selected organisms from a site are pooled as a bulk (composite) sample prior to analysis. This is usually performed to provide sufficient sample for analysis, to take account of within-site variation of contaminant concentrations in individual bivalves, and of course, to save the costs involved in chemical analysis. Of the remaining papers, 30% of studies took between 2 and 4 replicate samples, and only 24% of the studies took >5 replicate samples (Fig. 2).

One of the primary goals in measuring field concentrations of POPs is to detect spatial and/or temporal differences between samples. As we mentioned earlier, in doing so it is extremely important that the chosen sampling design is sufficiently robust to detect differences that are relevant to the monitoring goals. Using power analysis, we asked the question "how big a difference can one detect, and to what extent does this difference depend upon replication?" In undertaking these analyses, we took into consideration three factors: (a) the variance among treatments (i.e. the "signal" strength between samples taken at different sites and/or times; (b) the variance within treatments (i.e. the "noise" within samples taken at single sites and /or times); and (c) a given hypothetical number of replicates (n = 2, 5 and 10) taken for each site and/or time. 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, 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% to 33%.
- for *n* = 5 replicates, the probability of detecting a 20% difference ranged from 4% to 40% in 8 cases, and only in one out of 9 cases was the detection power >50%.
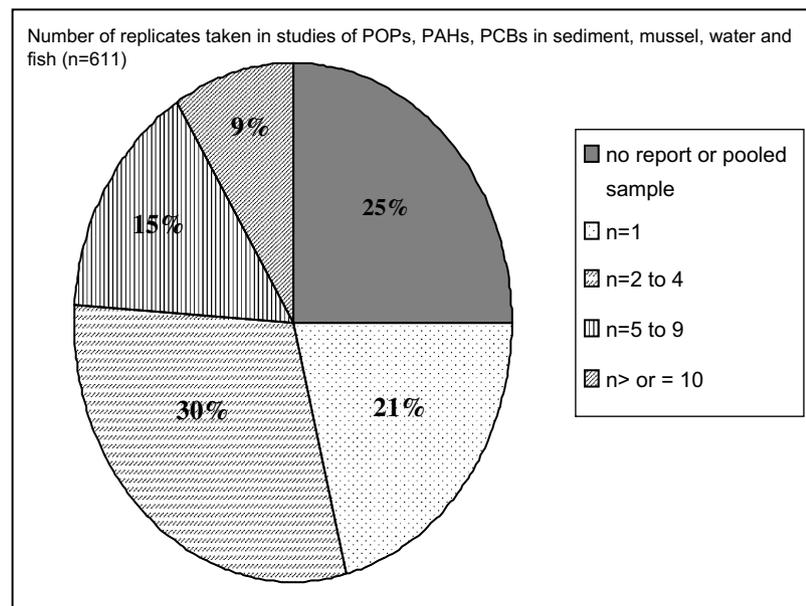
Fig. 2. An analysis of replications taken for analysis of POPs, PAHs and PCBs in sediment, fish and mussels (based on a total of 611 studies since 1970).

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	ΣPOPs	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, US	PCBs	0.23	17	40	71
	Salton Sea, US	HCHs	0.25	14	34	63
	Oregon, US	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

- for $n = 10$ replicates, the probability of detecting a 20% difference ranged from 5% to 28% in 5 cases, and in 4 out of 9 cases the detection power was >50% (67% to 96%).

Using the same set of field data, power analysis was further performed to determine the percent difference that 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% to 1089% 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.

