

# Certified reference materials for organic contaminants for use in monitoring of the aquatic environment

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Over the last three decades organic contaminants have been of increasing importance in environmental monitoring. Dioxins, furans, polychlorinated biphenyls and organochlorine pesticides have determined the environmental research agenda. This has led to an increasing demand for certified reference materials (CRMs). However, CRMs have only been made available in limited numbers, as the production and certification of CRMs is normally a relatively slow process. This paper gives an overview of the available CRMs for biota and sediments for these contaminants and the developments in their quality. ©2001 Elsevier Science B.V. All rights reserved.

Keywords: Certified reference materials; PCBs; Dioxins; Pesticides; Chlorinated benzenes; Organotin; PAHs; Environmental monitoring

## 1. Introduction

The analysis of organic contaminants such as polychlorinated dibenzo-p-dioxins (PCDDS), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), chlorinated benzenes, and organochlorine pesticides in environmental matrices is complex. The contaminants are often complex mixtures consisting of many different congeners. A determination of the total concentration of, for example, PCBs leads to significant errors as, due to weathering effects and metabolism, the patterns in the environmental samples are different from those in the technical mixtures. A congener-specific approach is therefore desirable, as only then can

possible toxic congeners be specifically determined. However, chromatographic separation is often insufficient to offer a full separation of all congeners present. In addition, the environmental matrices are relatively difficult to handle. All these factors make the analysis of organic contaminants in environmental samples rather complicated. Laboratories performing this type of analysis and trying to cope with the high degree of analytical difficulty are obviously in need of a good quality control system. International monitoring programmes, which include the analysis of many of these organic contaminants have regularly stressed the need for a good comparability of the laboratories [1]. Consequently, for many years there has been a continuous request for reliable certified reference materials (CRMs). Although the production of CRMs for this field has increased, the available number of CRMs is still too small to cover the needs of the laboratories [2,3]

One of the first initiatives to develop CRMs for PCBs in Europe was taken by the Community Bureau of Reference of the European Union (BCR). In the mid 1980s a programme of stepwise designed interlaboratory studies was started, finally resulting in the production of two CRMs for PCBs: PCB in cod liver oil (CRM 349) and PCBs in mackerel oil (CRM 350) [4]. This approach to improve the agreement between laboratories using different methods was also used in the ICES IOC OSPARCOM PCB interlaboratory study, in which over 60 laboratories participated and which was very successful in improving the performance of participating [5-7]. Later several laboratories involved in the ICES IOC OSPAR-COM study and the BCR work initiated the QUASI-MEME programme (Quality Assurance of Information for Marine Environmental Monitoring in

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Table 1 RMs for hydrocarbons in biota

Code	SRM 1974a	SRM 2974	SRM 2977	SRM 2978	140/OC
Organisation	SRM NIST <sup>2</sup>	SRM NIST <sup>2</sup>	SRM NIST <sup>2</sup>	SRM NIST <sup>2</sup>	IAEA <sup>2</sup>
Country of origin	USA	USA	USA	USA	Monaco
Matrix	Mussel tissue	Mussel tissue	Mussel tissue	Mussel tissue	Fucus (sea plant homogenate)
Units	μg/kg	μg/kg	μg/kg	μg.kg	μg/kg
As	Dry weight				
[ ± ] expressed as	± 95% CI	± 95% CI	± 95% CI	± 95% CI	95% CI
Units of issue	3×15 g	8 g	10 g	10 g	30 g
Form	Frozen tissue	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried and micronised
Resolved aliphatics					*13 000 (6400-24 000)
Unresolved aliphatics					*26 000 (12 000-48 000)
Total aliphatics					27 000 (25 000-42 000)
n-C14	*83.8 ± 3.0				_,, (,
n-C15	*108 ± 12				
n-C16	*161 ± 28				
n-C17	*280 ± 57				890 (300-1300)
n-C18	*153 ± 17				99 (45-140)
n-C19	*40.4 ± 1.1				( ,
n-C20	*65.1 ± 6.0				
п-C22	*46.7 ± 1.9				
п-C24	*57.2 ± 5.7				
п-С26	*49.3 ± 6.3				
n-C28	*64.5 ± 3.3				
n-C30	*47.8 ± 7.3				
n-C32	*55.9 ± 4.2				
n-C34	*28.5 ± 1.9				
Pristane	*74.1 ± 5.8				50 (15-69)
	*56.9 ± 6.8				56 (25-100)
Phytane Sum alkanes (C14-C34)	30.910				11 000 (5600-21 000)
Total aromatics					*5800 (750-16000)
Resolved aromatics					
Unresolved aromatics					*350 (150-500) *8100 (3900-17000)
	*3 15±0 26	*2.74 ± 0.52	*4_2 ± 0.4	*6 ± 2	
Acenaphthene	*3.15 ± 0.26	*4.60 ± 0.88	4-2 1 0.4	*4 ± 1	*3.4 (3.3–7.0)
Acenaphthylene	*5.25 ± 0.38		*8 ± 4	*5.4 ± 2.2	14 /4 02 \
Anthracene	6.1 ± 1.7	6.1 ± 1.7	"0 I 4	"3.4 I 2.2	14 (4-93)
Anthranene	*1.15 ± 0.31	*1.15 ± 0.31	20 24 : 0 70	*25   7	25 (14 22)
Benz[a]anthracene	32.5 ± 4.7	$32.5 \pm 4.8$	20.34 ± 0.78	*25±7	25 (14–32)
Benzo[b]chrysene	*1.60 ± 0.15	*40.10	$1.07 \pm 0.15$	*2.1 ± 0.4	
Benzo a fluoranthene	*4.0 ± 1.9	*4.0 ± 1.9	11.01.000	*50.45	×07 /22 25)
Benzo[b]fluoranthene	46.4 ± 3.7	46.4 ± 4.0	11.01 ± 0.28	*58 ± 15	*37 (33-37)
Benzo[j]fluoranthene	*20.5 ± 1.7	*20.5 ± 1.8	*4.6 ± 0.2	*23 ± 2	10 (15 07)
Benzo[k]fluoranthene	20.18 ± 0.84	$20.2 \pm 1.0$	*4 ± 1	24.1 ± 3.4	19 (15–27)
Benzo[ghi]fluoranthene	*28.3 ± 5.5	220.22	0.50 0.40	107 11	
Benzo[ghi]perylene	22.0 ± 2.2	$22.0 \pm 2.3$	$9.53 \pm 0.43$	19.7 ± 4.4	20 (17-35)
Benzo[c]phenanthrene	*19.5 ± 6.7	45.50 0.00	*9.4 ± 0.3	*31 ± 2	
Benzo[a]pyrene	$15.63 \pm 0.65$	$15.63 \pm 0.80$	$8.35 \pm 0.72$	*7 ± 3	20 (16–22)
Вепzо[е]ругепе	$84.0 \pm 1.9$	$84.0 \pm 3.2$	13.1 ± 1.1	$89.3 \pm 6.3$	26 (19–33)
Biphenyl	$*5.11 \pm 0.32$	$*4.68 \pm 0.56$	$*6.8 \pm 0.6$	*8 ± 1	
Chrysene	$44.2 \pm 2.3$	$44.2 \pm 2.7$	*49 ± 2	*59 ± 10	40 (25-49)
Dibenz[a,h]anthracene			$1.41 \pm 0.19$		*4.5 (2.6-160)
Dibenz[a,h]anthracene/	*3.00 ± 0.20	*3.00 ± 0.16	* 2.0 ± 0.2	$*3.5 \pm 0.5$	
dibenz[a,c]anthracene					
Dihenz[a,j]anthracene	*1.247 ± 0.075	*1.247 ± 0.084			
Fluoranthene	$163.7 \pm 9.1$	$163.7 \pm 10.3$	$38.7 \pm 1.0$	166 ± 12	88 (57-110)
Fluorene	$*5.72 \pm 0.91$	*4.69 ± 0.34	$10.24 \pm 0.43$	*7 ± 1	*6.5 (4.6-1600)
Indeno[ 1,2,3-cd ]pyrene	$14.2 \pm 2.8$	$14.2 \pm 2.8$	$4.84 \pm 0.81$	$12.2 \pm 2.9$	33 (20-53)
1-Methylnaphthalene	$*5.3 \pm 1.8$	$*3.47 \pm 0.85$	*16 ± 5	*21 ± 5	*13 (6.5-15)
2-Methylnaphthaleпе	*10.2 ± 1.5	*6.48 ± 0.85	*18 ± 5	*23 ± 4	*16 (9-23)

(Continued on next page)

Table 1 (continued)

Code	SRM 1974a	SRM 2974	SRM 2977	SRM 2978	140/OC
1-Methylphenanthrene	*10.5 ± 4.8	*10.5 ± 4.8	*44±2	*6.8 ± 0.1	11 (9-14)
2-Methylphenanthrene	$*20.6 \pm 8.0$	$*20.6 \pm 8.0$	*43 ± 1		19 (15-40)
3-Methylphenanthrene	*13.5 ± 9.7	*13.5 ± 9.7	$*44.2 \pm 0.4$		,
4-Methylphenanthrene/	*14.7 ± 9.2	*14.7 ± 9.2	*36 ± 2		
9-methylphenanthrene					
Naphthalene	$23.5 \pm 4.4$	$*9.63 \pm 0.61$	*19 ± 5	*31 ± 6	17 (9-43)
Perylene	$7.68 \pm 0.27$	$7.68 \pm 0.35$	$3.50 \pm 0.76$	$4.09 \pm 0.32$	*5 (2.5-9.8)
Phenanthrene	$22.2 \pm 2.4$	22.2 ± 2.5	$35.1 \pm 3.8$	*74 ± 7	76 (40-110)
Ріселе			$2.29 \pm 0.27$	$*4.5 \pm 0.5$	. ,
Ругепе	151.6 ± 6.6	$151.6 \pm 8.0$	$78.9 \pm 3.5$	$256 \pm 21$	67 (46-79)
Triphenylene	$50.7 \pm 5.9$	$50.7 \pm 6.1$	*39 ± 1	*63 ± 9	, ,
UVF chrysene					*3500 (1200-5400)
UVF ROPME oil					*29 000 (11 000-39 000)

For non-IAEA materials, values preceded by an asterisk (\*) are non-certified; all other values are certified. For IAEA materials, values preceded by an asterisk are classified as information values; all other values are classified as recommended.

