MONITOOL
new tools for water quality monitoring

Simulation of Chemical status assessment using DGT results

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Report/Deliverable by

Isabelle Amouroux
Stéphane Guesdon

Disclaimer

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Table of Contents

Introduction

The overarching objective of the MONITOOL project is to improve the implementation of the European Water Framework Directive (WFD, 2000/60/CE) for the assessment of chemical status of transitional and coastal waters, allowing the use of passive sampling devices in a regulatory context.

The MONITOOL project provides a robust database of dissolved and labile metal concentrations in transitional and coastal waters, which is used to adapt existing Environmental Quality Standards (EQS; 0.45 µm filtered) to suitable EQS_{DGT} for passive sampling devices.

In the framework of the WP6 - action 1, it has been proposed two approaches to use the DGT results for the chemical status assessment: either interpret DGT results to EQS_{DGT} or predict metals concentration in the dissolved fraction from their concentration in DGT and compare it to their $EQS_{marine\ water}$. DGT_{EQS} are proposed for cadmium, nickel and lead, and a model can be used to predict the concentration in the dissolved fraction from DGT results.

Currently, to assess the chemical status of a waterbody regarding Pb, Cd or Ni, the Directive requires to compare the average monthly concentrations measured in spot water samples (analysis on filtered water) for one year (12 results) per WFD cycle (every 6 years) to the $EQS_{marine\ water}$ (AA - Annual Average - EQS).

Scope

In this document a simulation of the "chemical status" assessment based on the MONITOOL results is done for each sampling site, using i) results from spot water samples compared to $AA\text{-}EQS_{marine\ water}$, ii) using the DGT results compared to the proposed EQS_{DGT} and iii) using the predicted metal concentration in the dissolved fraction from its DGT results and compare to the $EQS_{marine\ water}$.

The aim of this work is to check the agreement of the assessment using these different approaches, and, in case of mismatching, to check whether the use of DGT results is at least as protective as the current assessment for the Directive.

1. Simulation of "Chemical status assessment" per metal and site using EQS $_{DGT}$

1.1. Data processing method

For each substance, an average of the results obtained in a year is calculated and compared to the AA-EQS. For the average calculation of concentrations, the Directive states: "*where the amounts of physico-chemical or chemical measurands in a given sample are below the limit of quantification, the measurement results shall be set* ***to half of the value of the limit of quantification concerned for the calculation of mean values*** (article 5-Directive 2009/90/CE)" (2).

The "chemical status" of coastal and transitional is assessed per sampling sites for the three metallic priority substances: cadmium, nickel and lead.

The MONITOOL data are considered on an annual basis in order to be compared to the AA-EQS defined for "other surface waters", which corresponds to the EQS applicable to marine waters (EQS $_{marine\ water}$) (3), and proposed EQS $_{DGT}$ determined in WP6- action 1 are indicated in Table 1, with and without the Prediction interval ($PI_{95\%}$).

Table 1: AA-EQS $_{marine\ water}$ and proposed AA-EQS $_{DGT}$ for Cd, Pb and Ni (cf WP6 - Action 1 report)

WFD number	CAS number	Substance	AA-EQS $_{marine\ water}$ ($\mu g \cdot L^{-1}$)	AA-EQS $_{DGT}$ n°1 Linear model regression ($\mu g \cdot L^{-1}$)	AA-EQS $_{DGT}$ n°2 Linear Model Regression minus low Prediction interval (PI $_{95\%}$) ($\mu g \cdot L^{-1}$)
6	7440-43-9	Cadmium	0.2	0.20	0.18
23	7440-02-0	Nickel	8.6	4.60	3.08
20	7439-92-1	Lead	1.3	0.23	0.12

For this simulation, two EQS $_{DGT}$ are considered: the value determined by the linear model regression, namely EQS $_{DGT}$ n°1; and, in order to be more protective, the value determined by the linear model regression minus predictive intervale 95, namely EQS $_{DGT}$ n°2.

- MONITOOL dataset used: WP4 – dataset v24, provide results for each sampling site and each season (wet and dry season, WS and DS respectively).
- For each sampling site (Map 1 and Table 2), the following calculations were done:

  - annual average concentration for spot-sampling results "dissolved fraction" (ICPMS).

