13th International SedNet Conference
Faculty of Sciences of the University of Lisbon, Lisbon, Portugal
6 - 8 September 2023

The Importance of Reviewing the Portuguese Legislation for the Assessment and Management of Dredged Materials: The Case of Butyltins

Mário Mil-Homens*[1,2], C. Marisa Almeida[2], Miguel M. Santos[2] & Miguel Caetano[1,2]

[1] Divisão de Oceanografia e Ambiente Marinho, Instituto Português do Mar e da Atmosfera, Lisboa, PORTUGAL
mario.milhomens@ipma.pt , mcaetano@ipma.pt
[2] Interdisciplinary Centre of Marine and Environmental Research, of the University of Porto, Matosinhos, PORTUGAL
calmeida@ciimar.up.pt , santos@ciimar.up.pt

Background 1

Maintenance of harbors, marinas & navigation channels

Implies regular dredging operations

Significant amounts of contaminated dredged materials

THE ASSESSMENT OF THE LEVELS OF CONTAMINANTS

TO PREVENT

TO REDUCE

THE RELEASE OF HAZARDOUS SUBSTANCES IN THE MARINE ENVIRONMENT

Background 2

2007

Portugal implemented environmental legislation for the management of dredged materials **(Ordinance 1450-2007)**

5-category scheme

Trace metals (As, Cd, Cu, Cr, Hg, Ni, Pb & Zn), **POP** (PAHs, PCBs & HCH)

CONCENTRATION RANGE

CLASS 1 (CLEAN DREDGED MATERIAL)

CLASS 2 (TRACE CONTAMINATED DREDGED MATERIAL)

CLASS 3 (SLIGHTLY CONTAMINATED DREDGED MATERIAL)

CLASS 4 (CONTAMINATED DREDGED MATERIAL)

CLASS 5 (HEAVILY CONTAMINATED DREDGED MATERIAL)

Butyltin compounds (TBT, DBT, and MBT) could be monitored but were not measured since there are no screening levels available for monitoring.

Study framework

THE CSS PROJECT

CHARACTERIZE SPATIAL PATTERNS & RECENT TEMPORAL TRENDS

SEDIMENTARY PARAMETERS (GRAIN SIZE, ORGANIC CARBON)

CHEMICAL CONTAMINANTS (BTS, TRACE METALS, PAHS & PCBS)

