



Organotins monitoring strategies in the European Water FrameWork Directive: Challenges and limitations

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Water bodies in Europe:
Integrative Systems to assess Ecological status and Recovery

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Water Framework Directive

The ¹ [Water Framework Directive](#) commits European Union member states to achieve good ecological status of all inland and coastal water bodies by 2015. The Water Framework Directive changed European water management fundamentally. First, management is coordinated at the level of entire river basins - countries need to cooperate now in cross-border basins. Second, assessment accounts for ¹ [ecological quality](#) and includes the status of aquatic animal and plant communities: phytoplankton, phytobenthos and macrophytes, benthic invertebrates and fish. And third, the ecological status is expressed as the deviation of the current conditions from undisturbed ¹ [reference conditions](#).



Monitoring programmes account for these aspects and were developed and published by 2007. At present, ¹ [river basin management plans](#) are being finalised and prepared for publication at the end of 2009. In parallel, programmes of measures are developed to deliver environmental objectives in each river basin district.

Despite considerable progress that has been made since 2000, significant knowledge gaps still hinder implementation. Monitoring schemes still do not cover all relevant organism groups and lack for some regions. These gaps also affect the European ² [intercalibration](#) exercise that aims at ensuring the comparability of monitoring results.



DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

on environmental quality standards in the field of water policy and amending Directive 2000/60/EC

(presented by the Commission)

{COM(2006) 398 final}
{SEC(2006) 947}

PART A: Environmental Quality Standards (EQS) for Priority Substances in surface water

AA: annual average;

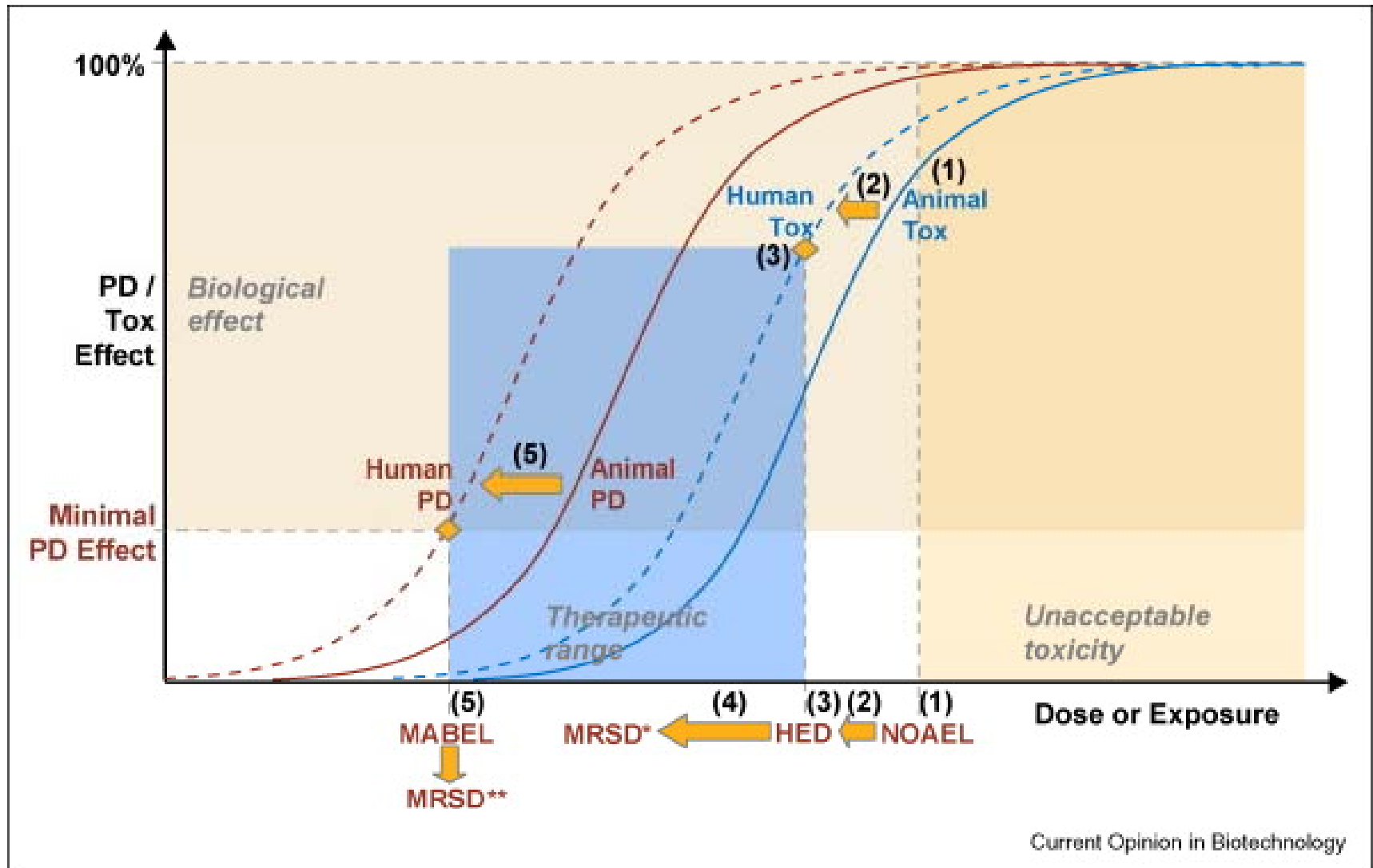
MAC: maximum allowable concentration.

Unit: [µg/l]

(1)	(2)	(3)	(4)	(5)	(6)	(7)
N°	Name of substance	CAS number	AA-EQS ²¹ Inland surface waters	AA-EQS ²¹ Other surface waters	MAC- EQS ²² Inland surface waters	MAC-EQS ²² Other surface waters
(1)	Alachlor	15972-60-8	0.3	0.3	0.7	0.7
(2)	Anthracene	120-12-7	0.1	0.1	0.4	0.4
(3)	Atrazine	1912-24-9	0.6	0.6	2.0	2.0
(4)	Benzene	71-43-2	10	8	50	50
(5)	Pentabromodiphenylether ²³	32534-81-9	0.0005	0.0002	<i>not applicable</i>	<i>not applicable</i>
(6)	Cadmium and its compounds	7440-43-9	≤ 0.08 (Class 1) 0.08 (Class 2)	0.2	≤ 0.45 (Class 1) 0.45 (Class 2)	
(29)	Simazine	122-34-9	1	1	4	4
(30)	Tributyltin compounds	688-73-3	0.0002	0.0002	0.0015	0.0015
(31)	Trichlorobenzenes (all isomers)	12002-48-1	0.4	0.4	<i>not applicable</i>	<i>not applicable</i>