<sup>1</sup>The following comments apply to these tables: the compiled tables are for information. Although every effort has been made to ensure that these tables are accurate, users of CRMs should consult vendors for full and accurate information; certified calibration materials and standards are not included; these tables do not purport to be complete and all the CRMs listed may not be commercially available; methyl mercury is not considered as an organic contaminant for the purposes of this list.

<sup>2</sup>NIST: USA National Institute of Standards and Technology. IAEA: International Atomic Energy Agency. BCR: EC Bureau of Community Reference, now EC Institute for Reference Materials and Measurements (IRMM). NRC: Canada National Research Council, Institute for National Measurement Standards (INMS). NWRI: National Water Research Institute, Environment Canada. CIL: Cambridge Isotope Laboratories, USA. NIES: National Institute for Environmental Standards, Environment Agency, Japan; LGC: Laboratory of the Government Chemist.

Europe), which started as a European research project, but later continued on its own as a proficiency testing scheme [8]. This QUASIMEME programme not only includes organic contaminants, but also trace metals, nutrients and many other parameters which are relevant in marine environmental monitoring. Meanwhile, the IAEA (International Atomic Energy Agency) had conducted several interlaboratory studies which resulted in a number of CRMs. Other developments took place in the USA and Canada and also in Japan, resulting in a number of CRMs for organic contaminants which will be discussed below.

The criteria used by the organisations responsible for producing CRMs are sometimes different and are often subject of debate. One of the best definitions of a CRM is presumably the following: a CRM is a reference material (RM), one or more properties of which are certified, with a stated uncertainty, by a technically valid procedure, which are traceable to a stated reference and accompanied by a certificate or other documentation issued by an accreditation body, to be used for the evaluation of the method(s) used by the laboratory [9]. Not all CRMs discussed below comply

with this definition. Some materials were just 'certified' as a result of an interlaboratory study only. Obviously, that did not include a technically valid procedure. Such materials should not be confused with CRMs which have been submitted to a very thorough process of certification by expert laboratories only followed by an extensive technical discussion. Laboratories should inform themselves about the background of available CRMs before they buy these relatively expensive materials. If a CRM is bought which has e.g. relatively wide uncertainties for a number of parameters, this could even be counter-productive as the laboratory might soon conclude that their methods comply with the certified values whereas in reality the results produced are only at one end of the wide uncertainty range and therefore relatively far away from the target value. Awaiting a definition of minimum requirements for the production of CRMs and the registration and accreditation of producers, laboratories should be very critical when buying and using the available CRMs. This is particularly true for the field of organic contaminants as errors can easily be made, and uncertainty ranges may soon become relatively wide.

Table 2 RMs for chlorinated pesticides in biota

	SRM 1974a	SRM 1588a	SRM 1945	SRM 2974	SRM 2977	SRM 2978	140/OC	BCR 598
Organisation	SRM NIST	SRM NIST	SRM NIST	SRM NIST	SRM NIST	SRM NIST	IAEA	BCR <sup>2</sup>
Country of origin	USA	USA	USA	USA	USA	USA	Monaco	EC
Matrix	Mussel tissue	Cod liver oil	Whale blubber	Mussel tissue	Mussel tissue	Mussel tissue	Fucus (sea plant homogenate)	Cod liver oi
Units	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg	μg/kg
As	Dry weight	Wet weight	Wet weight	Dry weight	Dry weight	Dry weight	Dry weight	Wet weight
[ ± ] expressed as	± 95% CI	± 95% CI	± 95% CI	± 95% CI	± 95% CI	± 95% CI	95% CI	95% CI
Units of issue	3×15 g	5×1.2 ml/ ampoule	Set 2, 15 g/ ampoule	8 g	10 g	10 g	30 g	5 g
Form	Frozen	Oil	Frozen	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried and micronised	Oil
Hexachloro- benzene		157.8 ± 5.0	$32.9 \pm 1.7$				*1.3 (0.35-3.3)	55.7 ± 2.0
α-HCH		$85.3 \pm 3.4$	$16.2 \pm 3.4$				*1.4 (1.3-1.5)	42 ± 3
В-НСН			*8.0 ± 1.4				4.6 (2.4-9.5)	16±3
γ-HCH		24.9 ± 1.7	$3.30 \pm 0.81$				*11 (5.4-16)	23 ± 4
Aldrin							*0.76 (0.5-4.5)	
trans-Chlordane	$16.6 \pm 1.7$	*52 ± 7		$16.6 \pm 1.8$		$11.38 \pm 0.56$	,	6.9 ± 1.6
cis-Chlordane	$17.2 \pm 2.8$	167.0 ± 5.0	$46.9 \pm 2.8$	$17.2 \pm 2.9$	$1.42 \pm 0.13$	$15.56 \pm 0.83$	*1.4 (0.36-2.8)	24.4 ± 1.8
Heptachlor							*3 (0.99-4.4)	
Heptachlor		$31.6 \pm 1.5$	$10.8 \pm 1.3$				*0.79 (0.32-1.4)	
epoxide							,	
trans-Nonachlor	$18.0 \pm 3.6$	$214.6 \pm 7.9$	$231 \pm 11$	$18 \pm 3.6$	$1.43 \pm 0.10$	$11.5 \pm 1.0$		$39 \pm 4$
cis-Nonachlor	$6.84 \pm 0.90$	$94.8 \pm 2.8$	$48.7 \pm 7.6$	$6.84 \pm 0.92$		$8.23 \pm 0.56$		
Dieldrin	*6.2 ± 1.3	$155.9 \pm 4.5$	*37.5 ± 3.9	*6.2 ± 1.3	$6.04 \pm 0.52$	$6.30 \pm 0.67$	1.7 (0.72-2.8)	$59 \pm 4$
Oxychlordane		*38 ± 4	$19.8 \pm 1.9$			$2.13 \pm 0.27$		$11.0 \pm 1.8$
2,4'-DDE	*5.26 ± 0.27	$22.0 \pm 1.0$	$12.28 \pm 0.87$	$*5.26 \pm 2.8$		$4.41 \pm 0.56$		
4,4'-DDE	$51.2 \pm 5.5$	651 ± 11	$445 \pm 37$	$51.2 \pm 5.7$	$12.5 \pm 1.63$	$37.5 \pm 1.5$	1.2 (0.86-1.6)	$610 \pm 40$
2,4'-DDD	*13.7 ± 2.8	$36.3 \pm 1.4$	$18.1 \pm 2.8$	*13.7 ± 2.8	$3.32 \pm 0.29$	$10.5 \pm 1.0$	` ′	$30 \pm 4$
4,4'-DDD	$43.0 \pm 6.3$	254 ± 11	$133 \pm 10$	$43 \pm 6.4$	$4.30 \pm 0.38$	$38.8 \pm 2.3$	0.7 (0.61-0.90)	400 ± 30
2,4'-DDT	*8.5 ± 1.9	$156.0 \pm 4.4$	$106 \pm 14$	*8.5 ± 1.9		9.2 ± 1.6	,	
4,4'-DDT	$3.91 \pm 0.59$	$524 \pm 12$	$245 \pm 15$	$3.91 \pm 0.60$	$1.28 \pm 0.18$	$3.84 \pm 0.28$	2.2 (1.4-3.6)	179 ± 18
Mirex		*16 ± 3	$28.9 \pm 2.8$					
Endrin							*0.71 (0.43-1.6)	

For non-IAEA materials, values preceded by an asterisk (\*) are non-certified; all other values are certified. For IAEA materials, values preceded by an asterisk are classified as information values; all other values are classified as recommended.

## 2. CRMs for PAHs

An overview of the available CRMs for organic contaminants in biota is given in Tables 1–5. A similar overview for organics in sediments in given in Tables 6–13. Only five materials are available for PAHs in biota: four mussel tissues of the US National Institute for Standards and Technology (NIST) and a sea plant homogenate of the IAEA (Table 1). Two mussel materials are almost similar, showing only some minor differences in their certified values due to freeze-dry losses. One material (1974a) is offered as wet, frozen material [10], the other one (2974) is freeze-dried. The wet material is, however, not shipped to Europe. The freeze-dried material is available in Europe, but is rela-

tively expensive (\$ 470 for 8 g). Two new NIST freeze-dried mussel tissue materials, SRM 2977 and 2978, are available and SRM 2977 has lower PAH values than the other three NIST mussel tissue materials. Obviously, this very limited number of PAH CRMs is insufficient to serve the market. PAHs are metabolised in fish, so there is no need for that matrix, but more shellfish CRMs are required, particularly in Europe. The analysis of PAHs in mussels is included in several international marine monitoring programmes. In addition, the analysis of PAHs in shellfish is often required during surveys following oil pollution incidents. The production of CRM PAHs in shellfish, preferably a wet material, is therefore of high priority.

Tables 6 and 7 show that there are 18 CRMs for PAHs in sediment. These include harbour sediments, estuarine sediment, and lake sediments. Remarkably, no marine sediment is included, not even from coastal waters, in spite of the fact that PAHs are regularly analysed within the framework of various marine monitoring programmes. Apparently, relatively low PAH levels as occur in marine sediments, still cause problems for the laboratories, so certification of PAHs in such materials was not possible until now. The Canadian materials EC-1 to EC-8 also have PAH values. However, generally the materials with relatively low PAH levels (below 1 mg/kg) provide only non-certified values. This situation of course also rises doubt on the quality of data obtained for PAHs in marine monitoring programmes.

The NIST 1944 sediment is the most complete CRM with 56 PAHs, most of which have been certified, and includes non-certified reference values for many alkylated PAHs.

# 3. CRMs for OCPs

Eight CRMs are available for OCPs in biota (Table 2). These include two cod liver oils, four mussel tissues, a whale blubber, and a sea plant homogenate. As described above, the two NIST mussel samples 1974a and 2974 are identical, one being a wet material and one being the same material, but freezed-dried (see Section 2). The other wet material is the whale blubber [11]. Unfortunately, the whale blubber cannot be sent to countries outside the USA, due to restrictions on transportation of marine mammal materials. The availability of more wet CRMs would be beneficial to the laboratories. Wet materials have the advantage of allowing the user to control his extraction step, which cannot be done with an oil and which is normally less reliable when using a freeze-dried material. In addition, wet materials have realistic concentrations which are lower than those in oils or freezedried materials, and are therefore better comparable with samples that are being analysed in the laboratory's routine monitoring work. Table 2 shows that most CRMs indeed have OCP concentrations that are much higher than concentrations which can normally be found in marine fish samples (ca. 0.1-2 ng/g).