A further source of error in field measurements may stem from chemical analysis. Table 4 shows that the coefficients of variation

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	ΣPOPs	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

Table 4
Coefficient of variations in laboratory determination of selected POPs in marine sediment (NIST-SRM, 1941b)

Contaminant	CV (%)	Contaminant	CV (%)
PCB170	6.67	Benzo[a]pyrene	4.75
PCB180	15.74	Dibenz[a,h]anthracene	18.8
PCB206	7.85	*cis*-Chlordane	12.94
PCB209	9.26	HCB	6.52
Naphthalene	11.2	*p,p*′-DDE	8.70
Benz[a]anthracene	7.46	*p,p*′-DDD	9.87

Table 5
Environmental concentration ranges and detection limits of DDT, PCBs and PAHs

Sediment/soil	Environmental concentration range	Detection limit
DDT	0.005–18.5 ng/g	0.0001–0.0012 ng/g (Wang et al., 2007)
PCBs	1.7–124.6 ng/g	0.1–0.6 ng/g (Basheer et al., 2005)
PAHs	0.052–66.7 ug/g	0.001 ug/g (Bihari et al., 2007)

(CV) of chemical analysis for 12 different types of POPs ranged from 4.8 to 18.8 (mean = 9.9, median = 9) (NIST-SRM, 1941b) which are very small compared with the coefficients of variance in field sampling as calculated based on the 9 field studies that provided replication (ranging from 16 to 107, mean = 44.8, median = 39). The results of our analysis clearly suggest, therefore, that the major errors in environmental measurements are from field heterogeneity rather than from chemical analysis. As such, to obtain a reliable estimate of environmental POPs distributions, major efforts should arguably be devoted to increasing the sample size.

There have been marked advances in analytical capability since the 1970s (when POPs first began to capture attention), and these new methods have frequently been considered to be of great importance and are therefore followed in marine environmental monitoring. With improved analytical capability, the detection limits for many POPs have been lowered from ppm concentrations (in the 1970s) to ppb concentrations in the 1980s, ppt in the 1990s and to ppq in the new millennium. Of course, advances in analytical techniques enable the detection of contaminants that only occur at very low concentrations, which were extremely difficult (if not impossible) to detect previously (e.g. dioxins and furans, PFCs, PBDEs). However, as it is now common practice to measure virtually all POPs down to the lowest possible detection limit, the question needs to be asked: "is measurement to such low limits necessary, or even meaningful?" This also elicits another query: "should we not challenge the necessity of lowering detection limits (or further improving the accuracy of measurements) beyond threshold concentration that can elicit any adverse environmental concerns in field measurements and monitoring?"

Table 5 shows that there is a considerable gap between observed environmental concentrations and current detection limits. We argue that there is little merit in lowering detection limits beyond concentrations of environmental concern (with perhaps only a few exceptions, such as mass balance studies) especially if analytical costs increase substantially as detection limits fall.

In summary, we conclude that concentrations of POPs in the vast majority of existing studies were measured without sufficient replication. This does not enhance (or in most instances enable) the detection of spatial differences or temporal changes. Even worse, current practices may not only defeat the purpose of the study and monitoring, but may lead to erroneous conclusions (both false positive and false negative). Because the major errors in field measurements stem from spatial and temporal heterogeneity, as opposed to chemical analyses, future efforts should be devoted to improving sampling design rather than further enhancing the accuracy of chemical measurements after meeting good QA/QC requirements, or lowering detection limits beyond thresholds of environmental concern.

4. A critique of current standards and guidelines

Contamination is very different from pollution, the latter being defined as "the introduction by man, directly or indirectly, of substances or energy into the environment, which results in such harmful effects as harm to living resources, hazard to human health, impairment of environmental quality and reduction of

amenities" (GESAMP, 1990). 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 able to enter biological systems (i.e. they are biologically available), others may not (and hence exert no effects).

Further, even if contaminants enter biological systems, they may not necessary elicit any adverse biological effects, provided they occur below certain threshold concentrations, or if depuration or metabolism occur faster than uptake. Thus, concentrations of contaminants below thresholds of adverse effects are of little environmental concern (except, perhaps, for identifying the source of contamination to ensure early prevention).

This suggests that establishing a reliable threshold of concern is of utmost importance, since it underpins the primary objective of all field monitoring activities. We would 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 general approach to determine the threshold concentrations of concern is to conduct toxicity tests and derive the "no observable effects level" (NOEL) of a contaminant. Fig. 3 shows an example of the use of a toxicity database for phenanthrene used to derive sediment quality guidelines (SQGs) in which ERL (Effects Range Low) and ERM (Effects Range Medium) were determined.