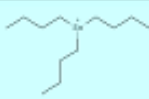
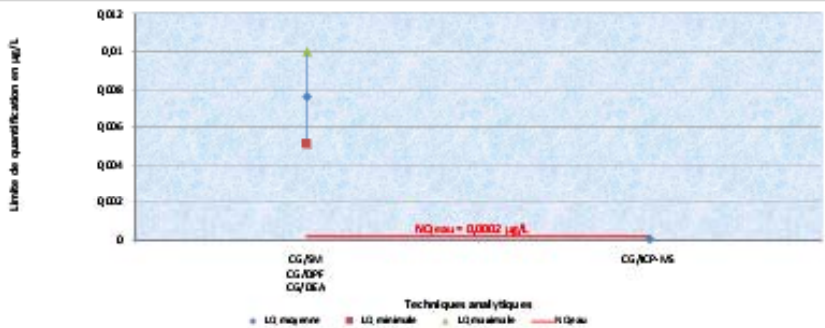
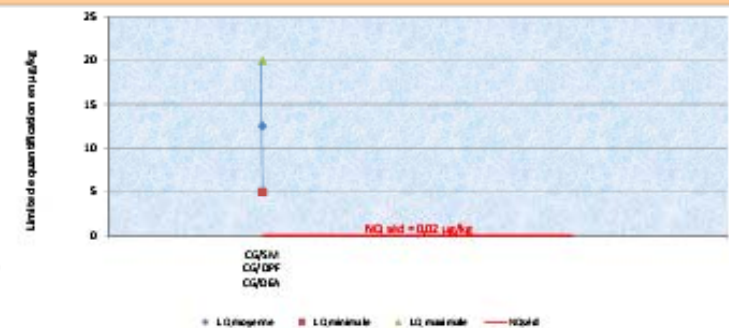


Why such low levels?



SUBSTANCES DE LA DIRECTIVE CADRE EAU



Composé				Formule développée ou élément chimique			
Tributylétain-cation Composés du Tributylétain				$(n-C_4H_9)_3Sn^+$ 			
Code Sandre		Numéro CAS		Log Kow		Solubilité dans eau (mg/L)	
Tin(1+), tributyl- : 2879 Tributylétain : 1820		Tin(1+), tributyl- : 36843-28-4 Composé du Tributylétain : 688-73-3		3,1 - 4,1		très peu soluble dans l'eau, dépend du pH Tributylétain : entre 18 et 61,4	
Support de surveillance, fraction à analyser et codes Sandre associés							
Support	Code Support	Fraction	Code fraction	Support	Code Support	Fraction	Code Fraction
Eau (1)	3	Eau brute	23	Sédiment	6	particules < 2 mm (1)	32
Valeur seuil nationale en µg/L		NQE-Moy (µg/L)		NQE-CMA (µg/L)		NQE-Moy (µg/kg de matière sèche)	
Eaux souterraines		Eaux de surface intérieures	Autres eaux de surface	Eaux de surface intérieures	Autres eaux de surface	Sédiment	
su		0,002	0,002	0,0015	0,0015	0,02 (1)	
(donnée indicative dans sédiment, non réglementaire calculée à partir de la valeur seuil de l'eau en fonction du coefficient de partage avec la phase organique du sol)							
Avis AQUAREF sur NQE - Matrice eau				Avis AQUAREF sur NQ - Matrice sédiment			
NQE atteinte		Commentaires LQ		NQ/3 atteinte		Commentaires LQ	
0		chromatographie en phase gazeuse couplée à un spectromètre de masse avec plasma à couplage inductif (CG/CP-MS) : atteignable (1) chromatographie en phase gazeuse à spectromètre de masse (CG/SM) : non atteignable chromatographie en phase gazeuse à détecteur par photométrie de flamme (CG/DPF) : non atteignable chromatographie en phase gazeuse à détecteur par émission atomique (CG/DEA) : non atteignable		N		chromatographie en phase gazeuse couplée à un spectromètre de masse avec plasma à couplage inductif (CG/CP-MS) : non atteignable chromatographie en phase gazeuse à spectromètre de masse (CG/SM) : non atteignable chromatographie en phase gazeuse à détecteur par photométrie de flamme (CG/DPF) : non atteignable chromatographie en phase gazeuse à détecteur par émission atomique (CG/DEA) : non atteignable	
Commentaires - Matrice eau				Commentaires - Matrice sédiment			
(1) Le logKow étant compris entre 3 et 5, le tributylétain est recherché dans l'eau et les sédiments (2) Filtré en microfiltrés de verre (3) méthode MA-33 : www.aquaref.fr				(1) Selon la norme XPPT 90-250 préciser la fraction à analyser (2) NQE sédiment : La valeur seuil dans les sédiments est une valeur calculée à partir de la valeur seuil de l'eau selon (base d) = (base a) x (0,896 + 0,022 Koc) - Circulaire DCE 2005/12 relative à la définition du bon état et à la consultation des référentiels pour les eaux douces de surface, en application de la directive européenne 2000/60/CE du 23 octobre 2000, ainsi qu'à la démarche à adopter pendant la phase transitoire (2005-2007)			
Performances des techniques sur la matrice Eau				Performances des techniques sur la matrice sédiment			
							
Note : Les données dans les graphes sont issues des limites de quantification (LQ) usuelles précitées en verso - matrice eau				Note : Les données dans les graphes sont issues des limites de quantification (LQ) usuelles précitées en verso - matrice sédiment			



Challenges in the accurate quantification of TBT in water samples

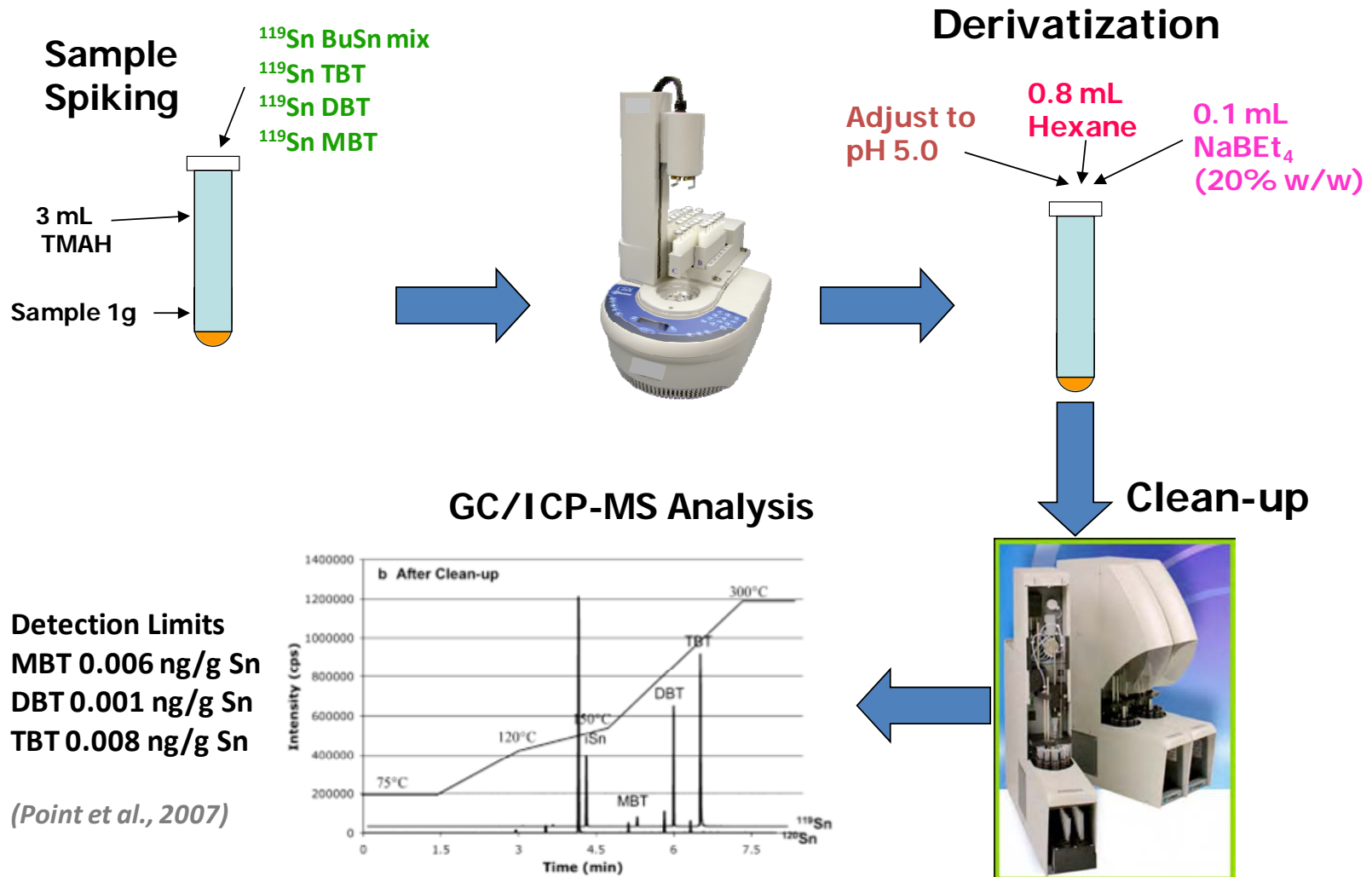
Typical detection limits for TBT for water samples