SURFACE SEDIMENTS & SHORT ^{210}Pb DATED SEDIMENT CORES

IN THE AREA THAT NOT REACHED THE GOOD ENVIRONMENTAL STATUS (GES) IN THE FIRST MSFD REPORT

THE CONCENTRATIONS OF BTS (TBT, DBT & MBT) WERE NOT ASSESSED

LACK OF INFORMATION AVAILABLE ON BTS IN THE PORTUGUESE SHELF SEDIMENTS

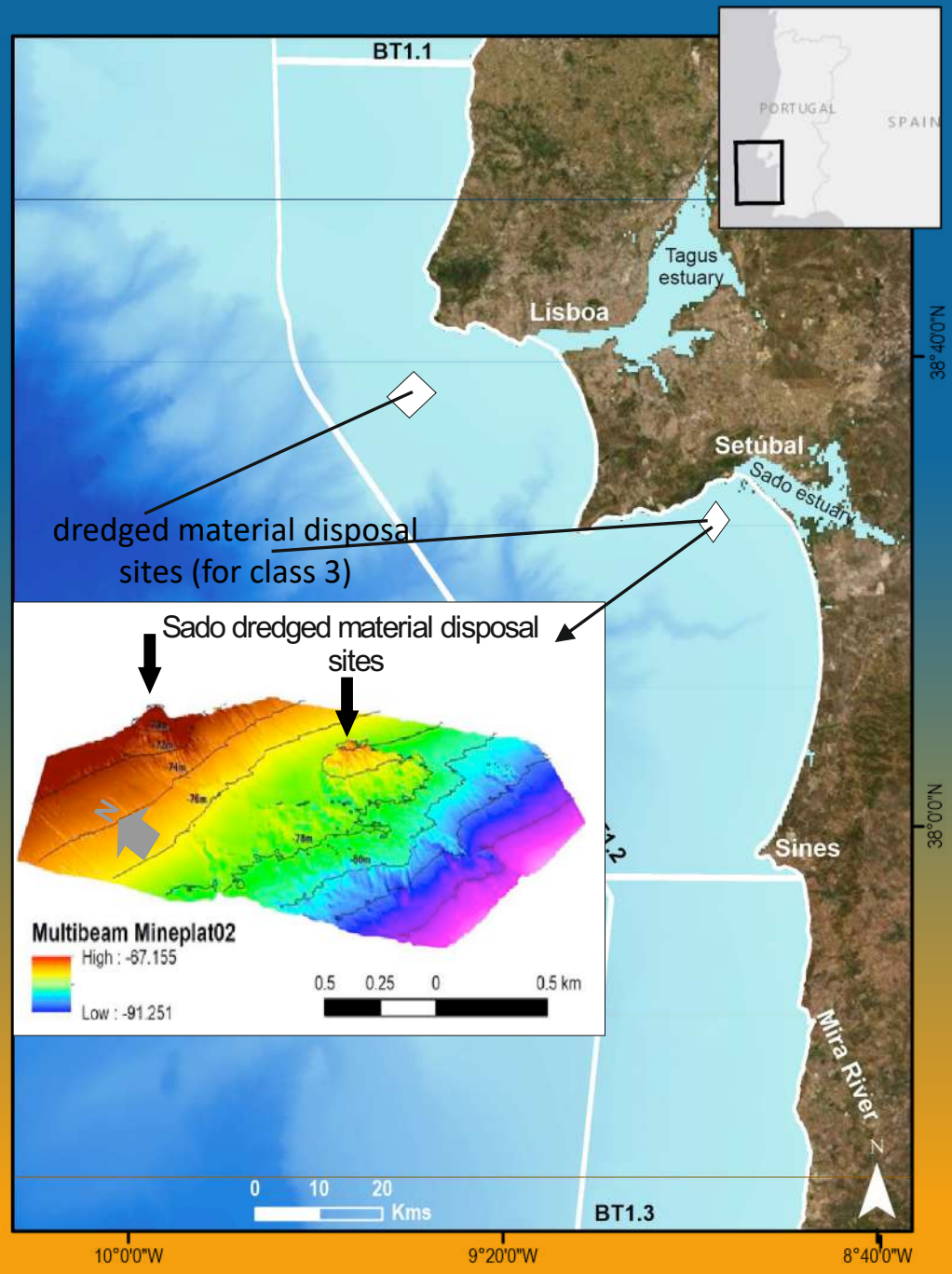
Main goals

- Filled the gap of butyltin compounds (BTs) data in marine sediments
- Collected data was compared to international Sediment Quality guidelines (SGG) and Action Levels (ALs) of contaminants for managing disposal of dredged materials

Study area

- THE AREA THAT NOT REACHED THE GES IS THE AREA BT1.2
- DUE TO:
  1) THE PROXIMITY OF THE TAGUS AND SADO ESTUARIES
  2) ESTUARINE AREAS MARKED BY INTENSE URBAN AND PAST INDUSTRIAL OCCUPATION (E.G., SHIPYARDS, CHLORALKALI, PYRITE ROAST PLANT, SMELTER)
  3) HISTORICALLY CONTAMINATED PARTICLES WERE EFFICIENTLY TRANSFERRED FROM THE ESTUARIES TO ADJACENT SHELF AREAS.
  4) SINES HAS THE LARGEST PORTUGUESE HARBOR, AN OIL REFINERY AND A THERMOELECTRIC POWER PLANT