Table 6 shows the effects range low (ERL) and effects range median (ERM) of a range of POPs. Fewer than 25% of studies indicated that there were adverse effects when concentrations were less than the ERL. Similarly, Table 7 shows that (a) despite the fact that no significant toxicity was found in 68% of samples when exposed to concentrations below the ERL, 11% of samples did show great toxicity; and (b) despite the fact that 85% of samples showed great toxicity when ERM values were exceeded, 10% of samples were found to be non-toxic. The above data analysis clearly shows that albeit ERLs and ERMs may provide useful guidelines, they may not necessarily be indicative of toxicity in every case.

Indeed, in a review by NOAA (1999a), it has been clearly pointed out that present guidelines do not account for geochemical factors in sediments that may affect concentrations and bioavailability; further, they cannot predict toxic thresholds, bioaccumulation and interactions of toxicants; cannot be used as regulatory standards; should be used with caution and common sense; and should be supplemented by laboratory toxicity tests, bioaccumulation tests and benthic community analyses for risk assessment purposes.

So, are there definitive concentrations that can lead to harmful effects by POPs? At present, there exists a paucity of concrete data regarding the threshold concentrations of POPs which should elicit

Table 6
Guidelines for effect-range low (ERL) and effect-range medium (ERM) (in ppb, dry wt.) verus percentage incidence of biological effects of various types of POPs (data from NOAA, 1999a)

Chemical	Guidelines		Percent incidence of effects		
	ERL	ERM	<ERL	ERL–ERM	>ERM
Acenaphthene	16	500	20.0	32.4	84.2
Acenaphthylene	44	640	14.3	17.9	100
Anthracene	85.3	1100	25.0	44.2	85.2
Fluorene	19	540	27.3	36.5	86.7
2-Methyl naphthalene	70	670	12.5	73.3	100
Naphthalene	160	2100	16.0	41	88.9
Phenanthrene	240	1500	18.5	46.2	90.3
ΣLPAH	552	3160	13.0	48.1	100
Benz(a)anthracene	261	1600	21.1	43.8	92.6
Benzo(a)pyrene	430	1600	10.3	63.0	80
Chrysene	384	2800	19.0	45.0	88.5
Dibenzo (a,h) anthracene	63.4	260	11.5	54.5	66.7
Fluoranthene	600	5100	20.6	63.6	92.3
Pyrene	665	2600	17.2	53.1	87.5
ΣH PAH	1700	9600	10.5	40.0	81.2
ΣTotal PAH	4022	44,792	14.3	36.1	85
p,p'-DDE	2.2	27	5.0	50.0	50
ΣDDTs	1.58	46.1	20.0	75.0	53.6
ΣPCBs	22.7	180	18.5	40.8	51.0

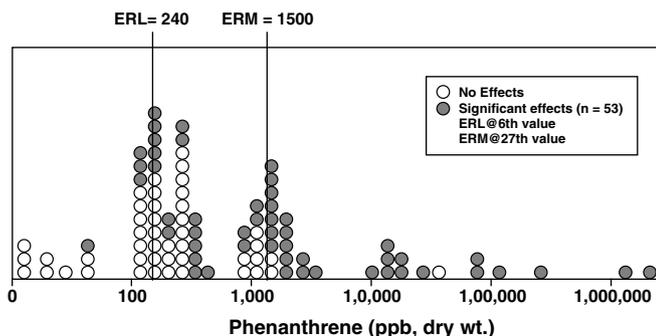Note that 27.3% of studies showed adverse effects despite ERLs not being exceeded.

Table 7
Percentages of samples in which no significant toxicity, marginal toxicity, and highly significant toxicity was observed in amphipod survival tests (after Long et al., 1998)

Chemical category	Number of samples	Percent not toxic	Percent marginally toxic	Percent greatly toxic
No ERLs exceeded	329	68	21	11
1 or more ERLs exceeded	448	63	20	18
1 or more ERMs exceeded	291	48	13	39
1–5 ERMs exceeded	225	53	15	32
6–10 ERMs exceeded	46	37	11	52
11–20 ERMs exceeded	20	10	05	85

environmental concern. It is noteworthy that most existing toxicity data on POPs are derived from acute rather than chronic toxicity tests, despite the fact that the majority of our concerns for POPs are on their sub-lethal and/or chronic effects. Indeed, concentrations leading to acute toxicity rarely occur under natural conditions. 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.