Matrix	Sample preparation	Separative method/Detection	System type	Species	LOD	References
Fresh water	Extraction: solvent Pr	GC-AED	On-line	MBT, DBT, TBT	7-12 ng l ⁻¹	Schubert <i>et al.</i> , 2000
Fresh water	Extraction: SPME Eth	GC-ICP-MS	On-line	MBT, DBT, TBT	0.3-2 ng l ⁻¹	Moens <i>et al.</i> , 1997
Natural water	Extraction: SPME Eth	GC-FPD	On-line	MBT, DBT, TBT	0.006-0.031 ng l ⁻¹	Aguerre <i>et al.</i> , 1999
Fresh and seawater	Extraction: HS-SPME Eth	GC-MIP-AES	On-line	MBT, DBT, TBT	5 ng l ⁻¹	Carpinteiro Botana <i>et al.</i> , 2002
Sea water	Extraction: HS-SPME Eth	GC-MS	On-line	TBT, DPhT, TPT, TET	0.025 - 1 ng l ⁻¹	Segovia-Martinez <i>et al.</i> , 2010
Sea water	Eth	GC-ICP-MS (IDMS)	On-line	MBT, DBT, TBT	0.04 – 0.27 ng l ⁻¹	Rodriguez-Gonzalez <i>et al.</i> , 2002
Sea water	Eth	GC-MS (IDMS)	On-line	MBT, DBT, TBT	0.18 – 0.25 ng l ⁻¹	Centineo <i>et al.</i> , 2004
Sea water	Eth	GC-ICP-MS (IDMS)	On-line	MBT, DBT, TBT	0.019 – 0.032 ng l ⁻¹	Monperrus <i>et al.</i> , 2005b

- Following the EWFD, the EQS for TBT is 0.2 ng l⁻¹ therefore the LQ < 0.06 ng l⁻¹
- Only few GC-ICPMS methods able to reach such analytical performances
- Need for a validated measurement procedure for TBT in whole water samples at a concentration level required by the EU
- Need for a reference material for the validation



Need for ultra low levels of detection: Biological tissues



Preconcentration techniques applied for TBT analysis

Liquid liquid extraction techniques



Speciation of butyltin compounds in environmental and biological samples using headspace single drop microextraction coupled with gas chromatography-inductively coupled plasma mass spectrometry

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ARTICLE INFO

ABSTRACT



Available online at www.sciencedirect.com



JOURNAL OF
CHROMATOGRAPHY A

Journal of Chromatography A, 1048 (2004) 81–88

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Liquid-phase microextraction of tributyltin and triphenyltin coupled with gas chromatography–tandem mass spectrometry
 Comparison between 4-fluorophenyl and ethyl derivatizations

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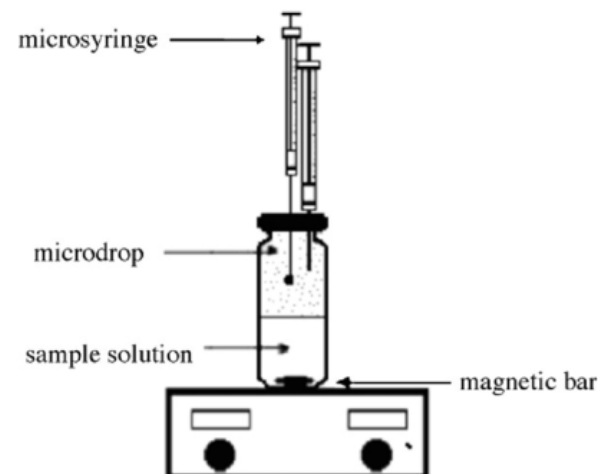


Fig. 1. Schematic of experimental set-up of HS-SDME.

U. Shioji et al.

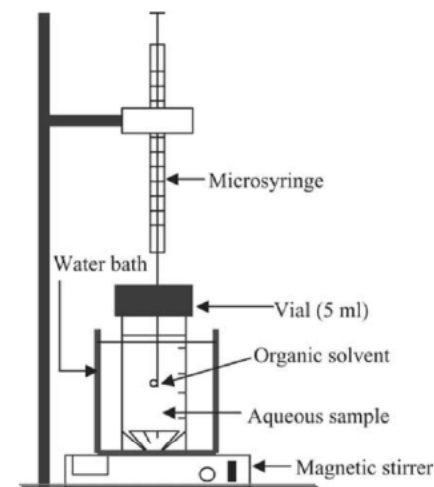


Fig. 2. LPME apparatus.

Liquid liquid extraction techniques

Journal of Chromatography A, 1193 (2008) 19–25

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Speciation of butyl and phenyltin compounds using dispersive liquid–liquid microextraction and gas chromatography–flame photometric detection

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Table 1
 Enrichment factor of different extraction solvents evaluated for extraction of butyl and phenyltins by DLLME^a

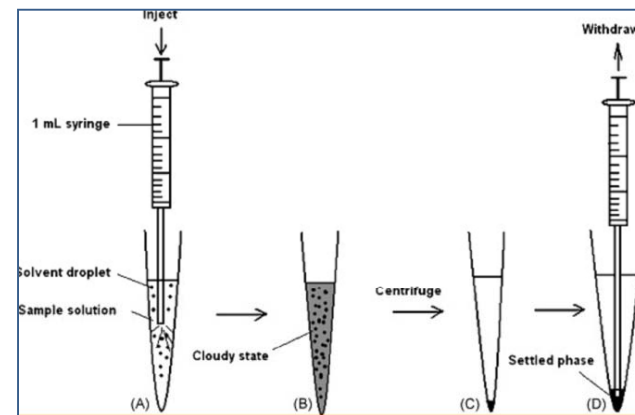
Compounds	Enrichment factor		
	Chlorobenzene, mean (SD ^b , n = 3)	Tetrachloroethylene, mean (SD ^b , n = 3)	Carbon tetrachloride, mean (SD ^b , n = 3)
MBT	611 (16)	759 (20)	923 (25)
DBT	672 (15)	820 (19)	987 (18)
TBT	739 (19)	893 (23)	1036 (23)
MPhT	760 (25)	684 (26)	825 (31)
DPhT	803 (28)	717 (27)	874 (29)
TPhT	865 (23)	744 (22)	951 (28)

^a Extraction conditions: water sample volume, 5.00 ml; disperser solvent (ethanol) volume, 500 μ L; extraction solvent volumes, 10.5 μ L chlorobenzene, 7.5 μ L tetrachloroethylene and 11.5 μ L carbon tetrachloride; sedimented phase volume, 5.0 ± 0.2 μ L; amount of NaBEt₄, 0.25 mg; pH 5; concentration of each butyl and phenyltins, 20 ng L⁻¹ (as Sn).