Proper CRMs for OCPs in sediments are hardly available (Table 8). In fact only the NIST SRM 1944

is certified for four OCPs: HCB, *cis*-chlordane, *trans*-nonachlor and *p,p'*-DDT and SRM 1939a has only three certified values. Two new IAEA sediments, IAEA 383 and IAEA 408, have information values for a wider range of OCPs. So, for a large number of OCPs there is no sediment CRM at all. Although OCP concentrations are decreasing in many coastal waters, OCPs are still being monitored, which is also true for many freshwater locations. Consequently, CRMs for OCPs in sediments is another high priority item for CRM producers.

# 4. CRMs for PCBs

Twelve materials are available as CRMs for PCBs in biota (Table 3). These include two cod liver oils, a mackerel oil, five mussel tissues, a carp, a whale blubber and a sea plant homogenate. The mussels are the NIST materials 1974a, 2974, 2977 and 2978 discussed above and BCR 682. The whale blubber has also been discussed as regards its transport restrictions (see CRMs for OCPs). As for OCPs the fish oil has the disadvantage of unrealistic high levels of PCBs. In addition, the cod liver oil (BCR 349) and the mackerel oil (BCR 350) originate from 1986 and are relatively old now. As newer analytical techniques such as newer gas chromatography (GC) mass spectrometry systems and multidimensional GC techniques were not available at the time of production, some of the certified values may be biased to some extent as some co-elution, e.g. for the CBs 101 and 138 were not observed during the certification [12,13]. The recently produced sterilised wet mussels (BCR CRM 682) are presumably of a better quality. This is the first wet, sterilised material that was produced as CRM for PCBs. It has realistic PCB concentrations which correspond with values which have to be determined by laboratories in marine monitoring programmes. The CRM is packed in tins which can easily be transported and stored at room temperature for a long time. It is also the only CRM for PCBs with a certified value for CB 138. In the other CRMs CB 138 was determined as the sum of the CBs 138 and 163 or 138, 163 and 164. The IAEA sea plant homogenate does not include more detailed information on a possible separation of these CBs, but most likely the certified value is only valid for the sum of the three CBs. Another CRM PCB in wet sterilised herring has recently been certified for 13 PCBs, including CB 138 as a single compound. This

Table 3 RMs for PCBs in biol

Code	SRM 1974a	SRM 1588a	SRM 1945	SRM 2974	SRM 2977	SRM 2978	140/OC	CARP-1	BCR 349	BCR 350	BCR 682	EDF 2524	EDF 2525
Organisation Country	SRM NIST USA	SRM NIST USA	SRM NIST USA	SRM NIST USA	SRM MIST USA	SRM NIST USA	AEA Monaco	NRC Cana Ju	BCR	BCR EC	BGK	CIL USA	CIL USA
Matrix	Mussel	Cod liver	Whale	Mussell	Mussell	Mussel	Fucus (sea plant homogenate)	Сатр	Cod fiver	Mackerel	Mussela	Cilan natural matrix (5 h	Chan Contaminated natural natural natural natural
Units. As [3]	µg, g Dryweig i ±95% C	µg/ r Wet eight +95% C	We weight	118 12 Dry Will 11 ± 9 %	ju. kg D. weigit + 15% C.	ug/kg Dry w ± 95%	L <sup>k</sup> g Dyw <sub>B</sub> l 9.%Cl	eith: -95% C	Wet weight ±95% CI	μg/kg We weight ± 95% C	weight Weight	ng/kg Wat weight 95% CI	Wet we put
Units of same	M) M)	5×1.2 ml/	Set 2, 15 g/ empoule	Mi KO	10 g	10.8	35 %	84, 25 X	2 g. Ampoules	2 g ampoules	tin.70g	Ser 1, 10 g/ ampoole	Ser 1, 10 g./. ampoule
Florm	Frazeri	Oil	Frozen	Freeze-dried	Freezh-drind	Freezendried	Freeze-dired micronised	andSlurry	75	10	Well,	Surry	Slumy
PCB 16/32		*2.6 ± 0.8											
PCB 17	425 × 11	*6.5+1.1	4 48 -0 88	*26 S . T . S	265-030	47.4+0.6	+1 € 11 3, 1 61						
PCB 22	100	*3.0±0.6	1000	-	200	B-11 + L/+							
PCB 2M PCB 31	724.15	28.3% (1.55 8.13+0.28	*14.1 = 1.4	*79±15	5 37 ± 0.44 3.92 ± 0.24	7.91 ± 0.90 21.40 ± 0.43	1.2 (1.3-2.5)		68±7	22.5 ± 4.0	0.30 + 0.07		
PCB 33		33±14											
208 42		5643											
PCB 44	72.2±7.4	35.1±1.4	12.2±1.4	72.7±7.7	3.25 ± 0.63	11.80±0.64	11.80±0.64 *2 (1.9-2,1)		175	*44			
P.CB 45	-	11122	0			1000							
PCB 52	115 ± 11	99±084	208±28 3.6±25	115 £ 12	8.37±0.54	15,84±0.85	3.8 (2.6-4.9)	1244.32	149±20	62 ± 9	0.78±0.09		
PCB 55/60		118811											
PCB 64		1441		4.60.00.00.00.00.00.00.00.00.00.00.00.00.	N . 74 .		1 1000						
PCB 50	101.424.0	247113	23.0 ± 1.0	1014194	3,54 ± 0.32	10,44	1.0 (1.1-4.0)	-					
PCB 70/76		+27 ± 4											
PCB 74		*40 ± 4											
PCB 83		21 # 5											
PCB 87	*54±14	56.3 = 1.7	16.7 ± 1.4	-54+14	2.15 ± 0.10	10.25+0.29	1.6 (1.2-2.0)						
PCB 95	83+17	36 5+1,1	318417	83±17	5.39±0.59	20.8 ± 2.1							
PCB 97	2000	47			. 40 . 44		100000000000000000000000000000000000000						
PCB 99	1903 203	1965-43	42.4 1.3.4		07.03 50.1	18.84 ± 9.44	(871-67-07-0-6)		440.44	40.00			
PCB 101790	128.3 = 9.7	120 0 2:403	2 + 5 5 6	2017	11 0+1 0	350+16	24(12-27)	124 + 27	3705-77	62.59			
PCB 105	D E + U E S	F C + C U9	30.1+23	53+38	3.76+0149	10.85 + 0.45	0.49 (0.4-0.7)	AC + AZ			20 50 + 0 10 0 2	322 + 90	43 KG7 ± 4 D1 3
PCB 110	127.3 ± 8.6	760+20	23.3 ± 4.0	127.3±9.4	4.03 ± 0.20	35.34 ± 0.71	0.17 (0.1-0.7)	r v			70:0 = 0c:n	06 T 070	7164776074
PCB 118	$130.8\pm3.6$	176.3±3.8	74.6 ± 5.1	130.8 ± 5.3	10.5 ± 1 0	35.1 ± 1.0	1 (0 97-11)	$132 \pm 60$	456+31	143 + 20	$2.6 \pm 0.3$	691±170	76 803 + 24 096
PCB 128	$22.0\pm3.4$	47.0 + 2.4	23.7 ± 1.7	22 ± 3.5	2.49+0.28	5,25 ± 0 17			*104	*41			

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Code	SRM 1974a	SRM 1588a	SRM 1945	SRM 2974	SRM 2977	SRM 2978	140/OC	CARP-1	BCR 349	BCR 350	BCR 682	EDF 2524	EDF 2525
PCB 136		*14±2											
PCB 137		*16±2											
PCB 138							1.7 (1.2-2.6)				4.6±0.8		
PCB 138/163									*765	*274			
PCB 138/	$133.5 \pm 9.5$	263,5 ± 9,1	131,5+7,4	134±10	16.6±1.6	35.7±1.5		102±23					
163/164													
PCB 141		*24 ± 4											
PCB 146		*39 ± 6											
PCB 149	87.6 ± 2.3	105.7 ± 3.6	106.6 + 8.4	87.6 ± 3.5	9,23 ± 0.12	$34.73 \pm 0.69$	1.2 (1.1-1.6)				5.7±0.6		
PCB 151	256±35	54.8 ± 2.1	28.7 ± 5.7	25.6+3.6	3.07 ± 0.18	10,92 ± 0,25							
PCB 153	$145.2 \pm 7.6$	273.8 + 7.7	213 ± 13	145.2 + B.B	14.1±1.0	56.9 ± 3.5	1.7 (1,3-3.1)	83 ± 39	938±40	317±20	9.2 ± 0.8		
PCB 156	7 43 ± 0 99	27.3 ± 1.8	10.3 ± 1.1	7.4+1.0	0.960 ± 0.085 1.97 ± 0.11	1.97 ± 0.11	0.17 (0.08-0.36)						
PCB 158		*21±2											
PCB 170	5.5+1.1	46.5±1.1		5.5 ± 1.1	2.95±0.23	*7±2	10.21 (0.16-0.76)				0.17 ± 0.05		
PCB 170 / 190			40.6+2.6					22 ± 8					
PCB 180	$17.1 \pm 3.8$	$105.0 \pm 5.2$	106.7 ± 5.3	17.1 + B.B	6.79±0.67	7.81±0.63	0.43 (0.38-0.52)	46±14	280 ± 22	73 ± 13	0.77 ± 0.07		
PCB 172 / 197		*17±4											
PCB 174		*41±10											
PCB 177		*4.8 ± 0.8											
PCB 178 129		*29±1											
PCB 179		*4.4 ± 1.2											
PCB 183	16.0 ± 2.4	$31.21 \pm 0.62$	36.6±4.1	16.0 + 2.4	1.33 ± 0.10	5.25±0.15							
PCB 187			105.1 ± 9.1				*0.38 (0.30-1.2)						
PCB 187 182								36±16					
PCB 187/	3 + 0 + 2 3	$35.23 \pm 0.83$		34.0 ± 2.5	4.76±0.38	16.7±1.3							
159/182													
PCB 189		*2.9 ± 0.6											
PCB 191		*4.5 ± 0.7											
PCR 193		*14±3											
PCB 194		15.37 ± 0.61	396+25		0.897±0.042				*38				
PCB 195		*4.6 ± 0.6	17.7 ± 4.3										
PCB 196/23		*24±3											
PCB 199		*17+2											
PCB 201		12.18 ± 0.46	16.96 + 0.89										
PCB 206		3.4±1.6	31.1+2.7										
PCB 209		*35±10	10.6 ± 1,1										

For non-IAEA materials, values preceded by an asterisk (\*) are non-certified; all other values are certified. For IAEA materials, values preceded by an asterisk are classified as information values; all other values are classified as, recommended.