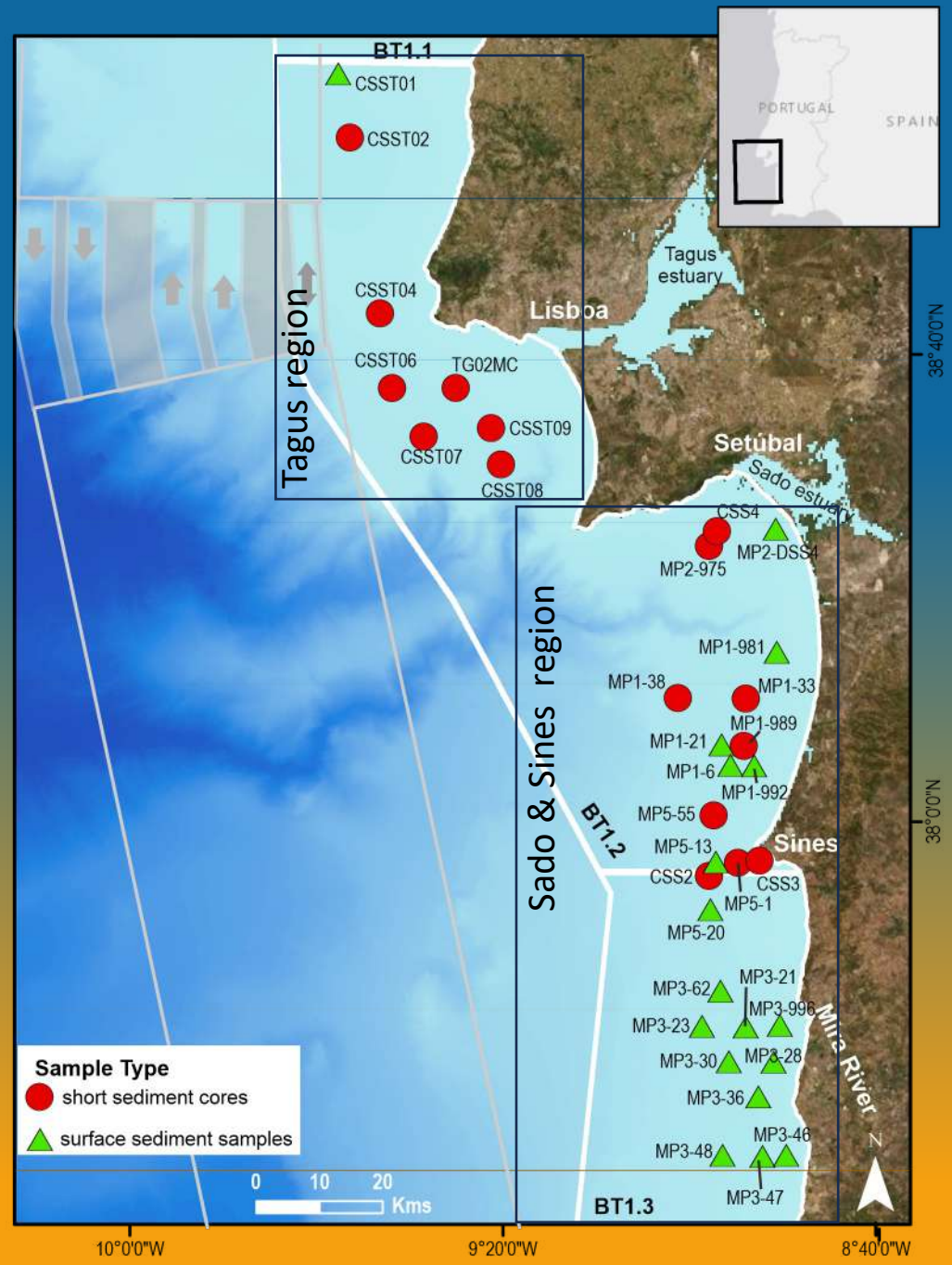
THIS AREA HAS THREE DMDS FOR CLASS 3 (SLIGHTLY CONTAMINATED DREDGED MATERIAL WITH A MONITORING PLAN FOR IMMERSION)



Sediment sampling

- Sediment samples were collected during two oceanographic campaigns occurred in 2019 & 2021

- For assessment of BT levels:
  1) eighteen surface sediment samples were collected using a Smith-McIntyre grab
  2) sixteen short sediment cores were sampled with multicorer and boxcorer
  3) total of 168 samples