^b SD, standard deviation.

Table 3
 Analytical characteristics of DLLME-GC-FPD for determination of butyl and phenyltins in water sample^a

Compounds	RSD ^b (% , n = 7)	RSD ^c (% , n = 7)	EF ^d	LR ^e (ng L ⁻¹)	r ² f	r ² g	LOD ^h (ng L ⁻¹)
MBT	3.7	6.4	923	2-1000	0.9992	0.9990	0.5
DBT	2.8	4.1	987	1-1000	0.9995	0.9989	0.3
TBT	2.3	5.0	1036	0.5-500	0.9997	0.9993	0.2
MPhT	5.9	8.8	825	2-1000	0.9992	0.9984	1.0
DPhT	4.5	8.1	874	1-1000	0.9990	0.9988	0.5
TPhT	3.2	7.3	951	2-1000	0.9993	0.9991	0.7



Preconcentration techniques not yet applied for TBT analysis

Solid phase extraction techniques

Micro extraction by packed sorbent MEPS

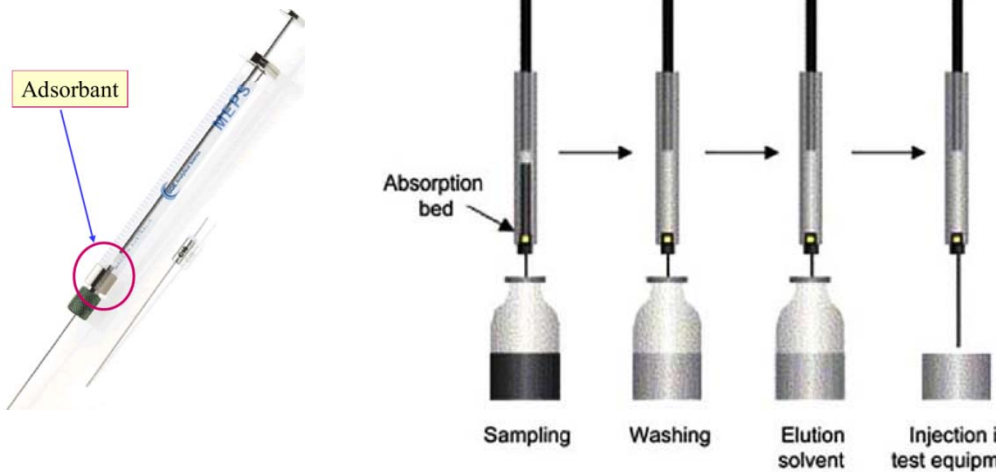


Figure 3.1 Automated GC SPME analysis with expansion of the SPME injection. Reproduced with permission from GERSTEL GmbH & Co. KG

Fig. (5). Automated MEPS process. Reprinted with permission from reference [94]. (© 2004 Elsevier Science).

Preconcentration techniques not yet applied for TBT analysis

Solid phase extraction techniques

Stired bar sorptive extraction SBSE

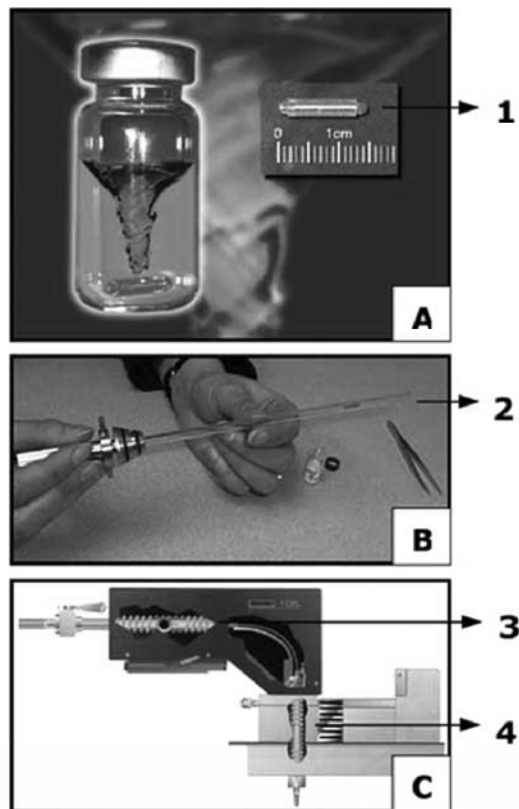


Fig. (6). Principle of SBSE. 1. Twister, 2. transfer to the thermal desorption tube, 3. thermal desorption unit, 4. programmed-temperature-vaporization injector. Reprinted with permission from reference [57]. (© 2002 Springer-Verlag).

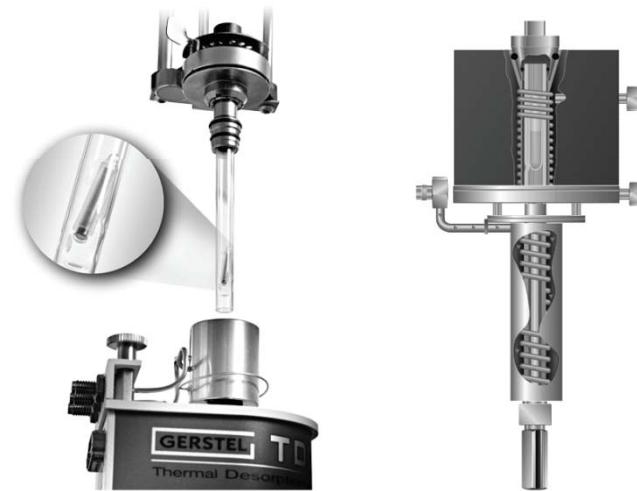
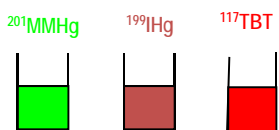


Figure 3.6 Twister bar being placed into the thermal desorption unit. Reproduced with permission from GERSTEL GmbH & Co.KG

Simultaneous speciation of organo- Hg and Sn compounds by isotopic dilution, microextraction in solid phase (SPME) in headspace and detection GC-ICPMS for waters