Action levels for POPs in seafood for various countries and guidelines for dioxin and dioxin-like PCBs adopted by various regulating authorities are shown in Tables 8 and 9, respectively. For the same contaminant, different standards have been adopted by different countries and organizations (even for countries with a similar food consumption pattern, such as the EU and the US); and (b) the standards may vary considerably (by up to an order of magnitude or more). As a further illustration, the maximum concentrations of dioxins and furans in fish and eel adopted by the EEC (EC, 2006) vary considerably (Table 10). For instance the standard for eel is 50% greater than that for fish. The above examples show that standards adopted may not only be based on toxicity, but also on other site specific/country-specific factors such as exposure level, political and economic factors, as well as potentially

ERL= 240   ERM = 1500

○ No Effects
● Significant effects (n = 53)
ERL@6th value
ERM@27th value

Phenanthrene (ppb, dry wt.)

Fig. 3. An example deriving sediment quality guidelines for phenanthrene (ERL = Effects Ranged-Low; ERM = Effects Range-Median) (after NOAA, 1999a).

Table 8
Action levels for various types of POPs in seafood (in μg/kg wet wt., except where specified)

	USFDA[a]	EU[b]/OSPAR	China[c]	Canada[d]	Japan[a]
ΣDDT	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	

[a] Food and Drug Administration, 2005.
[b] FAO Fisheries Technical Paper 473.
[c] GB18421-2001.
[d] Canadian Food Inspection Agency.

Table 9
Guidelines for dioxin and dioxin-like PCBs issued by different authorities and countries

Regulating body	Total daily intake (TDI) pg/kg body wt./day
EU[a]	2
WHO[b]	1–4
Japan[c]	5

[a] SCF (2001).
[b] WHO (1998).
[c] Report on tolerable daily intake (TDI) of dioxin and related compounds (Japan).

Table 10
Maximum concentrations of dioxins, furans and dioxin-like PCBs in fish and eel in EU (EC, 2006)

Food	Maximum concentrations sum of dioxins and furans (WHO–PCDD/F-TEQ)	Maximum concentrations sum of dioxins, furans and dioxin-like PCBs (WHO–PCDD/F–PCB-TEQ)
Muscle meat of fish and fishery products and products thereof with the exception of eel	4.0 pg/g fresh weight	8.0 pg/g fresh weight
Muscle meat of eel (*Anguilla anguilla*) and products thereof	4.0 pg/g fresh weight	12.0 pg/g fresh weight

Table 11
Sediment quality guidelines issued by different authorities and countries

Contaminants	USEPA[a]	NOAA[b]	Wisconsin Sediment quality guideline[c]	Netherlands[d]	China[e]	Canada[f]
ΣDDT	3.89	1.58	5.3	p,p′-DDT: 0.09	20	p,p′-DDT: 1.19
				p,p′-DDD: 0.02		p,p′-DDD: 1.22
				p,p′-DDE: 0.01		p,p′-DDE: 2.07
Total PAHs	LMW: 311.7 HMW: 655.3	4022	1610	1		B[a]P: 88.8
Total PCBs	21.55	22.7	60	0.02	20	21.5
Dieldrin	0.715		1.9	0.5		0.71
Endrin			2.2			2.67

All data in ng/g dry weight.
[a] National Sediment Quality survey.
[b] NOAA (1999b).
[c] Wisconsin Department of Natural Resources, 2003.
[d] MHSPE (1999).
[e] GB18668-2002.
[f] Canadian Environmental Quality Guidelines (2002).

approach is adopted by the US FDA to derive limits for PCBs in food (Table 12). To us, this approach makes much more sense, as in this case the limits depend upon (a) the amount consumed; (b) contaminant concentrations; and (c) risk of concern (for example, non-cancer versus cancer endpoints).