Table 4 RMs for chlorinated dioxins, furans and non-ortho PCBs in biota

Code	SRM 1588a	CARP-1	EDF 2524	EDF 2525	EDF 2526	140/OC
Organisation	SRM NIST	NRC	CIL <sup>2</sup>	CIL	CIL	IAEA
Country of origin	USA	Canada	USA	USA	USA	Мопасо
Matrix	Cod liver oil	Common carp	Clean natural matrix (fish)	Contaminated natural matrix (fish)	Fortified fish	Fucus (sea plant homogenate)
Units	μg/kg	ng/kg	ng/kg	ng/kg	ng/kg	µg/kg
As	Wet weight	Wet weight	Wet weight	Wet weight	Wetweight	Dry weight
[±] expressed as	± 95% CI	± 95% CI	95% CI	95% CI	95% CI	95% CI
Units of issue	5 × 1.2 ml/ ampoule	6×9 g	Set 1, 10 g/ ampoule	Set 1, 10 g/ ampoule	Set 1, 10 g/ ampoule	30 g
Form	Oil	Slurry	Slurry	Slurry	Slurry	Freeze-dried and
		,	/	,	/	micronised
2,3,7,8-TCDF		$11.9 \pm 2.7$	$2.5 \pm 0.16$	22 ± 1.6	17 ± 1.5 (25) <sup>b</sup>	
1,2,3,7,8-PCDF		$5.0 \pm 2.0$	NDa	$4.9 \pm 0.56$	$40 \pm 3.7 (50)$	
2,3,4,7,8-PCDF			ND	14 ± 1.3	38 ± 3.5 (50)	
1,2,3,4,7,8-HxCDF			ND	$8.2 \pm 3.7$	$80 \pm 8.4 (75)$	
1,2,3,6,7,8-HxCDF			ND	2.7 ± 1.2	63 ± 5.5 (75)	
1,2,3,7,8,9-HxCDF			ND	$0.76 \pm 0.35$	58 ± 7.0 (75)	
2,3,4,6,7,8-HxCDF			ND	2.3 ± 1.9	60 ± 5.5 (75)	
1,2,3,4,6,7,8-HpCDF			ND	$4.4 \pm 6.0$	83 ± 9.2 (100)	
1,2,3,4,7,8,9-HpCDF			ND	$0.63 \pm 0.23$	73 ± 7.7 (100)	
OCDF	*1.00		ND	2.6 ± 1.3	190 ± 22 (100)	
1,2, <b>7</b> -TriCDD	*0.32				, ,	
1,2,3,4-TCDD	*0.38					
2,3,7,8-TCDD	*0.21	$6.6 \pm 0.6$	ND	17 ± 1.4	19 ± 1.4 (25)	
1,2,3,7,8-PCDD		$4.4 \pm 1.1$	ND	$4.0 \pm 0.57$	40 ± 3.0 (50)	
1,2,3,4,7,8-HxCDD		$1.9 \pm 0.7$	ND	$0.77 \pm 0.27$	60 ± 4.8 (75)	
1,2,3,6,7,8-HxCDD	*0.39	$5.6 \pm 1.3$	ND	$3.0 \pm 1.2$	56 ± 4.8 (75)	
1,2,3,7,8,9-HxCDD	*0.22	$0.7 \pm 0.4$	ND	$0.79 \pm 0.26$	60 ± 4.4 (75)	
1,2,3,4,6,7,8-HpCDD		$6.5 \pm 1.8$	ND	$1.4 \pm 0.53$	76 ± 5.9 (100)	
OCDD	*1.01	$6.3 \pm 1.9$	ND	$7.2 \pm 3.7$	192 ± 14 (350)	
PCB 77			$13.8 \pm 7.0$	1945 ± 354	619±107 (600)	*0.19 (0.04-6.9)
PCB 126			$3.9 \pm 1.8$	647 ± 148	1140 ± 465 (600)	( 2.7/
PCB 169			1.8 ± 2.3	50 ± 12	1416 ± 553 (600)	

Table 5 RMs for organotin compounds in biota

Antifouling	BCR 477	NIES 11
Country of origin	EU	Japan
Matrix	Mussel tissue	Fish tissue
Units	mg/kg	mg/kg
As	Dry weight	Dry weight
[ ± ] expressed as	1/2-width of 95% CI of mean	2×S.D.
Units of issue	14 g	20 g
Form	Dried	Freeze-dried
Triphenyltin (as chloride)		*6.3
твт	$2.2 \pm 0.19$	$1.3 \pm 0.1$
DBT	$1.54 \pm 0.12$	
MBT	$1.50 \pm 0.28$	

Values preceded by an asterisk (\*) are πon-certified; all other values are certified.

<sup>&</sup>lt;sup>a</sup>ND – not detected.

 $<sup>^{\</sup>mathrm{b}}\mathrm{Figure}$  in brackets represents the amount of each analyte added to the matrix.

material (BCR CRM 718) is waiting for the last stability tests and is expected to become available in 2001. The advantage of the NIST materials is that they give certified values for a broad range of PCB congeners, whereas the BCR materials and the carp CRM of the National Research Council (NRC, Canada) have only certified values for a limited number of PCBs, although those PCBs are the ones which are being analysed for monitoring purposes. In particular, the cod liver oil, NIST SRM 1588a, contains a large suite of certified and reference values for PCBs. Recently, NIST has certified a new CRM, coded SRM 1946 [14]. This CRM has been certified for fatty acids but includes certified values for 10 PCBs and three OCPs.

There are 18 RMs for PCBs in sediment, of which eight contain certified values. Some of them (NRC CS-1, NWRI EC-1 and EC-2) have only been certified for total PCB (Tables 9 and 10). The list includes harbour sediments, estuarine sediments and lake sediments. As for OCPs, no marine sediment is available, whereas PCBs are frequently monitored in marine monitoring programmes such as the Joint Monitoring and Assessment Programme (JAMP) of the Oslo and Paris Commissions. The SRM 1944 offers the most complete set of certified values, including 35 PCBs (some in combination). Wet sediments have not been produced until now. Recently, wet sediments have successfully been used in interlaboratory studies within the QUASI-MEME programme [15]. This shows that in principle the technology for producing wet sediment CRMs is available. Wet sediment CRMs for PCBs would be a useful addition to the current list.

# 5. CRMs for PCDDs, PCDFs and dioxin-like PCBs

There are six CRMs for PCDDs, PCDFs and dioxin-like PCBs in biota: a cod liver oil, a carp, three unidentified fish samples of which one has been spiked, and a sea plant homogenate (Table 4). The NIST 1588a cod liver oil has only indicative values for these contaminants, whereas the carp CRM CARP-1 only has certified values for a limited number of PCDDs. The two fish CRMs produced by Cambridge Isotope Laboratories comprise a rather complete set of PCDDs, PCDFs and dioxin-like PCBs. The uncertainty ranges are, however, relatively large for the unspiked material (ca. 30–140% for some PCDDs and PCDFs and PCB 169)

and EDF 2524 mostly has values given as nondetected. A candidate CRM for non-ortho PCBs (77, 81, 126 and 169) in chub has been prepared for BCR. This material is currently being certified and, in case that will be successful, it will become available in 2002. Obviously, also here is a clear need for more CRMs. Particularly since the Belgian dioxin crisis in 1999 [16], discussions on new maximum residue limits for PCDDs, PCDFs and dioxinlike PCBs are taking place at national levels and in the European Union [17,18]. From these discussions it becomes clear that the highest risks can be found in fish and in animal feed based on fish products, particularly because the dioxin-like PCBs have relatively high contribution to the total TCCD equivalent. Although this rather serves the food control laboratories than environmental laboratories, it is clear that there is a need for CRMs for PCDDs. PCDFs and dioxin-like PCBs in fish, next to such CRMs for other food stuffs and animal feed. Such CRMs for fish should include certified values for all PCDDs, PCDFs and dioxin-like PCBs which have been given a TCDD equivalency factor by the World Health Organisation (WHO) [19]. Given the possible relatively strict maximum residue limits which may be proposed, such CRMs are of high priority.

Table 11 shows that there are seven sediment CRMs for PCDDs, PCDFs and dioxin-like PCBs. Unfortunately, the EC-1 to EC-3 sediments only contain indicative values for the three non-ortho PCBs, whereas the other five sediments only have indicative (NIST SRM 1944, NWRI DX-3) or certified values (NWRI DX-1 and DX-2) for the PCDDs and PCDFs. The CIL material has been fortified. A preferably unspiked sediment CRM in which both dioxin-like PCBs and PCDDs and PCDFs would be certified would be most welcome.

# 6. CRMs for chlorinated benzenes

There are no CRMs for chlorinated benzenes in biota. Only HCB is certified in a number of OCP CRMs (Table 2). Table 12 shows eight CRMs which all have predominantly indicative values for chlorinated benzenes, hexachlorobutadiene, and octachlorostyrene in sediments. These materials, EC-1 to EC-8, were all made available by the National Water Research Institute (NWRI), Canada. No European CRMs are available for chlorinated benzenes in biota. HCB is certified in three sedi-