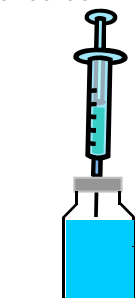
ANALYTICAL PROCEDURE

1-Enriched Standards



Determination of the relative abundances by reverse isotopic dilution

2-Spiking with enriched standards



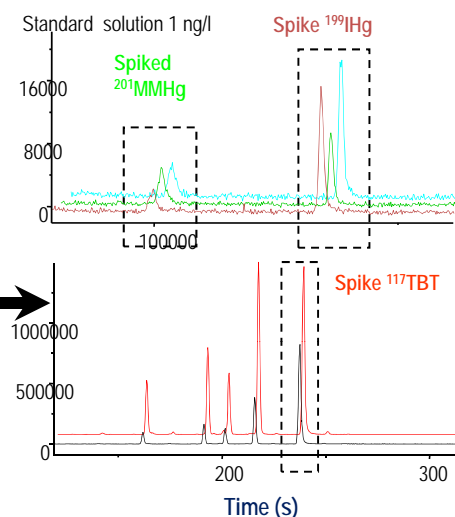
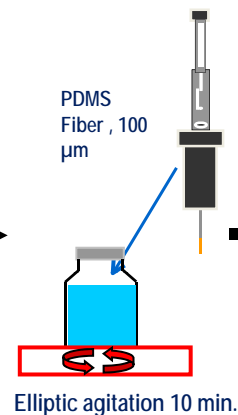
45 mL matrice
+ 5 mL acetate buffer
0.1M, pH=5,

3-Derivatization



NaBR₄, 50 µL at 1%
R= Propyl- or Ethyl-

4-Extraction



METHODE PERFORMANCE

Reproducibility

	MeHg	IHg	MBT	DBT	TBT
RSD (%) pic areas (n=4)	15	11	10	8	20
RSD (%) isotopic ratio (n=4)	3	2,3	2,2	1,4	2,4

☺
Improvement of the method by a factor of 5

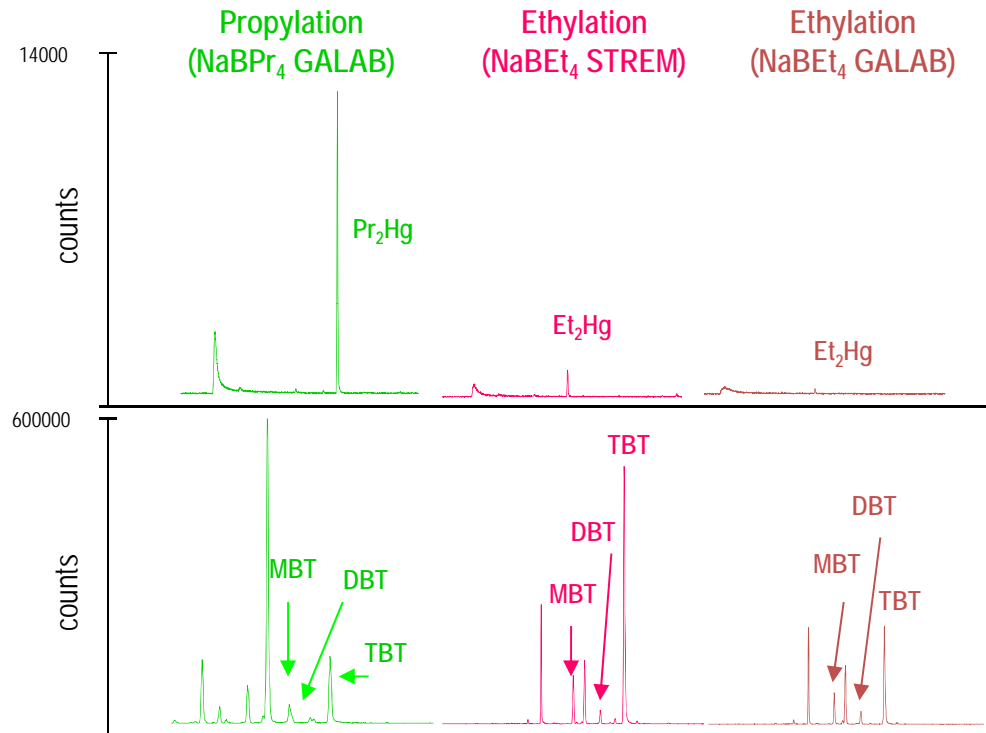
Detection limits

	MeHg	IHg	MBT	DBT	TBT
DL SPME (pg(Sn).l ⁻¹)	136	36	1,2	0,6	0,6
DL LLE (pg(Sn).l ⁻¹)	220	480	600	350	300

☺
Improvements of detection limits for bylltins

☹
Poor extraction by SPME for organo Hg

- Blanc contamination

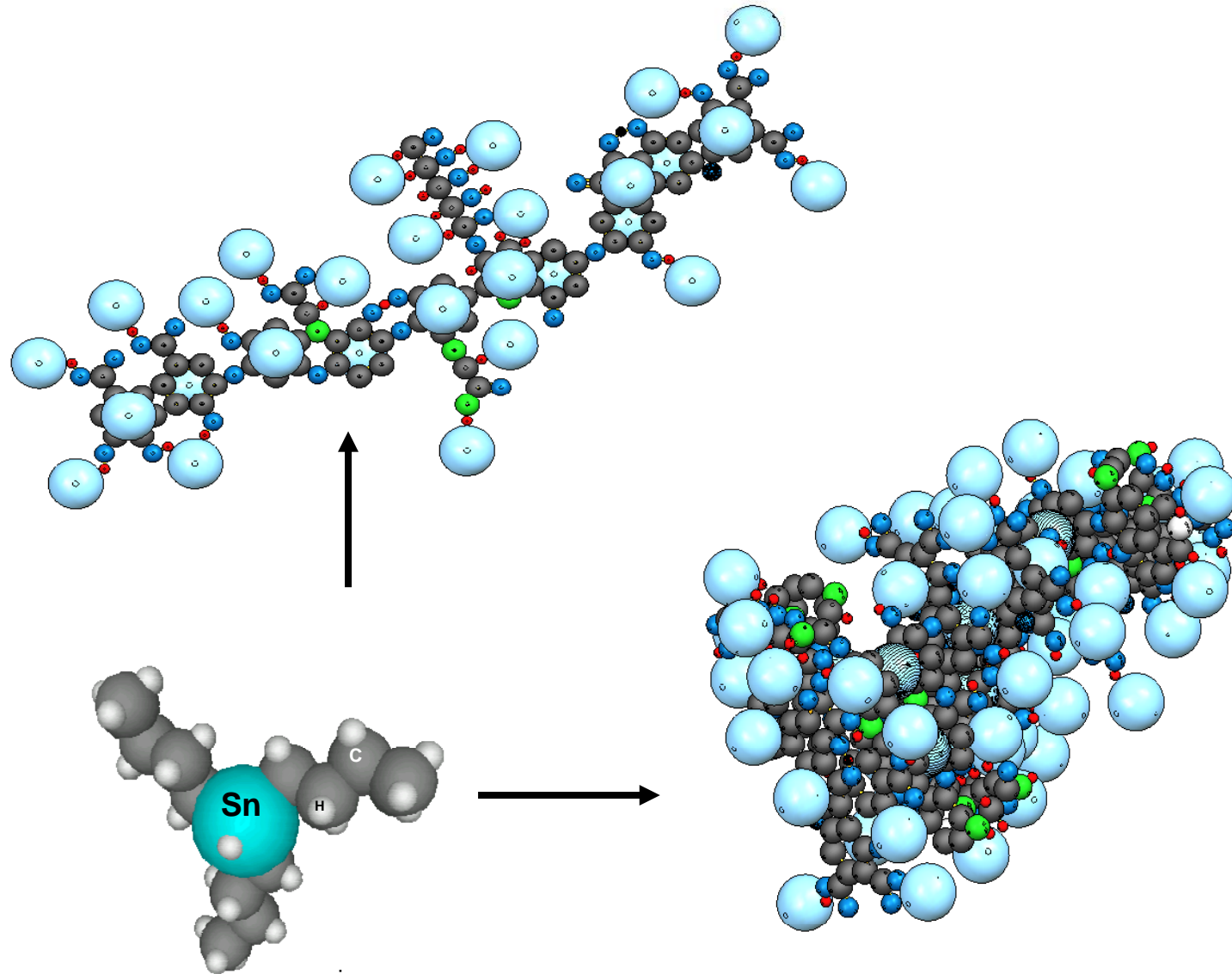


- Isotopic dilution allows to improve both the precision and accuracy of the method.
- SMPE preconcentration?
- Quality of the support