  - annual average for DGT results (mean of the replicates). In an operational way, only DGTs deployed for at least 4 days were considered (DGTs deployed for 2 days were not considered in this simulation).

  - Results below the LOQ were considered as equal to LOQ/2

- Annual average concentrations in the dissolved fraction were directly compared to the EQS $_{marine\ water}$.

- Annual mean DGT results were compared to EQS $_{DGT}$ n°1 in the simulation 1, and compared to the EQS $_{DGT}$ n°2 in the simulation n°2.
- The assessment was done for each sampling site annual mean, and for DS and WS separately.

Institute	Sampling points
AZTI	DEBA LEZO MUSEO PRACTICOS
CEFAS	BELFAST FAL LIVERPOOL X38A
DCU	ABW DUBLIN BAY BUOY M69 M70
IFREMER	PORT-EN-BESSIN FONTENELLE SAINT-NAZAIRE SAUMONARD TERENEZ LAZARET (EIL site) SILLON DES ANGLAIS (BAF study) ANTIFER (BAF Study) LE CROISIC (BAF study)
IPMA	AVEIRO PORTO SESIMBRA TAGUS
ITC	GANDO JINAMAR LUZ TALIARTE
MSS-SEPA	BRAEHEAD MONTROSE NEWHAVEN
UNICA	MOLODOGANA MOLOINCHUSA MOLORINASCITA SANTELMO

Figure 1: MONITOOL sampling sites: table and map

1.2. Cadmium

The graphical representation of the annual mean concentration of cadmium measured in DGT and in the dissolved fraction is presented in Figure 2, with the indication of the EQS $_{marine\ water}$ and the proposed EQS $_{DGT}$ n°1 and n°2.