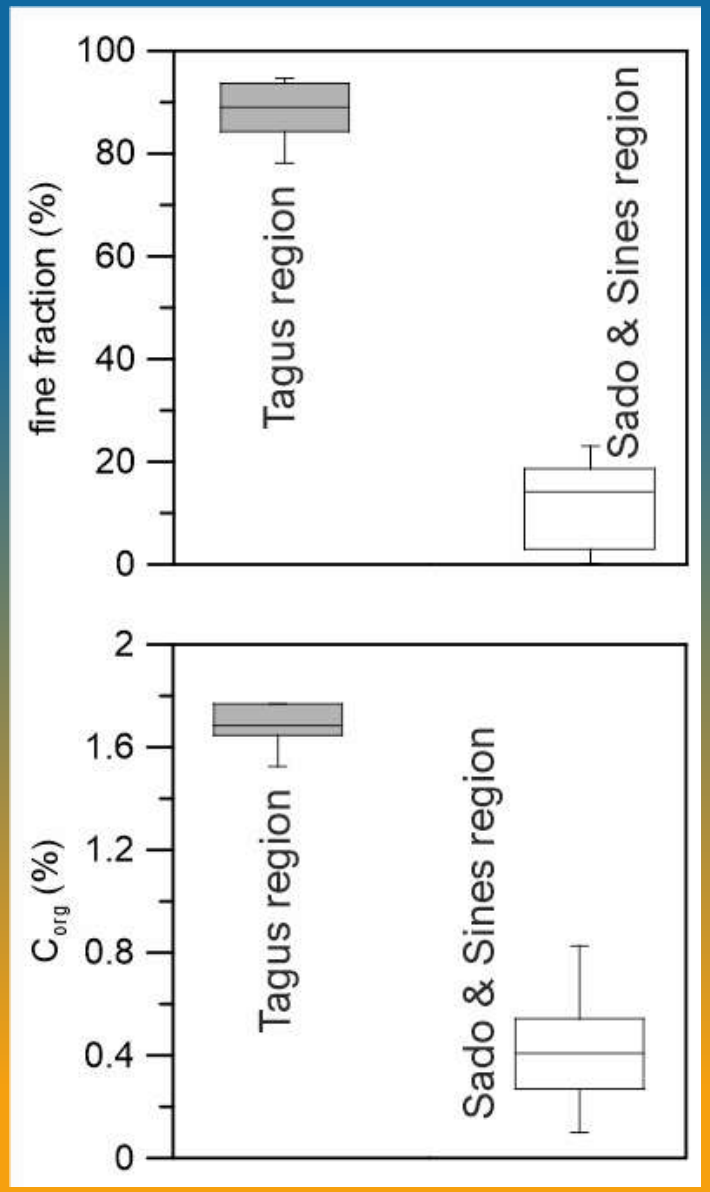


Methods

GRAIN SIZE	Mechanical sieving & Coulter LS-1320
ORGANIC CARBON (C_{ORG})	Leco Truspec micro-analyzer CHNS
BUTYLTIN COMPOUNDS (MBT, DBT & TBT)	solid-phase microextraction (SPME)-GC-MS
^{210}Pb & ^{226}Ra	α & γ spectrometry [sedimentation rates calculated using the Constant Flux and Constant Sedimentation Rate including a surface mixed layer]

Main results & discussion

Surface and down-core sediment characteristics



TAGUS REGION HAS HIGH FINE FRACTION & C_{org}

MAJOR TAGUS RIVER OUTFLOW & HIGHER EXPORT OF PARTICULATE MATERIAL

FINE FRACTION & C_{org} SHOWS LIMITED DOWN-CORE VARIABILITY

MAY REFLECT THE ABSENCE OF SIGNIFICANT CHANGES IN THE HYDRODYNAMIC CONDITIONS OF THE AREA.