In summary, the present standards and guidelines for POPs vary considerably between (and within) different countries. They tend to have been based on a combination of concrete data (e.g. dose-response relationships, NOAEL; records of the quantity of food items consumed, and consumption patterns) and assumptions (the acceptable risk, and safety factors to cover uncertainty, generally in the range of 0.1–0.01). Clearly, at least some of the considered factors are arbitrary and/or country or population specific; as we showed previously, political and economic factors may also have been taken into consideration. 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.

Table 12
Monthly fish consumption limits of PCBs (USEPA, 1999)

Risk-based consumption limit	Non-cancer health endpoints	Cancer health endpoints
Fish meals/month	Fish tissue concentrations (ppm, w/w)	Cancer health endpoints (ppm, w/w)
16	>0.006–0.012	>0.0015–0.003
12	>0.012–0.016	>0.003–0.004
8	>0.016–0.024	>0.004–0.006
4	>0.024–0.048	>0.006–0.012
3	>0.048–0.064	>0.012–0.016
2	>0.064–0.097	>0.016–0.024
1	>0.097–0.19	>0.024–0.048
0.5	>0.19–0.39	>0.048–0.097
None (<0.5)[a]	>0.39	>0.97

[a] None = no consumption is recommended.

unenforceable concentrations of contaminants due to the bioaccumulation potential of the organism concerned.

Guidelines for POPs in sediment also vary among countries and even between States in the USA (Table 11). This indicates that guidelines may not necessarily be based solely on toxicity and ecological risk. Indeed, existing sediment guidelines are considered to be far from adequate by NOAA (1999a), who state "NOAA scientists found it difficult to estimate the possible toxicological significance of chemical concentrations in sediments. Thus, numerical sediment quality guidelines were developed as informal, interpretive tools". They go further to say that "The guidelines were... intended for use in ranking chemicals that might be of potential concern... to compare the degree of contamination among sub-regions, and to identify chemicals elevated in concentration above the guidelines that were also associated with measures of adverse effects" and that "The guidelines were not promulgated as regulatory criteria or standards. They were not intended as cleanup or remediation targets, nor as discharge attainment targets. Nor were they intended as pass-fail criteria for dredged material disposal decisions or any other regulatory purpose. Rather, they were intended as informal (non-regulatory) guidelines for use in interpreting chemical data from analyses of sediments".

Is there a better way of setting reasonable and sensible environmental standards and guidelines? In this regard, a risk assessment

5. 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) (Fig. 4). On this basis, ecological risk (ER) is considered to be great if the value of the former is larger than that of the latter (i.e. ER > 1) and low if the ER value is less than 1.0. As such, the reliability of both values is of paramount importance in ecological risk assessment, and effort must be devoted to reducing 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 (as derived from toxicity tests). Similar to PEC/MEC, a great degree of uncertainty is normally associated with estimating PNECs, since (a) toxicological effects are normally extrapolated from test animals; (b) there are few toxicological data for humans; (c) there are few data regarding the effects of low exposures over long periods (even for test animals); (d) modeling and predictions involves assumptions and uncertainties; and (e) prediction of risk is usually not validated with actual data. Thus, application factors are normally required to cover uncertainty in estimating PNEC.

An application factor of 0.1 is normally applied to cover each of the following: limited reliability of data (i.e. limited species and/or

tests, $\times$ 0.1); extrapolation from one species (e.g. rat) to others (humans) ($\times$ 0.1); and intra-specific variability in human populations ($\times$ 0.1). Obviously, the use of application factors is subjective. In many cases, the error derived from the use of application factors is itself larger than the errors derived from toxicity testing. As mentioned before, there is s paucity in chronic toxicity data on POPs, and there is an imminent need to accumulate such data in order to reduce the uncertainties and provide a reliable estimate of PNEC, if the ecological risk approach is to be adopted in POPs monitoring.