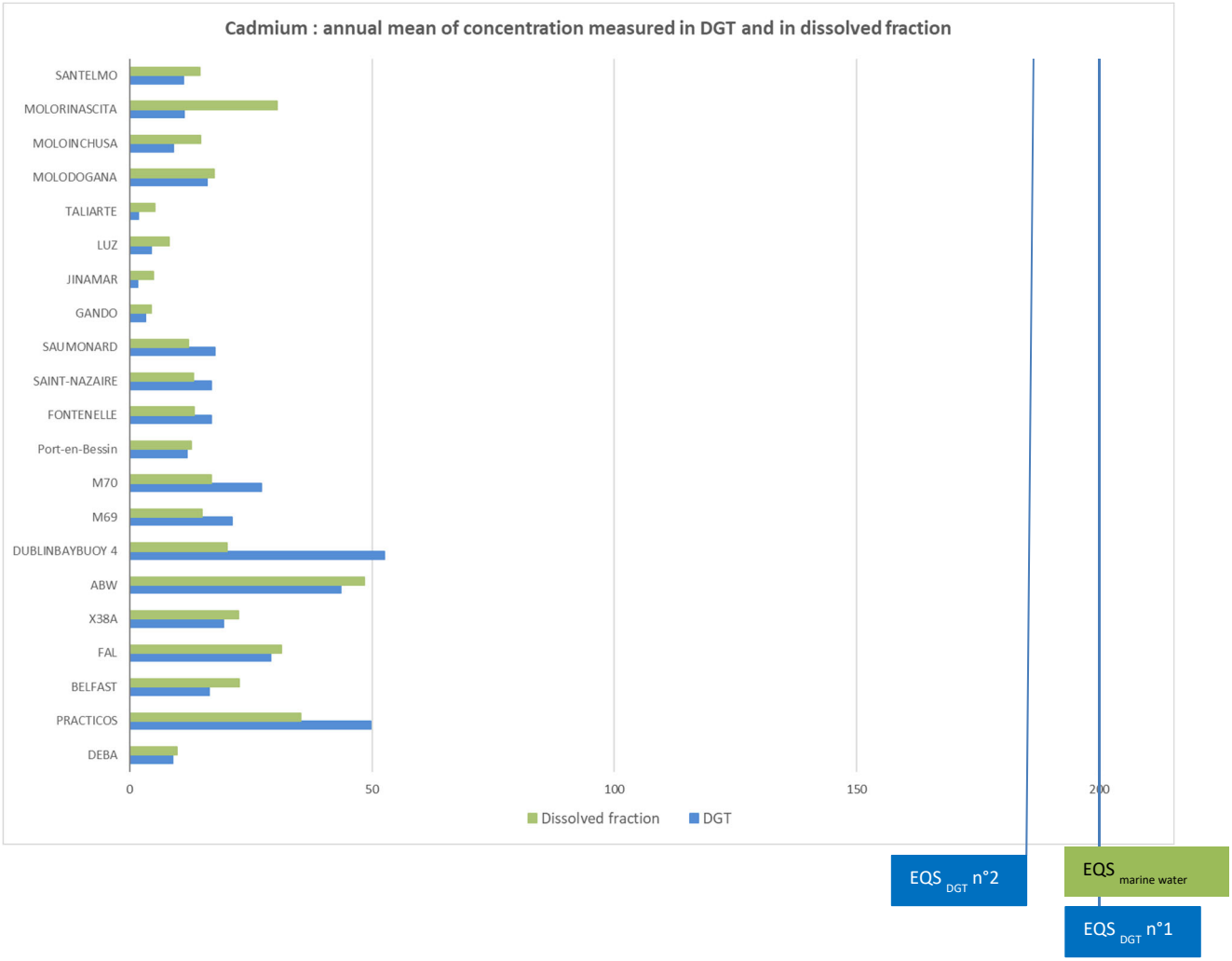

Figure 2: Cadmium: Annual mean concentration measured in DGT and in dissolved fraction (ng.L^{-1}) for the MONITOOL sampling points. EQS values are indicated.

The results of the three simulations of the chemical assessment for the MONITOOL sampling sites for cadmium are presented in Table 2 as the annual mean concentration of spot sample results on dissolved fraction compared to AA-EQS $_{marine\ water}$ and the annual mean of DGT results compared to proposed AA-EQS$_{DGT}$.

Table 2: Simulation of the chemical assessment of MONITOOL sampling sites for Cd: annual mean of dissolved concentration compared to AA-EQS $_{marine\ water}$ (200 ng.L^{-1}) and annual mean of DGT results compared to proposed AA-EQS$_{DGT}$. *WB = water body. Period results = number of DGT deployments during a year. Results number = total number of measurements in discrete water samples (dissolved fraction) during the DGT deployments.*

			Cadmium results and chemical assessment simulation						
				Annual Average (ng·L^{-1})	DGT Simulation EQS $_{DGT}$ n°1	Simulation EQS $_{DGT}$ n°2	Dissolved concentration		
Institute	Sampling points	WB Type	Period results				Results number	Annual average	Simulation Status
			DGT	DGT	200 ng.L^{-1}	180 ng.L^{-1}	Nb	Dissolved fraction	200 ng.L^{-1}
AZTI	DEBA	estuary	2	9	< EQS	< EQS	19	10	< EQS
AZTI	PRACTICOS	estuary	2	50	< EQS	< EQS	20	35	< EQS
CEFAS	BELFAST	estuary	2	16	< EQS	< EQS	22	23	< EQS
CEFAS	FAL	estuary	2	29	< EQS	< EQS	19	31	< EQS
CEFAS	X38A	coastal	2	19	< EQS	< EQS	6	22	< EQS
DCU	ABW	estuary	2	44	< EQS	< EQS	8	48	< EQS
DCU	DUBLINBAYBUOY	coastal	2	53	< EQS	< EQS	6	20	< EQS
DCU	M69	estuary	2	21	< EQS	< EQS	5	15	< EQS
DCU	M70	estuary	2	27	< EQS	< EQS	5	17	< EQS
IFREMER	Port-en-Bessin	coastal	2	12	< EQS	< EQS	10	13	< EQS
IFREMER	FONTENELLE	estuary	2	17	< EQS	< EQS	19	13	< EQS
IFREMER	SAINT-NAZAIRE	coastal	2	17	< EQS	< EQS	10	13	< EQS
IFREMER	SAUMONARD	coastal	2	18	< EQS	< EQS	8	12	< EQS
ITC	GANDO	coastal	2	3	< EQS	< EQS	6	5	< EQS
ITC	JINAMAR	coastal	2	2	< EQS	< EQS	6	5	< EQS
ITC	LUZ	coastal	2	4	< EQS	< EQS	6	8	< EQS
ITC	TALIARTE	coastal	2	2	< EQS	< EQS	6	5	< EQS
UNICA	MOLODOGANA	coastal	2	16	< EQS	< EQS	6	17	< EQS
UNICA	MOLOINCHUSA	coastal	2	9	< EQS	< EQS	5	15	< EQS
UNICA	MOLORINASCITA	coastal	2	11	< EQS	< EQS	6	31	< EQS
UNICA	SANTELMO	coastal	2	11	< EQS	< EQS	6	15	< EQS