Table 6 RMs for hydrocarbons in sediments

45.0	1 022	110.30	AR SH	2 30	2.30	CHEL ADDAR	THE YOUR	TAPA ADD	arm erc	2012
Code	SES-	HS-5H	HS-4B	AS O	HS-6	SIRM 1944"	IAEA 383	IAEA 408	BCR 535	CC 6188
Organisation	NRC-CNRC	NRC-CHRI	NRC CNRC	NRC-CARC	NRC-CMRC	SRM NIST	IAEA	IAEA	BCR	רמכ
Marrix	Estuarine sedim n	Karbur sedim m	H rbur	Harbour sediment	Harbour sediment	now York New Jersey, Waterway, sedimini	Scalment Tagus Estriary mudflats	voligeo Sediment Ven ce agoon		River sedi- ment
Units As [ x ] expressed as	mg, kg Dry wegiit	mg kg Dry weight 90% CI	mg/kg Dry weight 90% Cl	mg/kg Dry weight 90% Cl	mg / kg Dry weigrt 909. СІ	mg, kg D-y weignt 95 . СI	µв чевт Dr. we.grt 95% СІ	pe, kg Dryweight 959, Cl	mg kg D weigh 1/2-w-dth of 95% CI	mg / k. Dry vir.glii 1/2-width or 95% Cl
Units of Issue Form	700 g Freeze-dried	700 g 100 g Freeze-dried Freeze-dried	100 g Freeze-dried	100 g Freeze-dried	100 g Freeze-dried	50 g Freeze-dried	35 g Freeze-dried ∵. 250 µm	40 g Freeze-dried, 750 gm	40 g Dred	30g Ar-dred
Acenaphthene Acenaphthylme	127.	$1.25 \pm 0.02$ $0.6 \pm 0.10$	$0.09 \pm 0.02$ 0.3 + 0.10	0.23 ± 0.10	$0.23 \pm 0.07$ $0.19 \pm 0.05$	*0.57 ± 0.03	16 (13–21) 47 (31–59)	*3.3 (2 0-17) *3.6 (2 1-4 7)		*0.07±0.02 *0.1
Anthracene	1.63	$2.76 \pm 0.06$	0.46 ± 0.06	$0.38 \pm 0.15$	1.1 ± 0.4	$1.77 \pm 0.33$	30 (25-34)	9.8 (8 0-13)		*0.36±0.11
Benzo[a anmazene Benzo b chrysene	181	7 91 ± 0.09	46 ± 0.09	29±12	1,8 ± 0,3	$4.72 \pm 0.11$ $0.63 \pm 0.10$	105 (83-130)	53 (35-60)	154±0.10	*0.83±0.18
Binzo a filorarithene Binzo bifio a cheni Binio kifio antime				2.0±0.15	7.8 ± 0.6 43 ± 0.15	$0.78 \pm 0.12$ $3.87 \pm 0.42$ $2.30 \pm 0.20$	50 96-190) 73 (48-76)	46 (32-69) 46 (26-61)	2 29 ± 0.15 1 09 ± 0.15	*0.82±0.19
Benzol b,k Morambere (combined value)		12.8±0.12	3.32 ± 0.12							
Benzol Jfluoranthene Benzol a Javrene	*1.21	5,80 ± 0.15	1.55±0.15	1.7 ± 0.8	2,2 ± 0,4	2 U9 ± U.44 4.30 ± 0.3	120 (77–140)	48 (30-63)	1.16±0.10	*0.65±0.14
Bénzol e pyrene Benzol ghi Jperylene Birhenyl Chrysene / miphenylene	*1.27	$3.88 \pm 0.15$ $0.41 \pm 0.02$	$1.23 \pm 0.15$ $0.04 \pm 0.002$	1.3 ± 0.3	1,78±0,72	2,84±0.10	190 (120-210) 190 (69-230) *29 (19-30)		C	*0.36±0.13
Chrynen∉ Coronene	+1.32	$8.77 \pm 0.11$ $0.83 \pm 0.04$	$1.76 \pm 0.11$ $0.31 \pm 0.04$	2.8±0.9	2.0 ± 0.3	4.86±0.10	170 (120–220)	35 (25-56)		*0.83±0.16
Dibenz [a,h]anthracene Dibenz [a,c]anthracene Dibenz [a,j]anthracene Oibenz [a,j]aprene	+1.30	0.89 ± 0.04	0.34 + 0.04	0.2 ± 0.1	0.49±0.16	$0.424 \pm 0.069$ $0.335 \pm 0.013$ $0.50 \pm 0.044$	*20 (18-41)	*11 (7.8-14)		*0.13 ± 0.05
Dibenzoi uran Dibenzoi hiaphishe 2,a Dimethylnaphihalena		1.19±0.02	0.11 ± 0.02			*0.62 ± 0.01	*13 (7.1–2.3)			
Fluoranthene Fluorane Indeno[ 1,2,3-cd   pyrene	1.58	25.33±0,11	3.33 ± 0.11 0.15 ± 0.04	8.4±2.6 0.4±0.1	3.54±0.65 0.47±0.12 1.95±0.58	8.92±0.32 *0.85±0.03 2.78±0.10	290 (260-350) 27 (24-34) *150 (130-160)	84 (53-110) *6.7 (4.6-24) *51 (45-53)	1.56±0.14	-1.79±0.35 -0.12±0.04 -0.37±0.14
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Code	SES-1	HS-3B	HS-4B	HS-5	HS-6	SRM 1944*	IAEA 383	IAEA 408	BCR 535	LGC 6188
1-Methynaphthalene 2-Methynaphthalene 1-Methylphenanthrene 2-Methylphenanthrene 3-Methylphenanthrene		0.73 ± 0.02	0.16 ± 0.02			*0.52±0.08 *0.95±0.05 *1.7±0.1 *1.90±0.60 *2.1±0.1	14 (11-28) *36 (26-43) 24 (18-28) 31 (24-38)	*7.5 (4.7–12) *14 (13–33) *10 (9.2–11) *12 (12–14)		
4-Methylphenanthrene 9-methylphenanthrene Naphthalene	*3,62	2.14±0.02	0.22 ± 0.02	0.25 ± 0.07	4.1 + 1.1	*1.6±0.2	96 (52-110)	27 (16-47)		*0.22±0.11
Perylene Phenanthrene	* 1.37	18.8 ± 0.08	1.91 ± 0.08	5.2 ± 1.0	3.0 ± 0.6	1,17 ± 0.24 5.27 ± 0.22 6.70 ± 0.42	58 (41–130) 160 (140–190) 280 (210–350)	320 (140-420) 35 (21-43) 77 (57-93)	250+018	*1.04 ± 0.30
Pyrene Picene Triphenylerie Benzo[c]phenanthrene Pentaphene	¥4.	18 + 0.10	2.55 ± 0.10	5.64 + 1.60 - 1.60	3.U ± U.b	9.70±0.42 0.518±0.093 1.04±0.27 0.76±0.10 0.288±0.026	280 (210-350)	(26-22)	2.52±0.18	1.48±0.50
n-C17 n-C18 Pristane Phytane							380 (330-470) *83 (42-230) *87 (36-240) *57 (43-150)	74 (56-140) *90 (60-110) 69 (50-130) 78 (63-130)		
Resolved aliphatics Unresolved aliphatics							*9 600 (6700- 24000) *52 000 (11 000- 79 000)	11 000 (6400- 17 000) - *110 000 (68 000- 150 000)		
Total aliphatics							*52000 (14000- 85000)			
Sum alkanes (C14-C34)							*6100 (5300- 6800)	8100 (4300-		
Total aromatics							*8 800 (1500-	*3700 (1300-		
Resolved aromatics							*2500 (400- 6000)	*1900 (240- 6800)		
Unresolved aromatics							*6 600 (1100- 16 000)			
UVF chrysene							*13 000 (1800-	*6000 (4600-		
UVF ROPME oil							*96000 (12000- 225000)			

For non-IAEA materials, values preceded by an asterisk (\*) are non-certified; all other values are certified. For IAEA materials, values preceded by an asterisk are classified as information

values; all other values are classified as recommended. Reference values are also available for dimethylphenanthrenes, methylfluoranthenes and methylpyrenes for SRM 1944.

Table 7 RMs for hydrocarbons in sediments

Code	EC-1	EC-2	EC-3	EC-4	EC-5	EC-6	EC-7	EC-8
Organisation	NWRI	NWRI	NWRI	NWRI	NWRI	NWRI	NWRI	NWRI
Country of origin	Canada	Canada	Canada	Canada	Canada	Canada	Canada	Canada
Matrix	Freshwater	Lake	Lake	Freshwater	River	Lake Erie	Lake	Lake
	harbour	Ontario	Ontario	harbour	sediment	sediment	St. Clair	Ontario
	sediment	sediment	sediment	sediment			sediment	sediment
Units	μg/g	μg/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
As	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight
[ ± ] expressed as	± S.D.	± S.D.	± S.D.	± S.D.	± S.D.	± S.D.	± S.D.	± S.D.
Units of issue	100 g	100 g	100 g	100 g	100 g	100 g	100 g	100 g
Form	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried
Acenaphthene		$*0.20 \pm 0.04$	$*22 \pm 9$	*32±9	* 29 ± 9	*7 ± 2	*3±1	*13 ± 3
Acenaphthylene		*0.12 ± 0.02	*25 ± 8	*48 ± 12	*41 ± 9	*12 ± 4	*13 ± 7	*28 ± 4
Anthracene	$1.2 \pm 0.3$	*0.11 ± 0.02	*59 ± 11	*124 ± 16	*113 ± 17	*37 ± 5	*22 ± 5	*41 ± 6
Benzo[a]anthracene	$8.7 \pm 0.8$	$1.42 \pm 0.25$	$312 \pm 28$	*712 ± 117	*503 ±47	$184 \pm 27$	*110 ± 22	*168 ± 18
Benzo[b]fluor-	$7.9 \pm 0.9$	$2.48 \pm 0.043$	*505 ± 88	*753 ± 148	*480 ±88	$267 \pm 90$	*90 ± 32	*208 ± 24
anthene								
Benzo[k]fluoranthene	$4.4 \pm 0.5$	$1.93 \pm 0.36$	*271 ± 104	*560 ± 562	*419 ± 49	*159 ± 50	*84 ± 2	*294 ± 37
Benzo[ j ]fluoranthene								
Велго[а]ругеле	$5.3 \pm 0.7$	$1.21 \pm 0.28$	$386 \pm 50$	*675 ± 114	*449 ± 61	*250 ± 76	*103 ± 48	*207 ± 26
Benzo[e]pyrene	$5.3 \pm 0.6$	$1.91 \pm 0.36$	$450 \pm 49$	*747 ± 93	*440 ± 76			*531 ± 177
Benzal ghi perylene	$4.9 \pm 0.7$	$1.47 \pm 0.33$	*348 ± 70	*576 ± 122	*333 ± 53	*176 ± 43	*95 ± 8	*176 ± 32
Chrysene / tri-	*9.2 ± 0.9	*2.15 ± 0.86	*458 ± 59	*1073 ± 150	*619 ± 60	*279 ± 29	*182 ± 51	*378 ± 38
phenylene								
Dibenz[a,h]anthra-	$*1.3 \pm 0.2$	$0.49 \pm 0.10$	*109 ± 17	*241 ± 96	*195 ± 44	*42 ± 9	*34 ± 6	*316 ± 79
cene								
Fluoranthene	$23.2 \pm 2.0$	$3.55 \pm 0.41$	558 ± 46	*1087 ± 139	*823 ± 74	*297 ± 48	*196 ± 32	*462 ± 41
Fluorene		*2.14 ± 0.40	*42 ± 21	*88 ± 35	*84 ± 26	*17 ± 3	*16±4	*19 ± 2
Indeno[ 1,2,3-cd ]-	$5.7 \pm 0.6$	$1.55 \pm 0.26$	*359 ± 36	*564±101	*386 ± 66	*157 ± 53	*62 ± 14	*34±6
pyrene								
Naphthalene		*1_47 ± 1.05	*35 ± 20	*58±14	*26 ± 6	*75 ± 12	*40 ± 9	*10 ± 1
Perylene	*1.1 ± 0.2	*0.80 ± 0.26	*195 ± 21	*280 ± 93	*187 ± 28	*0.075	*0.040	*202 ± 25
Phenanthrene	$15.8 \pm 1.2$	*1.41 ± 0.16	293 ± 33	*732 ± 75	*612 ± 57	*138 ± 12	*180 ± 17	*234 ± 19
Ругепе	$16.7 \pm 2.0$	$2.92 \pm 0.31$	436 ± 47	*1085 ± 170	*987 ± 134	*337 ± 48	*306 ± 58	*327 ± 30

ment CRMs (NIST 1944, NWRI EC-2 and EC-3) for OCPs (Tables 8 and 12). The degree of difficulty of this type of analysis may be one of the reasons for the lack of good CRMs. Obviously, there is a need for more CRMs for chlorinated benzenes and octachlorostyrene in biota and sediments.