However, even though the use of application factors is subjective, subsequent analysis of data has lent some support for application factor "rules of thumb" (Dourson and Stara, 1983). In addition, the absence of widespread effects in exposed human populations provides circumstantial evidence of the adequacy of the application factors employed (USEPA, 1999).

A final point should be made here. Further sources of uncertainty and error can be incurred in field measurements of POPs, stemming from the selection of environmental components for measurement. An example of this phenomenon is provided by the profiles of PAHs in seawater, fish and mussels collected from the same monitoring sites (Fig. 5). The profiles of PAHs in waters, fish and mussels can be very different from each other, even though they were sampled from the same site. If not recognized and accounted for, such differences can also contribute significantly to variations in the estimation of field concentrations and resulting risk assessments.

6. Measuring POPs in the context of risk assessment: an example

Lysosomal integrity is a generic indicator of cellular well-being in eukaryotes. In bivalves, lysosomal integrity has been shown to correlate with total oxygen and nitrogen radical scavenging capacity (TOSC), protein synthesis, scope for growth and larval viability; and inversely correlated with DNA damage, as well as lysosomal swelling, lipidosis and lipofuscinosis (Moore et al., 2006). Here, we use lysosomal integrity in the green lipped mussel (*Perna virvidis*) as an example to illustrate the use of an ecological risk assessment approach to provide meaningful field measurements of POPs.

P. viridis were sampled from various locations in Hong Kong (representing a well-documented range of contaminant concentrations) and lysosomal integrity was determined using the neutral red assay. For each sampled mussel, total PCB concentrations (on a lipid weight basis) were determined. Lysosomal integrity showed a significant correlation with body burden of PCBs (Fig. 6). Based on
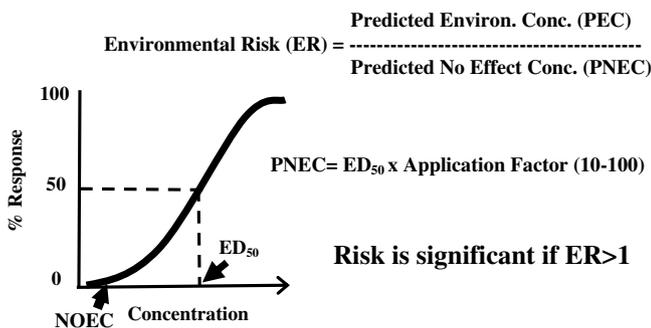
$$\text{Environmental Risk (ER)} = \frac{\text{Predicted Environ. Conc. (PEC)}}{\text{Predicted No Effect Conc. (PNEC)}}$$

$$\text{PNEC} = ED_{50} \times \text{Application Factor (10-100)}$$

Risk is significant if ER>1

Fig. 4. A schematic outline for deriving ED_{50}, NOEC, PNEC and ecological risk assessment.
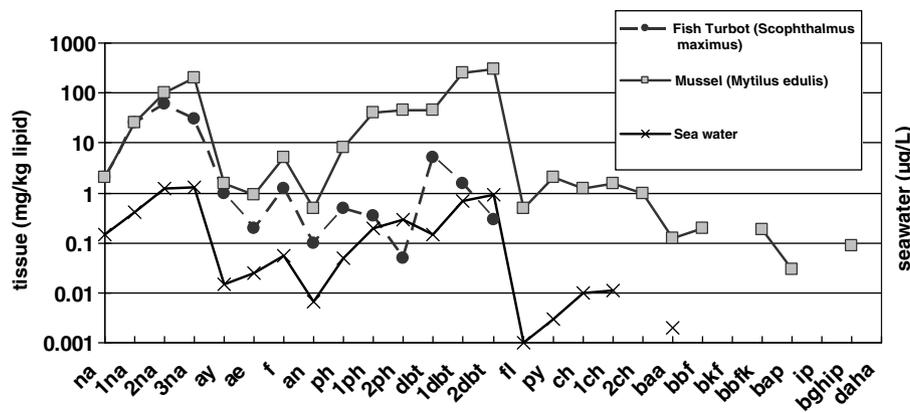
Fig. 5. Difference in congeners of PAHs in seawater, fish (Turbot, *Scophthalmus maximus*), and mussel (*Mytilus edulis*) collected from/deployed in the same environment, showing that different species take up different congeners (modified from Baussant et al., 2001).
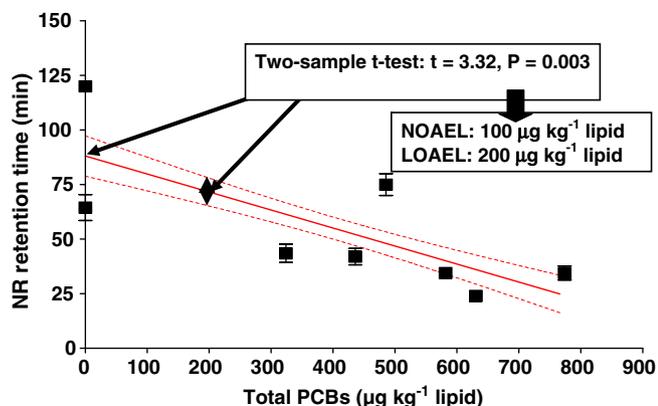
Fig. 6. Relationship between lysosomal stability (measured by neutral red (NR) retention time) and total PCBs concentration in the mussel, *Perna viridis*.