All the sampling sites (21) presented an annual average concentration of cadmium below the EQSs. The results are consistent between the assessments based on dissolved concentrations compared to EQS $_{marine\ water}$ and DGT labile concentration results compared with EQS $_{DGT}$ n° 1 or EQS $_{DGT}$ n°2.

The same results are obtained if we consider the results for each season. Detailed results are presented in Table 3.

All the sampling sites, even those located in potentially “contaminated areas” (like harbours) presented results below the EQS, whatever the season considered.

Table 3: Cd-Simulation of the chemical assessment per season for each MONITOOL site using DGT and dissolved concentrations. *WB = water body.*

				Cadmium results per season					
				DGT			Dissolved concentration		
Institute	Sampling points	Season	WB Type	Mean ($ng \cdot L^{-1}$) per season	Simulation EQS_{DGT} n°1 200 $ng.L^{-1}$	Simulation EQS_{DGT} n°2 180 $ng.L^{-1}$	Mean ($ng \cdot L^{-1}$) per season	Results number	Simulation Status 200 $ng.L^{-1}$
AZTI	DEBA	DS	estuary	12	< EQS	< EQS	17	9	< EQS
AZTI	DEBA	WS	estuary	6	< EQS	< EQS	3	10	< EQS
AZTI	LEZO	DS	estuary		< EQS	< EQS	43	10	< EQS
AZTI	LEZO	WS	estuary	120	< EQS	< EQS	115	10	< EQS
AZTI	MUSEO	DS	estuary		< EQS	< EQS	26	10	< EQS
AZTI	MUSEO	WS	estuary	25	< EQS	< EQS	28	10	< EQS
AZTI	PRACTICOS	DS	estuary	24	< EQS	< EQS	22	10	< EQS
AZTI	PRACTICOS	WS	estuary	76	< EQS	< EQS	48	10	< EQS
CEFAS	BELFAST	DS	estuary	14	< EQS	< EQS	26	11	< EQS
CEFAS	BELFAST	WS	estuary	19	< EQS	< EQS	19	11	< EQS
CEFAS	FAL	DS	estuary	15	< EQS	< EQS	26	9	< EQS
CEFAS	FAL	WS	estuary	44	< EQS	< EQS	36	10	< EQS
CEFAS	LIVERPOOL	DS	coastal				24	2	< EQS
CEFAS	LIVERPOOL	WS	coastal	30	< EQS	< EQS	29	3	< EQS
CEFAS	X38A	DS	coastal	19	< EQS	< EQS	26	3	< EQS
CEFAS	X38A	WS	coastal	20	< EQS	< EQS	19	3	< EQS
DCU	ABW	DS	estuary	53	< EQS	< EQS	53	5	< EQS
DCU	ABW	WS	estuary	34	< EQS	< EQS	41	3	< EQS
DCU	DUBLIN BAY BUOY	DS	coastal	82	< EQS	< EQS	21	3	< EQS
DCU	DUBLIN BAY BUOY	WS	coastal	23	< EQS	< EQS	20	3	< EQS
DCU	M69	DS	estuary	25	< EQS	< EQS	15	3	< EQS
DCU	M69	WS	estuary	17	< EQS	< EQS	16	2	< EQS
DCU	M70	DS	estuary	34	< EQS	< EQS	15	3	< EQS
DCU	M70	WS	estuary	21	< EQS	< EQS	20	2	< EQS
IFREMER	ANTIFER_BAF	WS	coastal	15	< EQS	< EQS	22	4	< EQS
IFREMER	PORT EN BESSIN	DS	coastal	10	< EQS	< EQS	11	5	< EQS
IFREMER	PORT EN BESSIN	WS	coastal	14	< EQS	< EQS	14	5	< EQS
IFREMER	FONTENELLE	DS	estuary	15	< EQS	< EQS	12	10	< EQS
IFREMER	FONTENELLE	WS	estuary	19	< EQS	< EQS	15	9	< EQS
IFREMER	LAZARET_EIL	DS	coastal	9	< EQS	< EQS	15	3	< EQS
IFREMER	LE CROISIC	WS	coastal	13	< EQS	< EQS	12	2	< EQS
IFREMER	SAINTNAZAIRE	DS	coastal	17	< EQS	< EQS	10	5	< EQS
IFREMER	SAINTNAZAIRE	WS	coastal	17	< EQS	< EQS	16	5	< EQS
IFREMER	SAUMONARD	DS	coastal	15	< EQS	< EQS	11	5	< EQS
IFREMER	SAUMONARD	WS	coastal	20	< EQS	< EQS	15	3	< EQS
IFREMER	SILLON DES ANGLAIS	WS	coastal	33	< EQS	< EQS	20	2	< EQS
IFREMER	TERENEZ	DS	estuary	52	< EQS	< EQS	33	10	< EQS