- Low efficiency for Hg

	MeHg	IHg	MBT	DBT	TBT
Slope (counts/pg)	90	350	14500	28000	28500

Environmental limitations



Organotins in Dutch waters

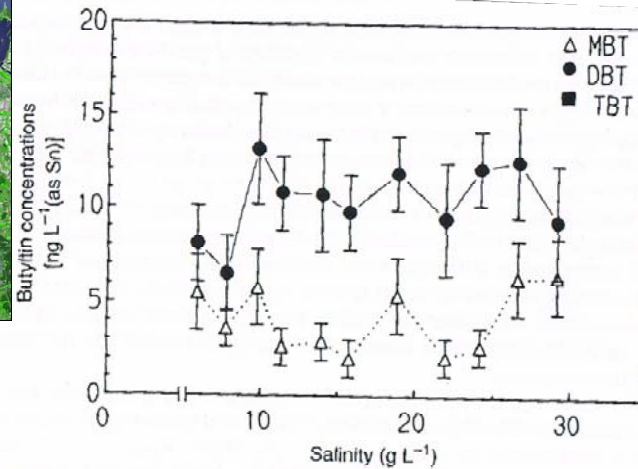


Figure 10.4. Distribution of butyl-Sn compounds in filtered water samples from the Western Scheldt (The Netherlands), October 1988. TBT was not present in any of the sample collected. (Adapted from ref. 95.)

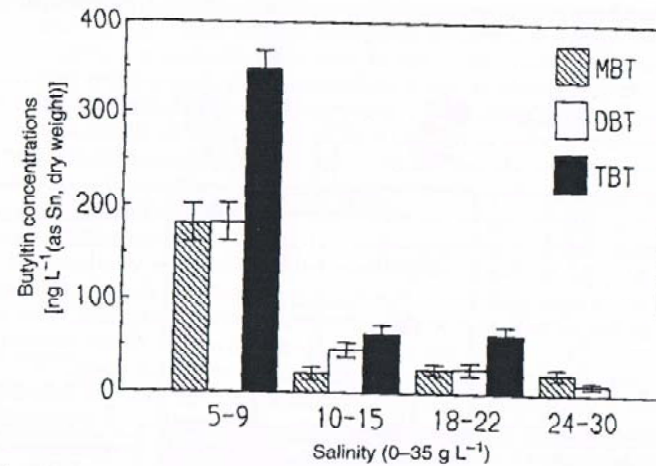
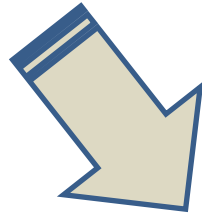


Figure 10.5. Distribution of butyl-Sn compounds in suspended matter collected by centrifugation in the Western Scheldt (The Netherlands), October 1988. Samples were collected by onboard continuous centrifugation. (Adapted from ref. 51.)

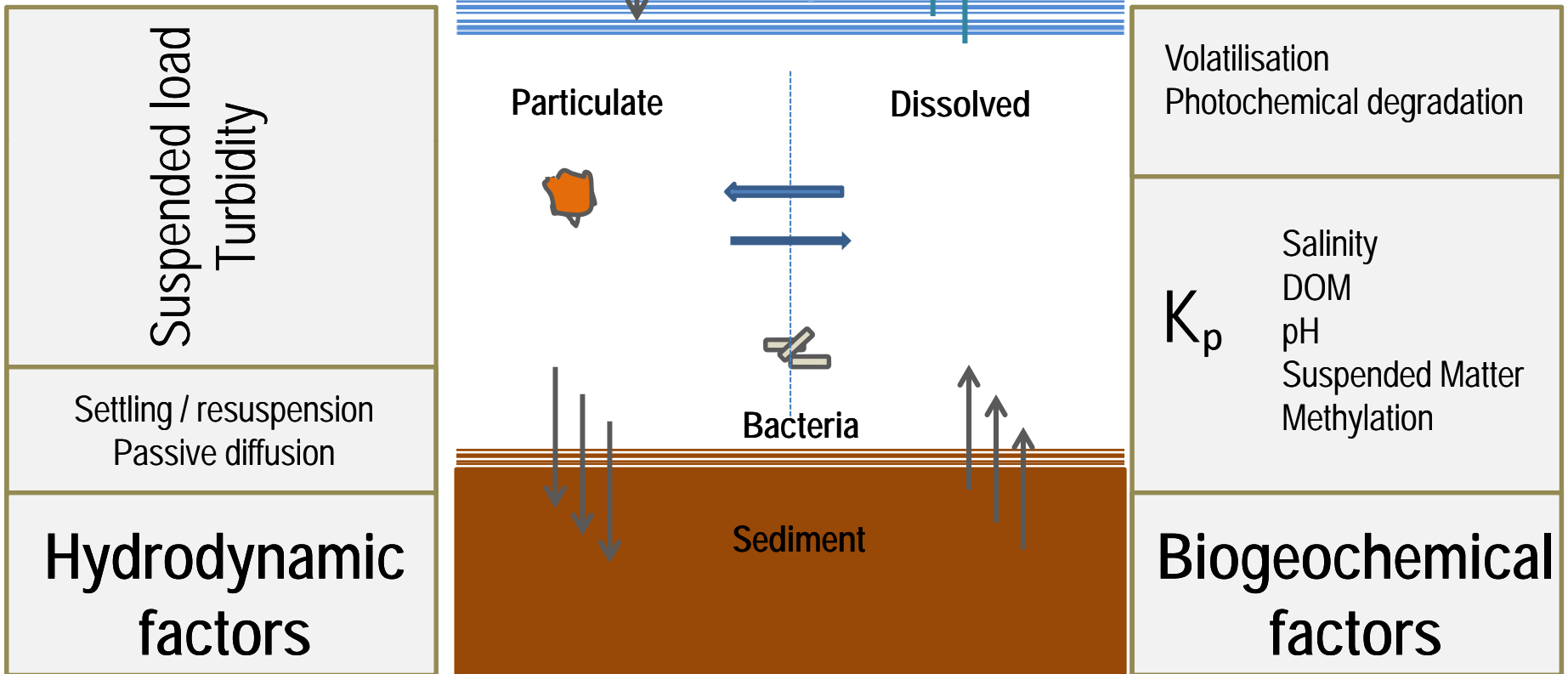
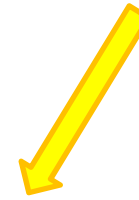