Main results & Discussion

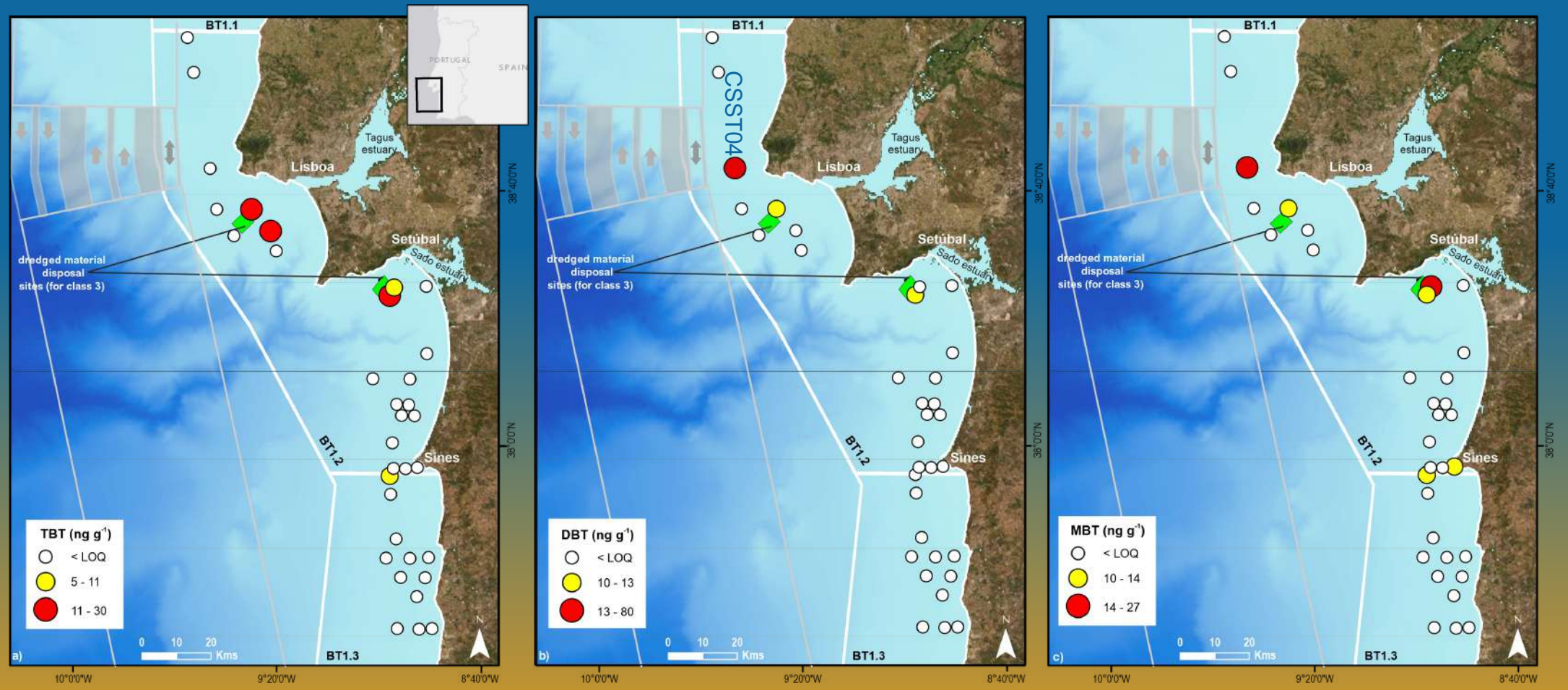
Characterization of Butiltyn compounds (BT) in sediments

Butiltyn Compounds	LoQ ($ng\ g^{-1}$)	Samples above the LoQ	Range ($ng\ g^{-1}$)	Correlation* with Corg and ff
Monobutyltin (MBT)	10	39	10 - 100	Not correlated
Dibutyltin (DBT)	10	25	10 - 300	Not correlated
Tributyltin (TBT)	5	19	5 - 41	0.65 & 0.51

* Spearman correlation coefficient

Main results & Discussion

Distribution of BT in surface sediments



- MAXIMUM TBT CONCENTRATIONS → VICINITIES OF THE DMDS
- MAXIMUM DBT CONCENTRATIONS → CSST04 & VICINITIES OF DMDS
- MAXIMUM MBT CONCENTRATIONS → CSST04, VICINITIES OF THE DMDS & SINES HARBOR