# 7. CRMs for organotin compounds

Two CRMs are available for antifouling compounds: BCR 477, showing certified values for tri-, di- and monobutyltin (TBT, DBT and MBT) and the Japanese material NIES 11 showing a certified value for TBT and an indicative value for triphenyltin (Table 5). Given the concern about environmental

levels of TBT in marine organisms, the production of more CRMs seems to be justified. Table 13 shows one CRM for antifouling compounds in sediment: BCR 462, which is a coastal sediment and has certified values for TBT and for DBT. Although, admittedly, only a few specialised laboratories study organotin compounds in sediments, tone CRM is a very small basis, even to serve this limited number of laboratories.

# 8. Conclusions

Although a number of good quality CRMs have been produced over the last two decades, there is still a need for a number of good CRMs to serve

Table 8
RMs for chlorinated pesticides in sediments

Code	SRM 1944	SRM 1939a	IAEA 383	IAEA 408
Organisation	SRM NIST	SRM NIST	IAEA	IAEA
Country of origin	USA	USA	Мопасо	Monaco
Matrix	New York, New Jersey,	River	Sediment	Sediment
	Waterway sediment	sediment	(Tagus Estuary mudflats)	(Venice Lagoon)
Jnits	mg/kg	μg/kg	μg/kg	μg/kg
As	Dry weight	Dry weight	Dry weight	Dry weight
±] expressed as	95% CI	95% CI	95% CI	95% CI
Jnits of issue	50 g	50 g	35 g	40 g
orm	Freeze-dried	Air-dried	Freeze-dried, -< 250 µm	Freeze-dried, < 150 μm
Hexachlorobenzene	$6.03 \pm 0.35$		*38 (17-57)	0.41 (0.30-0.57)
х-НСН	*2.0 ± 0.3		*0.29 (0.13-3.7)	*0.61 (0.21-1.5)
3-HCH			*0.57 (0.26-9.7)	*0.55 (0.38-1.7)
-HCH			*0.46 (0.16-1.1)	0.19 (0.11-0.20)
Aldrin			*1.4 (0.84-5.9)	*0.41 (0.2-0.23)
rans-Chlordane	*8 ± 2		*1.4 (0.8-1.9)	*0.27 (0.06-0.48)
cis-Chlordane	16.51 ± 0.83	$4.8 \pm 1.3$	*0.47 (0.06-0.73)	*0.12 (0.10-0.34)
Heptachlor			*1 (0.51-2.5)	*0.42 (0.23-0.70)
Heptachlor epoxide			*1.5 (0.42-5.9)	*0.64 (0.43-1.5)
rans-Nonachlor	$8.20 \pm 0.51$			
is-Nonachlor	*3.7 ± 0.7			
Dieldrin			*0.27 (0.1-0.57)	*0.3 (0.30-0.48)
2,4'-DDE	*1.9 ± 3		*0.21 (0.062-0.73)	
4,4'-DDE	*86 ± 12		1.2 (0.75-1.8)	1.4 (0.88-2.0)
2,4'-DDD	*38 ± 8		*1.2 (0.54-2.5)	*0.19 (0.18-0.33)
1,4'-DDD	*108 ± 16	$5.50 \pm 0.97$	*1.8 (0.8-3.6)	*0.87 (0.56-1.7)
2,4'-DDT			*0.39 (0.067-0.82)	*0.38 (0.09-3.8)
1,4'-DDT	119 ± 11	$2.72 \pm 0.42$	*2.4 (0.86-6.1)	0.67 (0.48-0.98)
- Endrin			*1.1 (0.4-1.8)	*0.57 (0.14-1.2)
x-Endosulfan			*0.31 (0.15-0.57)	*1.6 (0.3-6.2)
Endosulfan sulfate			*1.7 (0.92-7.1)	*1.6 (0.5-8.2)

For non-IAEA materials, values preceded by an asterisk (\*) are non-certified; all other values are certified. For IAEA materials, values preceded by an asterisk are classified as information values; all other values are classified as recommended.

Note: NWRI EC1-8 contain certified and reference chlorobenzene values in sediments and include hexachlorobenzene HCB. These results are presented in Table 12.

laboratories working in the field of organic contaminant analysis in the aquatic environment. In order of priority, there is a need for CRMs for PCDDs, PCDFs and non- and mono-ortho PCBs having WHO TEF values in biota and sediments, PAHs in shellfish, OCPs in wet biota and sediment, PCBs in wet sediment, chlorinated benzenes in biota and sediment and organotin compounds in biota and sediment. In addition, the production of CRMs for new contaminants such as brominated flame retardants should be considered. As regards the available CRMs, laboratories should critically evaluate the process of their production and certification, prior to using them, as there is a wide range in quality. Also, suppliers of CRMs should inform the users on how to use the available CRMs [20]. A definition of minimum requirements for the production of CRMs and registration and accreditation of producers, which would help the user to distinguish CRMs from RMs, is highly recommended.

# References

- [1] D.E. Wells, Fresenius Z. Anal. Chem. 332 (1988) 583.
- [2] E.A. Maier, Certified reference materials for quality control of measurements in environmental monitoring, in: D. Barceló (Editor), Sample Handling and Trace Analysis of Pollutants: Techniques, Apllication and Quality Assurance, Elsevier Science BV, Amsterdam, 1999.
- [3] S.A. Wise, M.M. Schantz, D.L. Poster, M.J. Lopez de Alda, L.C. Sander, Standard reference materials for the

Table 9 RMs for PCBs in sediment

Code	170	HS-1	HS-2	SRM 1944	SRM 1939a	IAEA 383	1AEA 408	BCR, 536	100 6114
Organisation	NRC-CNRC	NRC-CNRC	NRC-CNRC	SRM NIST	SRM NIST	IAEA	IAEA	BCR	100
Country of anom	Canada	Canada	Canada	USA	USA	Монасо	Мопасо	En	X
Matrix	Harbour	Harbour	Harbour	New York,	River	Sediment (Tagus	Sediment	Freshwater	Naval
	sediment	sediment	sediment	New Jersey.	sediment	Estuary mudflats)	(Venice Lagoon)	harbour	Dockvard
				Waterway			0	sediment	harbour
				sediment					sediment
Units	Mg, 'S	mg/lg	87/BH	mg/kg	ug/kg	54 S1	Lg/kg	By/Bm	hg/kg
As	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight	Dry winght	Dry weight	Dry weight	Dry weight
[±] expressed as	±5.D.	± S.D.	±5.D.	95% CI	95% CI	95% CI	95% CI	1 / 2-width	1 / 2-width
								of 95% CI	of 95% CI
Units of issue	100 E	100 g	100 g	20 g	50 g	35 8	40 %	40 g	50 B
Fоrт .	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried	Air-dried	Freeze-dried,	Freeze dried	Direct	Air-dried,
						< 250 µm	< 150 µm		<150 µm
PCB 8				$22.3 \pm 2.3$			*0.24 (0.22-4.6)		
PCB 18				$51.0 \pm 2.6$	*3210 ± 940	*0.5 (0.27-0.78)	*0.74 (0.13-1.9)		
PCB 28				80.8 ± 2.7	*2461±78	1 (0.77-1.4)	0.79 (0.35-0.98)	44 ± 5	*15±8
PCB 31				78.7 ± 1.6	*6440±490	0.76 (0.38-1.2)	*0.43 (0.09-1.5)		
PCB 44				$60.2 \pm 2.0$	1131 ± 74	*1.1 (0.92-1.2)	*0.47 (0.23-30)		
PCB 49				53.0 ± 1.7	3740 ± 280	*1.1 (0.89-13)	*0 35 (0.22-0.38)		
PCB 52				$79.4 \pm 2.0$	4320 ± 130	2,5 (1,1-2,8)	0.6 (0.38-0.93)	38±4	+337±57
PCB 66				71.9 ± 4.3	840±130	*2 (1.8-31)			
PCB 87				29.9 ± 4.3		*0.7 (0.55-0 91)	*0.87 (0.26-1.1)		
PCB 95				$65.0 \pm 8.9$	*1210 ± 420	*36 (27-4.5)			
PCB 97						*0.41 (0.26-0.9)			
PCB 99				37.5 ± 2.4	$380 \pm 96$	*1.3 (0.59-1.8)			
PCB 101/90				73.4 ± 2.5					
PCB 101		1.62±0.21	5.42±0.34			2,9 (1.3-4.2)	1.2 (0.81-1.7)	44+4	*810±193
PCB 105				24.5 ± 1.1	201 ± 28	0.99 (0.77-1.5)	0.57 (0.44-0.67)	3.5 ± 0.6	
PCB 110				63.5 ± 4.7	1068 ± 70	2.4 (1.8-3.6)	0.83 (0.50-0.90)		
PCB 118				58.0 ± 4.3	423 ±88	3.3 (2.2-4.1)	1.2 (0.9-1.6)	28±3	*688±200
PCB 128				8 47 ± 0.28	$91.2 \pm 8.4$	0.63 (0.52-0.87)	0.33 (0.27-0.53)	5.4±1.2	
PCB 137						*0.17 (0.09-0.22)			
PCB 138		1.98±0.28	6.92±0.52			4.4 (2.6-61)	1.6 (1.1-2.1)	27±4	*649 1164
PCB 138/163/164				62.1 ± 3.0	2581±69				
PCB 141						*0.64 (0.34-1.1)			
PCB 149				49.7 ± 1.2	427 ± 47	3.2 (2.3-3.7)	1.4 (1.3-1.6)	49 4 4	
PCB 151		0.48±0.0B	1,37 ± 0.07	$16.93 \pm 0.36$	192.1 ± 2.6	*0.58 (0.37-1.1)			
PCB 153		2.27 ± 0.28	6.15±0.67	74.0±2.9	297 ± 19	4.3 (2.3-5.4)	1.9 (0.98-2.1)	50 ± 4	*537 ± 127
PCB 156				$6.52 \pm 0.66$	$37.0 \pm 6.6$	*0.47 (0.24-0.78)	*0.36 (0.31-0.39)	3.0 ± 0.4	
PCB 158						*0.39 (0.18-0.57)			
PCB 163								17±3	

