OCCURRENCE OF ORGANOTIN COMPOUNDS IN WATERS OF THE SPANISH COAST UNDER THE EUROPEAN WATER FRAMEWORK DIRECTIVE

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INTRODUCTION

Organotin compounds (OTCs), such as tributyltin (TBT), are persistent organic pollutants that are present in water samples (surface water, river water, sea water, waste water, etc.) because of anthropogenic activities (antifouling agents in ship paints, biocides in polymers, etc.). The toxicity and endocrine disruption potential of these chemicals have been demonstrated even at very low levels (<1 ng L^{-1}) (Devos et al. 2012). Due to the extensive presence of OTCs in all environmental media as well as their adverse effects on human health and biota, these compounds are included in the list of priority substances according to the EU Directive 2013/39/EU amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. This directive specifies annual average environmental quality standard (AA-EQS) of 0.2 ng L^{-1} TBT and a maximum allowable environmental quality standard (MAC-EQS) of 1.5 ng L^{-1} TBT for all surface waters. Actually, achieving a reliable determination of these compounds in the range of a few ng L^{-1} continues to be an analytical challenge.

SAMPLING AND EXPERIMENTAL METHOD

Study area

Samples were collected in two semiconfined coastal areas, one of them an area with high industrial and port activities (Ría de Vigo). In this area, there are a number of small, dispersed population nuclei located along the margins of this estuary, together with the city of Vigo which exceeds 300,000 inhabitants and also possesses a modest industrial development and a significant port operation. All this, added to geographic and oceanographic characteristics that do not permit a good level of water exchange with the ocean, could lead to an accumulation of certain contaminants within the estuary. The other one with high touristic and agricultural activity (Mar Menor) is a hypersaline coastal lagoon located in the South East of Spain, with a mean depth of 4.5 m and a maximum depth of 6.6 m. As consequence of its relative isolation from the Mediterranean Sea, seasonal fluctuations of temperature and salinity are higher in the Mar Menor lagoon than those detected in the former, showing a water residence time of 0.79 years. Mar Menor lagoon (Murcia, SE Spain) is located close to the Campo de Cartagena area, characterized by intensive agriculture, recreational activities and a sporadic torrential rainfall regime.

Samples collection and treatment

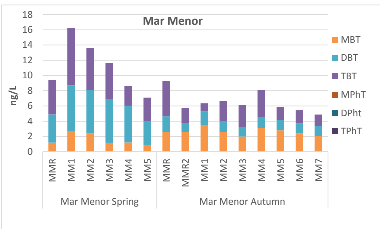
The sampling campaigns were performed in spring (P) and autumn (O) of 2015. In the spring campaign 5 sampling stations were selected within the Mar Menor (MM1 to MM5), and an external reference point (MMR). In the case of the Vigo estuary, 5 points were selected within the estuary (RV1 to RV5) and a reference point outside the estuary (RVR). In the autumn campaign two points were added within the Mar Menor (MM6 and MM7) and another external reference point (MMR2). Also in the Ría de Vigo two samples for the same point were taken: superficial (S) and bottom (F).

Sampling surveys in Ria de Vigo were carried out using the Oceanographic vessel J.M. Navaz. Surface (1m) and depth water samples (5m above the bottom) were collected in 1L amber glass bottles using a glass pitcher and stored at 10ºC until arrival at the laboratory, where they were stored at -20 ºC until further analysis.

Surface seawater sampling campaigns in the Mar Menor lagoon were performed using Posidonia II boat. Surface water samples (1-15 cm) were collected in 1L amber glass bottles using a glass pitcher and stored at 10ºC until arrival at the laboratory, where they were stored at -20 ºC until further analysis.

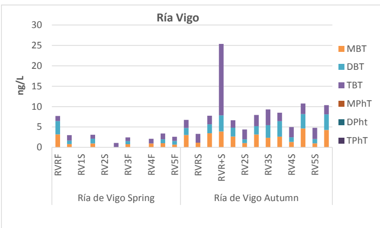
RESULTS

The levels of MBT, DBT, TBT, MPhT, DPhT and TPhT in the seawater samples were analyzed by HS-SPME-GC–QqQ-MS/MS method (Moscoso-Pérez et al. 2015).



As can be seen in the table, phenylated compounds of Sn (MPhT, DPhT and TPhT) were not found in concentrations above the limit of quantification in any of the samples. For butylated compounds (MBT, DBT and TBT), concentrations above the limit of quantification were detected in 100% of the samples analyzed in the Mar Menor. In the Vigo estuary, MBT has been detected in 20 of the 24 analyzed samples (83.3%), DBT in 18 samples from the total of 24 samples analyzed (75%) and TBT in 21 of the total of 24 samples analyzed (87.5%).

Higher values were found in spring than in autumn for Mar Menor, nevertheless for Ría de Vigo the highest values were found in autumn. This would be possibly due to the run-off or increase of the maritime traffic in the month before the sampling time.



TBT identified in the EU Water Framework Directive (2013/39/EU) as a priority hazardous substance with a maximum permissible concentration of 1,5 ng L-1 is present in 92.3% of the total 39 samples analyzed, being detected in 100% of Mar Menor samples and 87.5% of Ría de Vigo samples.

ng/L	MBT	DBT	TBT	MPhT	DPhT	TPhT	Ref.
Ría Vigo	1.83	1.65	2.37	<8.00	<15.0	<10.0	This reference
Mar Menor	2.22	2.81	3.30	<8.00	<15.0	<10.0	This reference
Saronikos Gulf (Grecia)	<2.00-17.0	7.00-45.0	8.00-70.0	nm	nm	nd	Thomaidis et al
Pagasitikos Gulf (Grecia)	<2.00-19.0	<2.00-159	<2.00-21.0	nm	nm	nd	Thomaidis et al
Gijón (España)	50	100	110	nm	nm	nm	Centineo et al
Jinhae Bay (Korea)*	1.10	0.70	0.20	nm	nm	nm	Kim et al
Adriatic Coast (Croacia)*	2.74	2.38	3.31	nm	nm	0.42	Furdek et al
Valencia (España)	nm	nm	1.30	nm	0.14	nd	Segovia-Martínez et al
Antwerp (Bélgica)	nm	nm	0.80-2.92	nm	nm	nm	Devos et al
Taiwan	Nd-99	Nd-160	Nd-287	Nd-148	nm	Nd-16.00	Chou et al
Francia*	0.49-151	<0.08-3.04	<0.08-0.25	17.6	nd	nd	Cavalheiro et al

Nd: no detected; nm: no measured; * ng/L Sn

The levels found are similar to those detected in other locations, and lower than the ones detected in ports near the coast of Taiwan, cost of Gijón or Greece gulf, near the cities of Athens and Volos, characterized by a great maritime traffic.

CONCLUSION

- MPhT, DPhT and TPhT were not detected in any sample at levels higher than LOQ.
- For butylated compounds, MBT, DBT and TBT were detected in 100% of the analyzed samples from the Mar Menor.
- In the Vigo estuary, MBT was detected in 83.3% of the samples, the DBT in 75% and the TBT in 88%.
- For TBT, the maximum permissible concentration of 1.5 ng L^{-1} proposed in the EU Water Framework Directive (2013/39 / EU) has been exceeded in 27 samples out of 39 analyzed. A monitoring of these compounds would be necessary to ensure the waters quality.

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