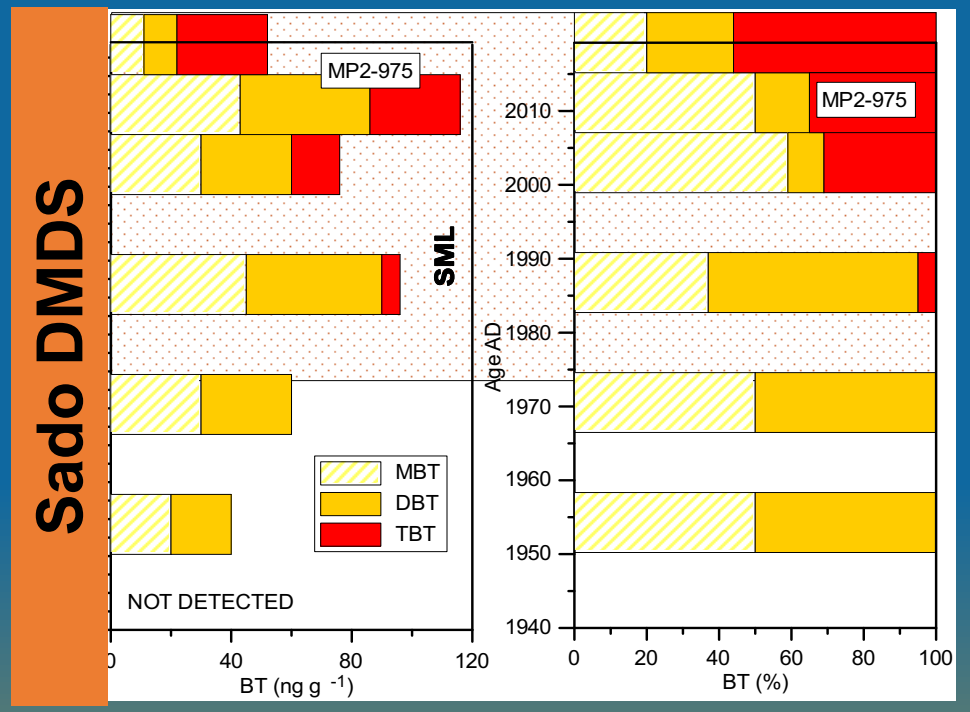
Main results & Discussion

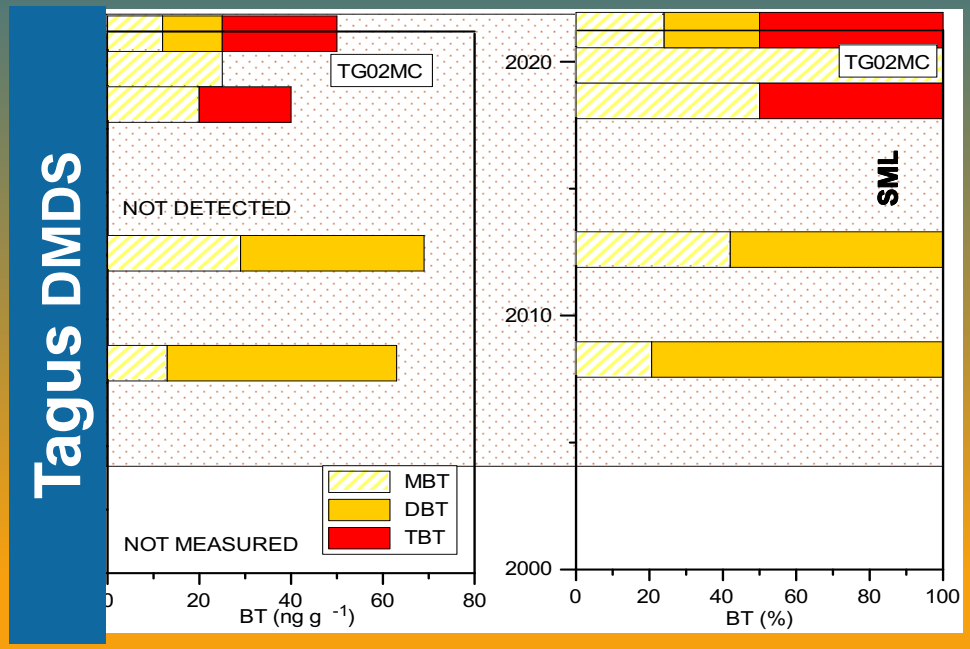
Down-core variability of TBT

MAJORITY OF THE SAMPLES [TBT] < LOQ

WHEN MEASURED ARE IN THE CORE LOCATIONS NEARBY THE DMDS AT CORE-DEPTHS REACHED BY THE SML

- MAY REFLECT SEDIMENT REWORKING
- MAY EXPLAIN THE IRREGULAR DOWN-CORE VARIABILITY





Main results & Discussion

Sediment Quality Guidelines (SQG) and evaluation of the potential ecological toxicity of TBT in marine sediments

ABSENCE OF SCREENING VALUES

↓

ACQUIRED DATA

- **TBT SITE CLASSIFICATION (DOWSON ET AL., 1992)**
- **ACTION LEVELS (AL)**
- **SEDIMENT QUALITY GUIDELINES (SQG)**

Main results & Discussion

DOWSON ET AL., (1992)

Site classification for levels of TBT (ng/g) in sediment samples

Classification	Range of TBT levels	Number of Sediment samples	
Uncontaminated	< 3	Surface	29*
		Down-core	120*
Lightly contaminated	3 - 20	Surface	3
		Down-core	9
Moderately contaminated	20 - 100	Surface	2
		Down-core	5
Highly contaminated	100 - 500	Surface & Down-core	0
Grossly contaminated	> 500	Surface & Down-core	0

* Our LoQ was 5 ng/g

TBT LEVELS FOUND IN PORTUGUESE SEDIMENTS ● LIGHTLY TO MODERATELY CONTAMINATED

Main results & Discussion

Action Level (AL) values for total concentrations of TBT (ng/g) in European countries from the OSPAR and HELCOM regions (adapted from MCWG, (2022) & Warford et al., (2022)).

	Belgium	United Kingdom	France	Germany	Finland
AL1 (lower)	3	100	100	20	3
AL2 (upper)	7	500	400	300	200

< AL1: generally considered acceptable for disposal at sea
>AL1 & < AL2: sediment evaluation using a weight of evidence approach
>AL2: unacceptable for uncontrolled dumping at sea without special handing and control

TBT levels found in Portuguese sediments

- Low risk: UK & France ALs