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ode CS-1		HS-1	HS-2	SRM 1944	SRM 1939a	IAEA 383	IAEA 408	BCR 536	LGC 6114
PCB 170		0.27 ± 0.05	1.07 ± 0.15		107±17	0.82 (0.62-1.3)	0.47 (0.34-0.59)	13,4±1,4	
PCB 170/190				22.6±1.4					
PCB 174						*0.67 (0.42-0.92)	*0.34 (0.20-0.44)		
PCB 177						*0.56 (0.35-0.73)	*0.35 (0.23-0.43)		
PCB 180		1.17 ± 0.15	3.70±0.33	44.3 ± 1.2	$140.3 \pm 6.1$	2.5 (1.9-3.4)	1.1 (0.85-1.2)	$22 \pm 2$	*119±22
PCB 183				12,19±0,57	$47.3 \pm 2.3$	0.47 (0.34-0.57)	*0.32 (0.26-0.33)		
PCB 185						*1.3 (0.073-0.18)			
PCB 187						1.3 (0.63-1.5)	0.68 (0.49-0.94)		
PCB 187/159/182				25.1 ± 1.0	156.4±2.6				
PCB 189						*0.07 (0.041-1.4)			
PCB 194		$0.23 \pm 0.04$	0.61 ± 0.07	$11.2 \pm 1.4$	35.5 ± 4.1	0.54 (0.31-0.73)	0.2 (0.2-0.23)		
PCB 195				3.75 ± 0.39		*0.24 (0.13-0.29)	*0.12 (0.06-0.16)		
PCB 196		0.45 ± 0.04	1.13±0.12				*0.22 (0.17-0.40)		
PCB 199						*0.091 (0.01-0.35)			
PCB 200						*0.16 (0.051-0.22)			
PCB 201		0.57 ± 0.07	1.39 ± 0.09			*0.71 (0.28-0.74)			
PCB 205						*0.033 (0.027-0.050)			
PCB 206 PCB 207				9.21 ± 0.51	29.7±5.6	*0.48 (0.44-1.1) *0.094 (0.05-0.19)			
PCB 209		0,33 ± 0.1	0.90 ± 0.14	$6.81 \pm 0.33$		2,1 (1,2-3.0)			
Total PCB 1.2±	$1.2 \pm 0.60$	21,8±1,1	111.8±2.5						

For non-IAEA materials, values preceded by an asterisk (\*) are non-certified; all other values are certified. For IAEA materials, values preceded by an asterisk are classified as information values; all other values are classified as recommended. LGC values for PCBs are classified as 'assessed' values.

Table 10 RMs for PCBs in sediments

Code	EC-1	EC-2	EC-3	EC-4	EC-5	EC-6	EC-7	EC-8 <sup>b</sup>	DX-3*
Organisation	NWR	NWR	NWRI	NWRI	NWRI	NWRI	NWRI	NWRI	NWRI
Country of origin	Canada	Canada	Canada	Canada	Canada	Carnada	Canada	Canada	Canada
Matrix	Freshwater	Lake Ontario	Lake Ontario	Freshwater	River	Lake Erie	Lake St. Clair	Lake Ontario	Great Lakes
	harbour	sediment	sediment	harbour	sediment	sediment	sediment	sediment	sediment
	sediment			sediment					
Units	ng/g	P8 P8	8/8u	B/Su	8/Bu	mg/g	8/80	8/8u	8/8u
5)	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight
±] expressed as	± S.D.	+ S.D.	± S.D.	± S.D.	± S.D.	± S.D.	± S.D.		Robust 95% pred intervals
Jnits of issue	100 g	100 g	100 g	100 g	100 g	100 g	100 g	100 g	50 g
Form	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried
PCB 18	*47.4±16.1	*17.5±7.1	*9.0±4.7	*3.7±1.6	*3.0 ± 1.1			*2.1	
PCB 28	*48.7±17.0	*25.6 ± 8.4	*18.6±8.6	*6.8 ± 1.8	*5.3 ± 1.3			*5.2	
PCB 44	*64.7 ± 31.4	*45.5 ± 25.3	$*32.6 \pm 15.3$	*75±29	*7.3±2.4			*10.4	
PCB 52	*99.4±43.2	*56.0±14.5	*35.6±12.9	*12.5 ± 5.7	*13.3 ± 4.1			*14.2	
PCB 81									*0.133 ± 0.247
PCB 87	*44.9±14.5	*24.7 ± 6.5	*16.8±3.7	*8.3 ± 1.5	*9.6 ± 1.4			£6.9	
PCB 101	*109.4±74.4	*59.7±29.1	*38.3±7.2	*22,4±9.5	$*24.6 \pm 6.0$			*18.2	
PCB 105	*34.2±13.5	*17.4 ± 4.8	*13.1±4.3	*8.1±3.2	*7.6±2.7			*5.9	$*6.097 \pm 1.467$
PCB 110	*120.1 ± 67.3	*77.8 ± 36.9	*52.5±21.4	*29,1±11,5	*33.3 ±11.9			*18,8	
PCB 114									$*0.284 \pm 0.242$
PCB 118	*79.8 ± 37.1	*40.5±11.6	*28.5 ± 5.4	*17.8±77	*17.0±7.4			*12.5	*13.48±7.40

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Table 10 (continued)

Code	EC-1	EC-2	EC-3	EC-4	EC-5	EC-6	EC-7	EC-8p	DX-34
PCB 123									*0.484±0.461
PCB 128	*14.5 ± 6.4	*7.9 ± 5.1	*73±32	*4.6 ± 2.2	*5.5 ± 2.3			*2.7	
PCB 137	*3.8±1.0	*2.4±0.8	*4.8±2.9	*1.7 ± 0.7	*1.7±0.8				
PCB 138	*72.0 ± 26.3	*35.1+11.8	$*25.2 \pm 6.3$	*28.7 ± 9.7	*28.6±9.1			*14.8	
PCB 141	*19.4±4.0	*9.2 ± 3.4	*6.2 ± 2.0	*8.3 ± 2.0	*8.4±1.9				
PCB 151	*16.6±4.9	*9.9±4.3	*8.1 ± 4.1	*9.4±3.7	*8.4+2.8			*2.5	
PCB 153	*68.2±22.1	*33.3 ±11.9	*24.2 ± 4.1	*27.3 ± 7.5	*27.2 ± 5.5			*	
PCB 156									*1,126±0.592
PCB 157									*0.332 ± 0.223
PCB 167									*0.587±0.438
PCB 170	*16.8±7.6	*8.4±2.4	*8.9±1.3	*11.8 ± 2.5	*10.1±1.6			*4.3	
PCB 180	*44.9 ± 23.2	*20.8 ± 9.6	*15.4±6.6	*26.1 ±11.0	*22.3 ± 7.6			4.7	
PCB 183	*15.2 ± 7.6	*6.7 ± 2.9	*4.9±1.8	*8.4±4.1	*7.2±2.8			*1.8	
PCB 189									*0.185±0.130
PCB 194	*13.1 ± 5.6	*14.3 + 26.0	*5.2 ± 2.1	*6.9 ± 3.1	*8.1 ± 10.1			*2.3	
PCB 201	*7.3 ± 5.0	*9.9 ± 4.8	*8.3 ± 2.4	*8.1 ± 2.0	*5.7±2.7			0.5	
PCB 206	$*7.0 \pm 3.0$	*5.6±3.0	*5.2 ± 2.1	*3.2 ± 1.6	*2.2 ± 0.9			*3.7	
PCB 209	*1,4+0.8	*16.1±10.5	*18.7±10.8	*1.6±2.0	*1.2 ± 0.9			.9.3	
Total PCB	2000 ± 50	1160±70	*660±54	*577±63	*597±82	*105±19	*21±3	*621±79	

For non-IAEA materials, values preceded by an asterisk (") are non-certified; all other values are certified. For IAEA materials, values preceded by an asterisk are classified as information values; all other values are classified as recommended.

afinformation' values for an additional 53 PCBs are also available for DX-3.

NWRI EC8 – these values are preliminary in nature and are provided as guideline only. "NWRI note – this distribution implies less than 95% confidence.