Cadmium results per season

Institute	Sampling points	Season	WB Type	DGT Mean ($ng \cdot L^{-1}$) per season	DGT Simulation EQS_{DGT} n°1 200 $ng.L^{-1}$	DGT Simulation EQS_{DGT} n°2 180 $ng.L^{-1}$	Dissolved concentration Mean ($ng \cdot L^{-1}$) per season	Dissolved concentration Results number	Dissolved concentration Simulation Status 200 $ng.L^{-1}$
IPMA	AVEIRO	DS	estuary		< EQS	< EQS	30	6	< EQS
IPMA	AVEIRO	WS	estuary	22	< EQS	< EQS	26	6	< EQS
IPMA	PORTO	DS	coastal				14	3	< EQS
IPMA	PORTO	WS	coastal	23	< EQS	< EQS	28	2	< EQS
IPMA	SESIMBRA	DS	coastal				11	3	< EQS
IPMA	SESIMBRA	WS	coastal	10	< EQS	< EQS	14	3	< EQS
IPMA	TAGUS	DS	coastal				13	3	< EQS
IPMA	TAGUS	WS	coastal	18	< EQS	< EQS	22	3	< EQS
ITC	GANDO	DS	coastal	1	< EQS	< EQS	4	3	< EQS
ITC	GANDO	WS	coastal	5	< EQS	< EQS	5	3	< EQS
ITC	JINAMAR	DS	coastal	1	< EQS	< EQS	5	3	< EQS
ITC	JINAMAR	WS	coastal	2	< EQS	< EQS	5	3	< EQS
ITC	LUZ	DS	coastal	3	< EQS	< EQS	8	3	< EQS
ITC	LUZ_WP4_2_D4	DS	coastal	6	< EQS	< EQS	10	3	< EQS
ITC	LUZ	WS	coastal	6	< EQS	< EQS	8	3	< EQS
ITC	TALIARTE	DS	coastal	1	< EQS	< EQS	5	3	< EQS
ITC	TALIARTE_WP4_2_D4	DS	coastal	5	< EQS	< EQS	6	3	< EQS
ITC	TALIARTE	WS	coastal	2	< EQS	< EQS	5	3	< EQS
MSS-SEPA	BRAEHEAD	DS	coastal	10	< EQS	< EQS	23	2	< EQS
MSS-SEPA	MONTROSE	DS	coastal	14	< EQS	< EQS	44	3	< EQS
MSS-SEPA	NEWHAVEN	NA	coastal	17	< EQS	< EQS	27	3	< EQS
UNICA	MOLODOGANA	DS	coastal	19	< EQS	< EQS	21	3	< EQS
UNICA	MOLODOGANA	WS	coastal	13	< EQS	< EQS	14	3	< EQS
UNICA	MOLOINCHUSA	DS	coastal	7	< EQS	< EQS	16	3	< EQS
UNICA	MOLOINCHUSA	WS	coastal	11	< EQS	< EQS	13	2	< EQS
UNICA	MOLORINASCITA	DS	coastal	13	< EQS	< EQS	47	3	< EQS
UNICA	MOLORINASCITA	WS	coastal	10	< EQS	< EQS	14	3	< EQS
UNICA	SANTELMO	DS	coastal	10	< EQS	< EQS	14	3	< EQS
UNICA	SANTELMO	WS	coastal	12	< EQS	< EQS	15	3	< EQS

1.3. Nickel

The graphical representation of the annual mean concentration of nickel measured in DGT and in the dissolved fraction is presented in Figure 3, with the indication of the EQS $_{marine\ water}$ and the proposed EQS $_{DGT}$ n°1 and n°2.