- Unacceptable for disposal: Belgian ALs

The difference in ALs among different countries can be explained by the level of precaution with which toxicity of the TBT is evaluated.

Main results & Discussion

LIMITATIONS IN USING SQG FOR EVALUATION OF THE ECOLOGICAL TBT TOXICITY

THIS APPROACH IS A PRACTICAL TOOL FOR SCREENING POSSIBLE ECOLOGICAL RISKS

Main results & Discussion

SQG → C_{org} is commonly used for normalizing BTs in marine sediments

Norwegian, Australian & USA SQG normalized to 1 % C_{org}

$TBT^* = TBT_{(sample)} \times 1\% / \%C_{org\ (sample)}$

		Portuguese sediments (9 ng/g<TBT*< 48 ng/g)
Norwegian SQG	CLASS 3 - Toxic effects following chronic exposure (5 < TBT* < 20 ng/g)	Moderately to badly contaminated
	CLASS 4 - Toxic effects following short term exposure (20 < TBT* < 100 ng/g)	
Australian SQG	Low Trigger Value (LTV) (9 ng/g)	Between LTV and HTV (possible adverse effects on benthic biota)
	High Trigger Value (HTV) (70 ng/g)	
USA SQG	Lower Screening Value (LSV) (5.2 ng/g)	Between LSV and HSV (Low ecological toxicity)
	Higher Screening Value (HSV) (72 ng/g)	

Final considerations

- This study demonstrates the occurrence of BTs in recent marine sediments of the Portuguese shelf.
- The sediments collected near disposal sites may be contaminated, causing harm to marine life in accordance with international guidelines.
- Monitor BT contamination in ports, marinas, shipyards, and shipping channels.
- Establish action levels of BTs and other booster biocides (e.g., Irgarol) for responsible disposal of dredged material.

Final considerations

- Portuguese legislation lacks proper regulations for BTs, which may result in the annual dredging and discharge of several thousand tons of contaminated sediments at sea disposal sites. This poses a potential threat to marine life.