Environmental limitations

Variable point sources



Photochemistry





Environmental limitations: partitioning variability K_p

Conditions	Salinity (g/L)	Susp. Matter (mg/L)	K_p
<i>Field</i>	10-30	10-50	20
<i>Field</i>	35	6	3.28
<i>Field</i>	35	50	0.34
<i>Field</i>	35	2	39.35
<i>Field</i>	35	9	4.61
<i>Mesocosm</i>	35	0.7	71
<i>Laboratory</i>	32	60	1.4
<i>Laboratory</i>	0	60	0.2
<i>Laboratory</i>	0	3 000-30 000	8
<i>Laboratory</i>	24	3 000-30 000	4.2
<i>Laboratory</i>	5	1 000	1.5
<i>Laboratory</i>	35	10	1 900
<i>Laboratory</i>	27	15-57	0.12

Adapted from:

Tin speciation monitoring in estuarine and coastal environments

Ph. Quevauviller & O.F.X. Donard

Element Speciation in Bioinorganic Chemistry

Chemical Analysis Series,

John Wiley V. 135, pp 331 (1996)





- **Differential sampling strategies**
 - Role of filtration
 - Filtered versus non filtered
 - Comparison of the performance of detector (ICP/MS versus PFPD)
 - Preconcentration strategies
 - Laboratory versus natural waters
 - Particules effects (natural versus models :e.g: humics, clays, colloids,...)
 - K_p values
 - **Improve the quality of reagents**
 - **Selection of the best preconcentration strategy**
 - **Implementation of isotopic dilution**
 - On the field versus in the laboratoy
 - **Computational approach**
 - Theoretical formulation/speciation – K_p – adsorptive behaviour and toxicity
 - **Investigation of time of « statilisation »**
 - **Preparation of a reference materail for « TBT Water reference material »**





APPLICATION NOTE

GC/ICP-MS

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Mercury Speciation in Biological Tissue and Sediments by GC/ICP-MS

Introduction

The chemical determination of mercury (Hg) species in the environment is gaining increasing interest both for improved understanding of their reactional pathways and also to meet regulation limits in both Europe and the U.S. Mercury species play an important role in environmental pollution because they can result from anthropogenic activities, as well as natural biomethylation processes.¹



Figure 1. Clarus S80 GC (right) connected to NexION 300D ICP-MS (left) via GC transfer line.

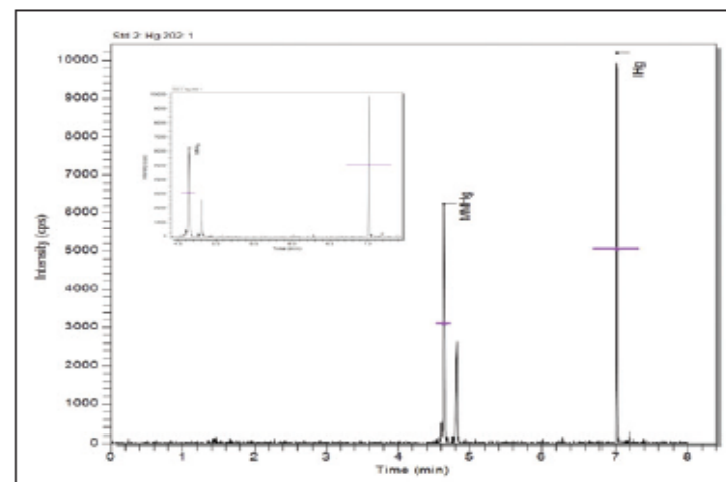


Figure 4. GC/ICP-MS chromatogram for ²⁰²Hg⁺ for 1 ng/mL standard solution of MMHg (1.2 ng/mL) and Hg²⁺ (1.7 ng/mL).

Analytical Performance

Once the optimization of the operational parameters for the GC transfer line was achieved, the analytical response characteristics were determined for MMHg and Hg²⁺ using standard solutions. The calibration curves were generated for the ²⁰²Hg⁺ peak areas for MMHg and Hg²⁺ through triplicate 1 µL injections across a concentration range from 0 (i.e. analytical blank) to 2 ng/mL. Good linearity and satisfactory coefficients of correlation (R² values) were observed for the ²⁰²Hg⁺ response functions (Figure 5). The limits of detections (LODs = 3σ_{blank}/n, where "n" is the number of readings) were determined from each calibration response function, and absolute LODs of 4 and 5 fg were obtained for MMHg and Hg²⁺ as ²⁰²Hg⁺, respectively.



Chemical reactivity

DFT based descriptors have found immense usefulness in the prediction of reactivity of atoms and molecules.

The prediction of the toxicity of chemicals requires the use of chemical descriptors that allow to understand how covalently reactive a given compound is.

For example, Chemical hardness (h) , Chemical potential (m) and global electrophilicity (w) are known as global reactivity descriptors

Thanks to Jean Marc SOTIROPOULOS and Laure TASTET

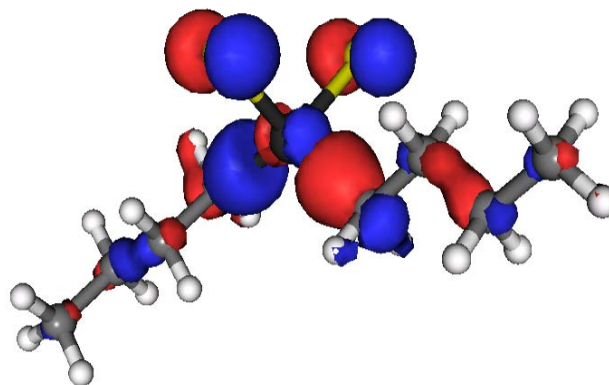


Example :

Dichloro Dibutyl Tin Frontier Molecular Orbital

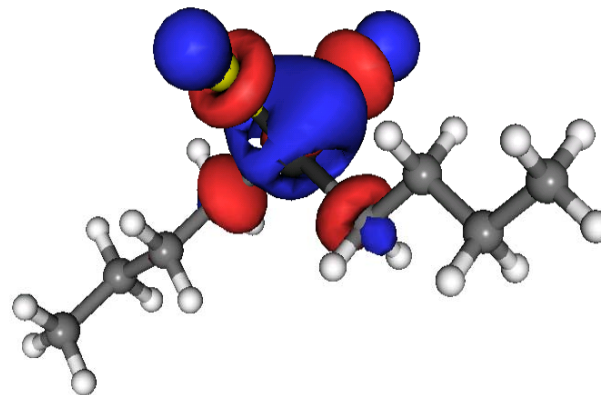
HOMO

$\sigma_{\text{SnC}}, n_{\text{Cl}}^{\pi^+}$



LUMO

σ_{Cl}^*



The LUMO in all chlorine derivatives are energetically more accessible than in the other calculated compounds which is coherent with a better electrophilicity (w)



Implementing molecular calculations

	μ (eV)	η (eV)	ω (eV)
DibutylTin	-2,948	3,956	0,368
Dibutyl Dichloro Tin	-4,201	3,276	2,693
Tributyl Tin	-2,759	2,763	1,378
AcetateTriPhenyl Tin	-3,687	3,006	2,261
TetraButyl Tin	-2,647	3,933	0,891
TriPhenyl Tin	-3,489	3,168	1,921
ChloroTriPhenyl Tin	-3,899	2,992	2,541