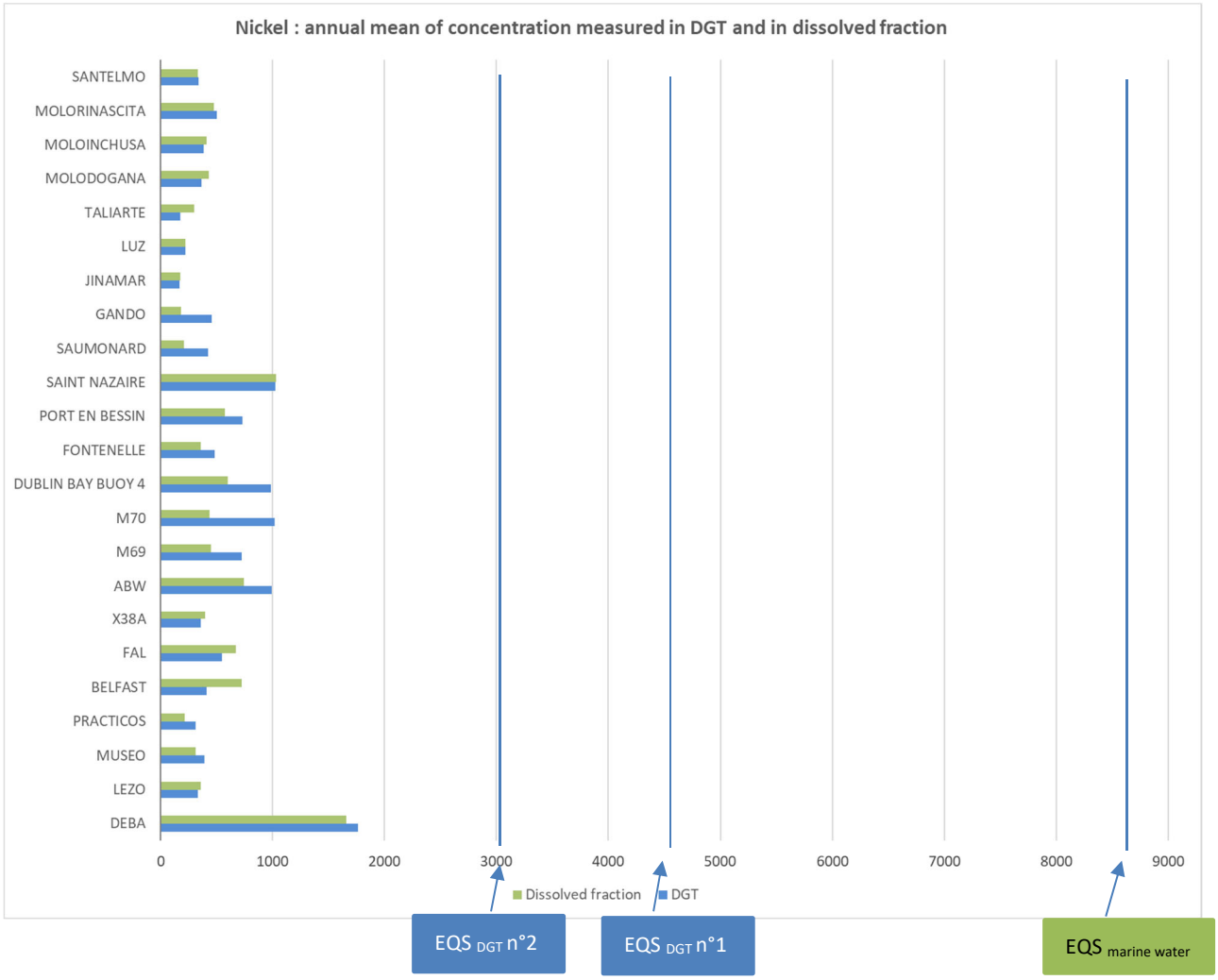

Figure 3: Nickel: Annual mean concentration measured in DGT and in dissolved fraction (ng.L^{-1}) for the MONITOOL sampling sites. EQS values are indicated.