lysosomal integrity, NOAEL and LOAEL values were determined using a 2 sample *t*-test. Our results indicated a NOAEL value of <200 μg/kg (lipid weight).

Assuming that the "safe" concentration derived from *P. virvidis* in this study (i.e. between 100 and 200 μg/kg lipid weight) was also applicable to similar species in other locations, we then compared our results to the concentrations reported in mussels from various other studies. Our data indicated that concentrations of PCBs in mussels from Japan, the Baltic Sea and Italy should be considered "at risk", whereas certain samples from China, Hong Kong, South Korea and Vietnam pose a potential "environmental concern". Overall, this experiment indicates that once thresholds of biological concern have been established, and linked to potential (and environmentally realistic) adverse biological effects, subsequent field measurements can be performed in a much more meaningful manner.

7. The way forward

Due to poor sampling design, POPs studies since the 1970s often did not provide reliable estimates of contaminant distribution and (perhaps of more relevance) nor has the ranking of the relative contaminant concentrations been accurately distinguished between sites. At the most, only very large differences can be discriminated, which defeats the purpose of measurement, or may even had lead to erroneous conclusions (both false positives and false negatives). Our analysis of the available data strongly suggests that future measurement and monitoring of POPs could be vastly improved through attention to sampling design with specific reference to the objective of the program and discriminating power desired, to provide statistically valid estimates of environmental concentrations. It is acknowledged that chemical analysis of POPs is expensive and number of affordable analysis is often restrictive. For the same reason however, we strongly argue that valuable analytical efforts may be in vain, unless chemical analysis can provide a reliable and statistical valid estimate of environmental levels. To this end, hierarchical sampling may be used in designing field sampling programs in order to maximize the power of estimation within in the given constraint of affordable numbers for analysis.

The present review has shown that current regulatory body standards and guidelines vary tremendously between countries and regions. Such discrepancies primarily resulted from a great degree of uncertainty in deriving exposure levels and thresholds of unacceptable biological effects, and the use of different Application Factor(s), which are often subjective and arbitrary. As such, guidelines need to be used with common sense mixed with an adequate

caution, but definitely not be interpreted in a mechanistic or pass/fail manner.

We argue that chemical measurements of POPs in the marine environment *per se* is of limited use, unless such data can be clearly related to biological effects *via* a risk assessment-based approach. Currently, there is a serious paucity of scientific data, which does not enable us to accurately estimate thresholds of unacceptable biological effects, especially at population and ecosystem levels. Future research should address this important deficiency and efforts be directed to providing relevant and solid scientific data so as to reduce the uncertainty. To this end, high research priorities should be accorded to determining threshold effects concentrations of POPs using sensitive receivers (especially keystone and commercial species, and populations with great energy flow value) in order to derive PNEC values and enable us to predict ecological risks.

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