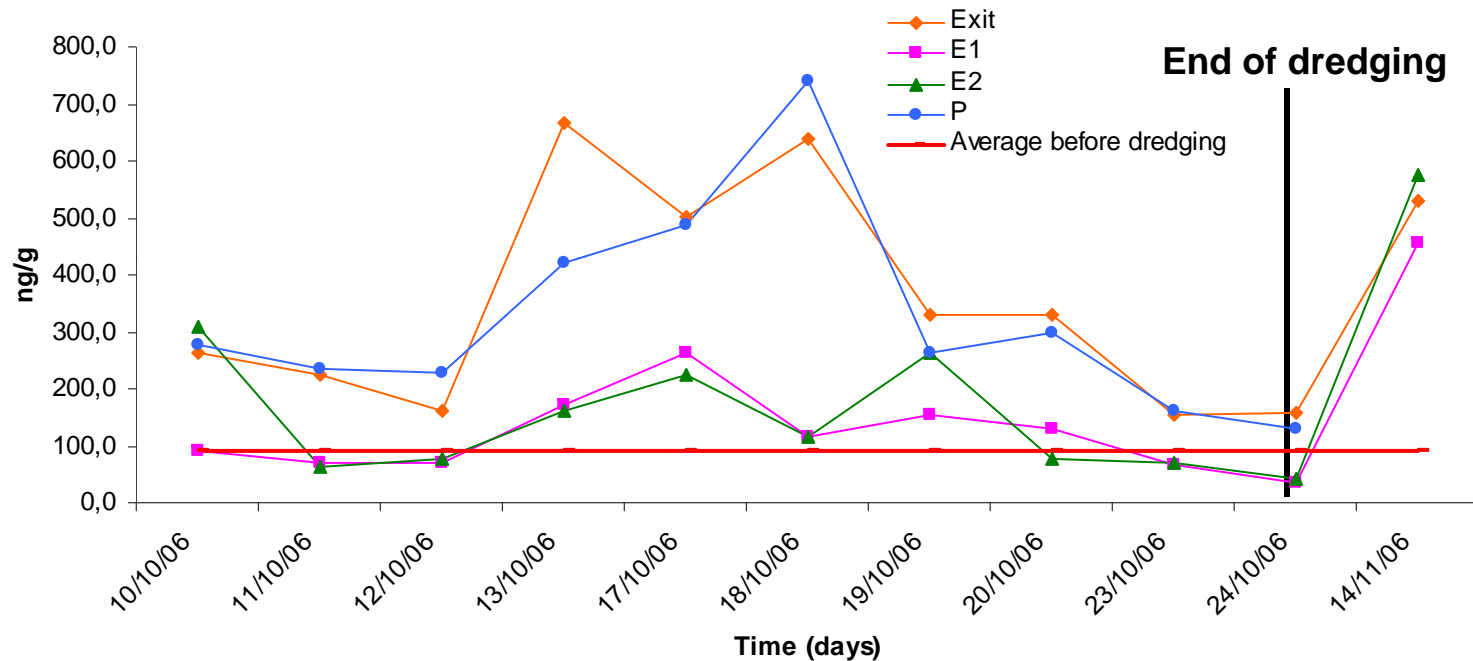
Thanks to Jean Marc SOTIROPOULOS and Laure TASTET



Real case situations: dredging of the Harbor of Arcachon



Dredging of the port of Arcachon: Environmental monitoring – TBT in suspended matters

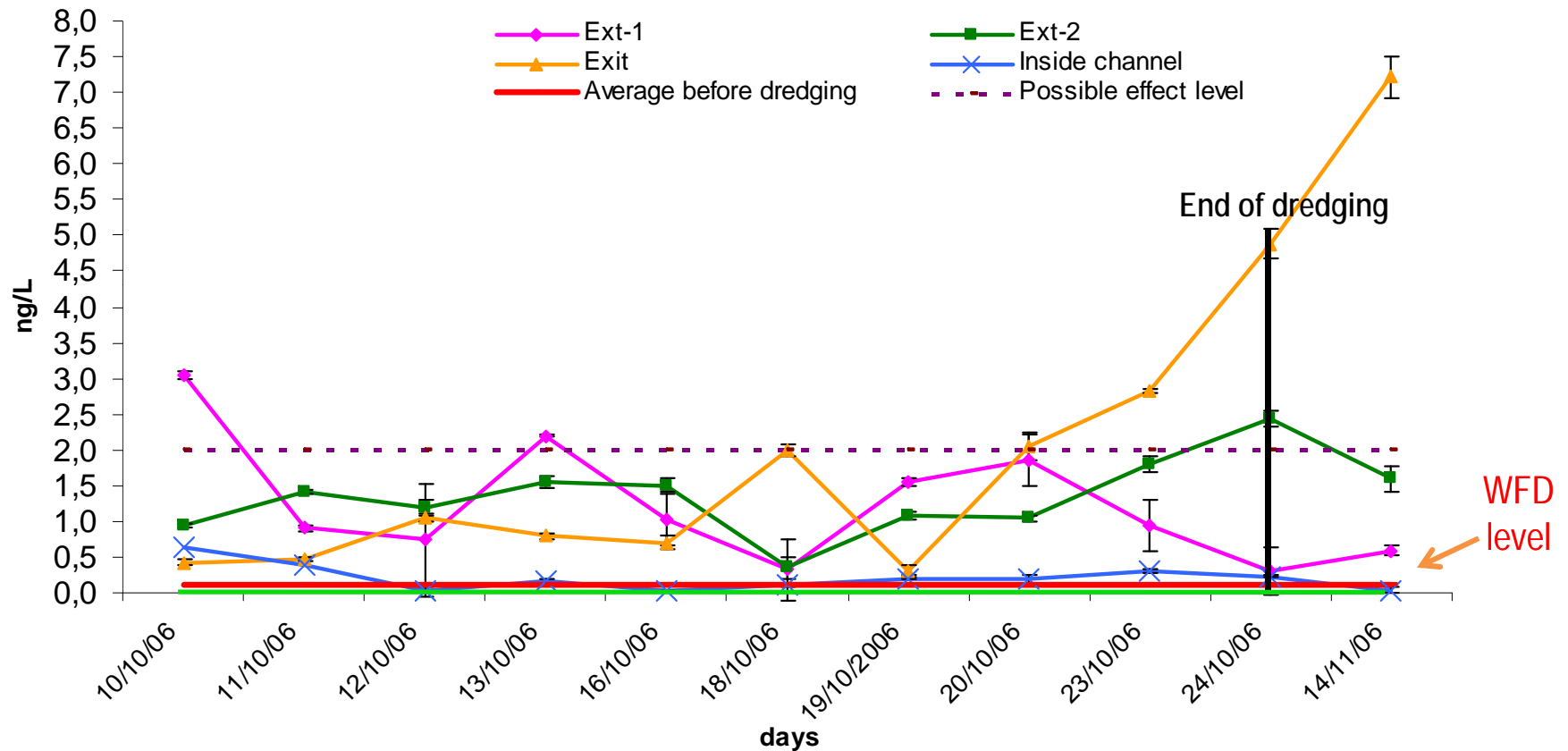


➡ Concentrations in SPM are above the concentration measured before the dredging operations

➡ Concentrations are in the same order of those measured in sediment

Dredging of the port of Arcachon:

Environmental monitoring – TBT in the dissolved phase by GC/IPC/MS



➡ Concentrations > 2ng/L could imply biological effects (calcification anomalies)

➡ Possible transfer of TBT from suspended particles to the dissolved phase