Table 11
RMs for chlorinated dioxins and furans and non-ortho PCBs in sediments

Code	SRM 1944	EC-1ª	FC-2 <sup>a</sup>	EC-3 <sup>a</sup>	DX-1	DX-2	DX-3
Organisation Country of origin Matrix	SRM NIST USA New York, New Jersey, Waterway	NWRI Canada Harbour sediment	NWRI Canada Lake sediment	NWRI Canada River sediment	NWRI Canada Great Lakes blend	NWRI Canada Lake Ontario sediments	NWRI Canada Great Lakes sediment
Units As [±] expressed as	sediment µg/kg Dry weight 95% Cl	ng/g Dry weight ± S.D.	μg/g Dry weight ±S.D.	μg/g Dry weight ± S.D.	pg/g Dry weight 95% Cl	pg/g Dry weight 95% Cl	pg/g Dry weight Robust 95% pred intervals
Units of issue Form  2,3,7,8-TCDF Total TCDF  1,2,3,7,8-PCDF 2,3,4,7,8-PCDF Total PCDF  1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-HxCDF Total HxCDF 1,2,3,4,7,8,9-HpCDF 1,2,3,4,7,8,9-HpCDF Total HpCDF OCDF 2,3,7,8-TCDD Total TCDD 1,2,3,7,8-PCDD Total PCDD 1,2,3,4,7,8-HxCDD 1,2,3,4,7,8-HxCDD 1,2,3,4,7,8-HxCDD 1,2,3,4,7,8-HxCDD 1,2,3,4,7,8-HxCDD Total HxCDD 1,2,3,4,6,7,8-HpCDD Total HxCDD 1,2,3,4,6,7,8-HpCDD Total CDFS Total CDFS Total CDDS	50 g Freeze-dried *0.039 ± 0.015 *0.7 ± 0.2 *0.045 ± 0.004 *0.74 ± 0.07 *0.025 ± 0.018 *0.09 ± 0.01 *0.019 ± 0.018 *0.054 ± 0.006 *1.0 ± 0.1 *1.0 ± 0.1 *0.040 ± 0.006 *1.5 ± 0.1 *1.0 ± 0.1 *0.133 ± 0.009 *0.25 ± 0.01 *0.019 ± 0.002 *0.19 ± 0.06 *0.026 ± 0.003 *0.056 ± 0.006 *0.053 ± 0.007 *0.63 ± 0.09 *0.80 ± 0.07 *1.8 ± 0.2 *5.0 ± 0.9 *8.7 ± 0.9 *8.7 ± 0.9 *0.25 ± 0.01	100 g Freeze-dried	100 g Freeze-dried	100 g Freeze-dried	50 g Freeze-dried *89 ± 44 659 ± 259 39 ± 14 62 ± 32 790 ± 489 714 ± 276 116 ± 37 *28 ± 42 *57 ± 36 1800 ± 809 2397 ± 796 137 ± 62 3567 ± 1165 7122 ± 2406 263 ± 53 416 ± 121 22 ± 8 226 ± 143 23 ± 7 77 ± 27 53 ± 24 669 ± 185 634 ± 182 1251 ± 933 3932 ± 933 13 676 ± 3777 6490 ± 1309	50 g Freeze-dried *134±61 975±588 46±10 88±28 916±351 825±348 153±61 *36±45 *70±47 2111±662 3064±745 152±84 4068±1306 7830±3087 262±51 418±125 28±14 253±150 25±8 85±33 58±19 739±218 757±320 1486±476 4402±1257 15 981±4177 7294±1783	pred intervals 50 g Freeze-dried *47 ± 31 *555 ± 359 *35 ± 17 *45 ± 16 *589 ± 369 *437 ± 151 *96 ± 46 *16 ± 32b *39 ± 31 *1241 ± 477 *1923 ± 558 *98 ± 39 *2455 ± 737 *3875 ± 1328 *121 ± 43 *251 ± 157 *19 ± 7 *204 ± 143 *20 ± 10 *60 ± 18 *37 ± 16 *547 ± 158 *501 ± 129 *942 ± 283 *3067 ± 888
Total toxic equivalent PCB 77 PCB 126 PCB 169	*0.25 ± 0.01	*4.1 *0.7 * < 0.016	*4.8 *0.175 *0.020	*4.5 *0.175 *0.018			*2560 ± 990 *107 ± 80 *14 ± 13

determination of trace organic constituents in environmental samples, in: D. Barceló (Editor), Sample Handling and Trace Analysis of Pollutants: Techniques, Apllication and Quality Assurance, Elsevier Science BV, Amsterdam, 1999.

[4] D.E. Wells, J. de Boer, L.G.M.Th. Tuinstra, L. Reutergårdh, B. Griepink, Fresenius Z. Anal. Chem. 332 (1988) 591.

- [5] J. de Boer, J.C. Duinker, J.A. Calder, J. van der Meer, J. Assoc. Off. Anal. Chem. 75 (1992) 1054.
- [6] J. de Boer, J. van der Meer, L. Reutergårdh, J.A. Calder, J. Assoc. Off. Anal. Chem. 77 (1994) 1411.
- [7] J. de Boer, J. van der Meer, U.A.Th. Brinkman, J. Assoc. Off. Anal. Chem. 79 (1996) 83
- [8] D.E. Wells, A. Aminot, J. de Boer, W. Cofino, D. Kirk-wood, B. Pedersen, Mar. Pollut. Bull. 35 (1997) 3.

PNWRI EC1-3 non-ortho PCBs - these values are preliminary in nature and are provided as guideline only.

hNWRI note - this distribution implies less than 95% confidence.

Table 12 RMs for chlorinated benzenes in sediments

Code	EC-1	EC-2	EC-3	EC-4	EC-5	EC-6	EC-7	EC-8
Organisation	NWRI	NWR	NWRI	NWR	NWRI	NWRI	NWP	NWRI
Country of origin	Canada	Canada	Canada	Canada	Canada	Canada	Canada	Canada
Matrix	Freshwater	Lake Ontario	Lake Ontario	Freshwater	River sediment	Lake Erie	Lake St. Clair	Lake Ontario
	harbour	sediment	sediment	harbour		sediment	sediment	sediment
	sediment			sediment				
nits	8/8u	ng/g	P	a/Su	1g/g	ng/g	g/gu	3/3u
	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight	Dry weight
± expressed as	+ S.D.	± S.D.	± S.D.	±5.D.	± S.D.	± S.D.	±5.D.	± S.D.
Inits of issue	100 g	100 g	100 g	100 g	3 00 L	100 g	100 g	100 g
Form	Freeze-dried	Freeze-dried	Freeze-dined	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried	Freeze-dried
2-Dichlorobenzene	*4.9 ± 1.8	18.1 ± 1.3	21±3	*6.8 ± 1.8	*7,4±2.5		*7.8 ± 4.1	*5±1
3-Dichlorobenzene	*5.9 ± 3.0	74.7 ± 5.1	$105 \pm 18$	*6_8 ± 1.4	*7.1 ± 1.9		*5.7±3.7	*43±3
4-Dichlorobenzene	*30.9 ± 9.5	844±88	*108 ± 12		*29.0 ± 5.5		*22.4 ± 10.5	*58±4
2,3 Trichlorobenzene	*2.3 ± 1.0	$6.1 \pm 0.7$	9±1	*1.9±0.4	$*3.8 \pm 0.8$		*4.4±4.1	*3 ± 0.3
2,4-Trichlorobenzene	*3.4±2.0	$80.7 \pm 5.4$	*141 ± 14	*6.7±1.1	*8.3 ± 0.7	$*2.1 \pm 0.8$	*5.7 ± 2.0	*67±4
3,5-Trichlorobenzene	*27±07	$34.3 \pm 2.6$	114±10	*4.4±0.9	*6.8 ± 1.3	*1.5 ± 0.7	*13.6±4.0	*46±2
2,3,4 Tetrachlorobenzene	*1.5 ± 0.4	36.5 ± 2.4	44 ± 5	*1.6±0.4	*2.5 ± 0.3	*0.4	*1.6±1.2	*17+1
2,3,5 Tetrachlorobenzene	$*0.8 \pm 0.4$	5.2±0.4	*14±1	$*0.3 \pm 0.2$	*0.6 ± 0.1			*6±03
1,2,4,5-Tetrachlorobenzene	*3.4±1.6	$84.0 \pm 4.9$	*156±17	*2.4±0.9	*3.3 ± 0.5	*1.5 ± 0.4	*19.2 ± 9.9	*57±4
Pentachlorobenzene	$*1.7 \pm 0.4$	$48.6 \pm 2.4$	65±8	*1.9±0.4	*2.2 ± 0.3	*1.4 ± 0.2	*9.1±3.9	*30±3
Hexachlorobenzene	*5.4±1.9	$200.6 \pm 13.2$	$279 \pm 33$	$*2.2 \pm 0.6$	*2,4±0,2	*3.6±1.1	*53,3±18,7	6∓86*
Hexachlorobutadiene	$*0.66 \pm 0.56$	$21.3 \pm 1.6$	61±7	*0.6 ± 0.1	*0.88±0.2	*1,7 ± 1.1	*7.0±3.3	*21±2
Hexachioroethylene						$*0.63 \pm 0.3$	*1.0 ± 0.4	
Octachlorostviene	*6.0±1.4	*30.6±4.6	*41±6	*1.0 ± 0.3	*0.89 ± 0.1	*3.4 ± 2.7	*17.5 ± 7.0	*22±4

Values preceded by an asterisk (\*) are non-certified; all other values are certified.

Table 13 RMs for organic compounds in marine sediments

Code	BCR 462			
Organisation	BCR			
Country of origin	EU			
Matrix	Coastal sediment			
Units	μg/kg			
As	Dry weight			
[ ± ] expressed as	Expanded uncertainty <sup>a</sup>			
Units of issue	25 g			
Form	Air-dried			
TBT	54 ± 15			
DBT	$68 \pm 12$			

[9] Ph. Quevauviller, C. Nieto de Castro, R. Morabito, M. Valcarcel, A. Voulgaropoulos, M. Walsh, Trends Anal. Chem. 18 (1999) 650.

- [10] M.M. Schantz, R. Demiralp, R.R. Greenberg, M.J. Hays, R.M. Farris, B.J. Potter, D.L. Poster, L.C. Sander, K.S. Sharpless, S.A. Wise, S.B. Schiller, Fresenius J. Anal. Chem. 358 (1997) 431.
- [11] S.A. Wise, M.M. Schantz, B.J. Koster, R. Demiralp, E.A. Mackey, R.R. Greenberg, M. Burow, P. Ostapczuk, T.I. Lillestolen, Fresenius J. Anal. Chem. 345 (1993) 270.
- [12] B. Larsen, J. Riego, Int. J. Environ. Anal. Chem. 40 (1990) 59.
- [13] J. de Boer, Q.T. Dao, Int. J. Environ. Anal. Chem. 43 (1991) 245.
- [14] C.S. Phinney, M.J. Welch, Proc. Intern. Symp. BERM-8, Bethesda, MD. 2000, p. 131.
- [15] QUASIMEME Report Round 18, Exercise 414, FRS Marine Laboratory, Aberdeen, 2000.
- [16] A. Bernard, C. Hermans, F. Broeckaert, G. Depoorter, A. de Cock, G. Houins, Nature 401 (1999) 231.
- [17] A.K.D. Liem, S. Atuma, W. Becker, P.O. Darnerud, R. Hogerbrugge, G.A. Schreiber, Organohalog. Compd. 48 (2000) 13.
- [18] Food and Drugs Act Regulation Dioxins in Eel, Staatscourant 211, The Netherlands, 30 October, 2000.
- [19] M. van den Berg, R.E. Peterson, D. Schrenk, Food Addit. Contam. 17 (2000) 347.
- [20] Ph. Quevauviller, Trends Anal. Chem. 18 (1999) 76.

<sup>&</sup>lt;sup>a</sup>Expanded uncertainty  $U = k u_c$  calculated according to ISO/BIPM guide with coverage factor k = 2.