- More research is required, contributing to adequate legislation and to reduce the risk of dispersion of TBT (and other booster biocides) through the disposal of dredged material.

MORE AND DETAILED INFORMATION CAN BE FOUND IN THE ARTICLE RECENTLY PUBLISHED AT THE SCIENCE OF THE TOTAL ENVIRONMENT JOURNAL

Science of the Total Environment 900 (2023) 165872

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Check for updates

Spatial distribution and temporal trends of butyltin compounds (TBT, DBT & MBT) in short sediment cores of the SW Portuguese Shelf (western Iberian Margin, NE Atlantic)

Mário Mil-Homens [a,b,*], C. Marisa R. Almeida [b,c], Sofia Dias [b,c], Warley Soares [d], Piet van Gaever [e], Henko de Stigter [e], Miguel M. Santos [b,f], André Santana [g], Mafalda Freitas [d], Fátima Abrantes [d,g], Miguel Caetano [a,b]

[a] IPMA, Divisão de Oceanografia e Ambiente Marinho, Instituto Português Do Mar da Atmosfera, I.P., Avenida Doutor Alfredo Magalhães Ramalho, 6 1495-165 Algés, Portugal
[b] CIIMAR/CIMAR-LA, Centro Interdisciplinar de Investigação Marinha e Ambiental, Universidade do Porto, Terminal de Cruzeiros de Leixões, Av. General Norton de Matos s/n, 4450-208 Matosinhos, Portugal
[c] Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal
[d] IPMA, Divisão de Geologia e Georecursos Marinhos, Instituto Português Do Mar da Atmosfera, I.P., Avenida Doutor Alfredo Magalhães Ramalho, 6, 1495-165 Algés, Portugal
[e] NIOZ, Royal Netherlands Institute for Sea Research, Department of Ocean Systems, Landsdiep 4, 1797SZ 't Horntje – Texel, the Netherlands
[f] Departamento de Biologia, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
[g] CCMAR, Centro de Ciências do Mar, Universidade do Algarve, Campus de Gambelas, 8005-139 Faro, Portugal

Acknowledgments

The authors would like to thank the FEAMP financial support through the CSS project (MAR-01.04.02-FEAMP-0013).

The CSS project and the TAGUSGAS project (PTDC/CTA-GEO/31885/2017) financed the 2021 sampling campaign.

The MINEPLAT project (ALT20-03-0145-FEDER-000013) supported the 2019 sampling campaign.

Special knowledge for the crews of the research vessels Noruega & NRP Gago Coutinho and for all participants in both cruise campaigns.

The authors thanks the technical staff of the IPMA's, CIIMAR and NIOZ laboratories involved in sampling, sample preparation, and all analytical determinations.

CO-FINANCED:

mar 2020

PROGRAMA OPERACIONAL MAR 2020

PORTUGAL 2020

UNIÃO EUROPEIA

Fundo Europeu dos Assuntos Marítimos e das Pescas

Classification of dredged materials according to the degree of contamination: trace metals (mg/kg), organic compounds (ug/kg) (Ordinance 1450/2007)

	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Hg (mg/kg)	ΣPCB (µg/kg)	ΣPAH (µg/kg)	HCB (µg/kg)
Class 1	< 20	< 1	< 50	< 35	< 30	< 50	< 100	< 0,5	< 5	< 300	< 0,5
Class 2	20 - 50	1 - 3	50 - 100	35 - 150	30 - 75	50 - 150	100 - 600	0,5 - 1,5	5 - 25	300 - 2000	0,5 – 2,5
Class 3	50 - 100	3 - 5	100 - 400	150 - 300	75 - 125	150 - 500	600 - 1500	1,5 – 3,0	25 - 100	2000 - 6000	2,5 - 10
Class 4	100 - 500	5 - 10	400 - 1000	300 - 500	125 - 250	500 - 1000	1500-5000	3,0 - 10	100 - 300	6000 - 20000	10 -50
Class 5	> 500	> 10	> 1000	> 500	>250	> 1000	>5000	> 10	>300	>20000	>50