The results of the three simulations of the chemical assessment for the MONITOOL sampling sites for nickel are presented in Table 4.

Table 4: Simulation of the chemical assessment of MONITOOL sampling sites for Ni: annual mean of concentrations measured in discrete water samples (dissolved concentration) by spot sampling compared to AA-EQS $_{marine\ water}$ and mean of DGT results compared to proposed AA-EQS$_{DGT}$. *WB = water body. Period results = number of DGT deployments during a year. Results number = total number of measurements in discrete water samples (dissolved fraction) during the DGT deployments.*

Nickel results and chemical assessment

Institute	Sampling points	WB Type	Period Results	Annual Average (ng·L-1) DGT	DGT Simulation EQS DGT n°1 4600 ng.L^{-1}	Simulation EQS DGT n°2 3080 ng.L^{-1}	Dissolved concentration Results number	Annual average	Simulation Status 8600 ng.L^{-1}
AZTI	DEBA	estuary	2	1761	< EQS	< EQS	20	1661	< EQS
AZTI	LEZO	estuary	2	333	< EQS	< EQS	20	360	< EQS
AZTI	MUSEO	estuary	2	390	< EQS	< EQS	20	311	< EQS
AZTI	PRACTICOS	estuary	2	315	< EQS	< EQS	20	218	< EQS
CEFAS	BELFAST	estuary	2	408	< EQS	< EQS	22	722	< EQS
CEFAS	FAL	estuary	2	545	< EQS	< EQS	19	672	< EQS
CEFAS	X38A	coastal	2	361	< EQS	< EQS	5	398	< EQS
DCU	ABW	estuary	2	990	< EQS	< EQS	8	742	< EQS
DCU	M69	estuary	2	725	< EQS	< EQS	5	451	< EQS
DCU	M70	estuary	2	1016	< EQS	< EQS	5	436	< EQS
DCU	DUBLIN BAY BUOY 4	coastal	2	984	< EQS	< EQS	6	599	< EQS
IFREMER	FONTENELLE	estuary	2	485	< EQS	< EQS	20	361	< EQS
IFREMER	PORT EN BESSIN	coastal	2	728	< EQS	< EQS	10	572	< EQS
IFREMER	SAINT NAZAIRE	coastal	2	1027	< EQS	< EQS	10	1030	< EQS
IFREMER	SAUMONARD	coastal	2	423	< EQS	< EQS	8	210	< EQS
ITC	GANDO	coastal	2	455	< EQS	< EQS	6	180	< EQS
ITC	JINAMAR	coastal	2	167	< EQS	< EQS	6	176	< EQS
ITC	LUZ	coastal	2	222	< EQS	< EQS	6	224	< EQS
ITC	TALIARTE	coastal	2	175	< EQS	< EQS	6	302	< EQS
UNICA	MOLODOGANA	coastal	2	364	< EQS	< EQS	6	431	< EQS
UNICA	MOLOINCHUSA	coastal	2	382	< EQS	< EQS	6	411	< EQS
UNICA	MOLORINASCITA	coastal	2	504	< EQS	< EQS	6	474	< EQS
UNICA	SANTELMO	coastal	2	340	< EQS	< EQS	6	336	< EQS

All the sampling sites (23) presented an annual average concentration of nickel below the EQS. The results are consistent between the assessments based on dissolved concentration compared to EQS $_{marine\ water}$ and DGT labile concentration results compared with EQS $_{DGT}$ n° 1 or EQS $_{DGT}$ n°2.

The same results are obtained if we consider the average of results for each season. Detailed results are presented in Table 5.

All the sampling sites, even those located in potentially “contaminated areas” (like harbours) presented results below the EQS, whatever the season considered.

Table 5: Ni- Simulation of the chemical assessment per season for each MONITOOL site using DGT and dissolved concentrations. *WB = water body.*

				Nickel results per season					
				DGT			Dissolved concentration		
Institute	Sampling points	Season	WBType	Mean (ng·L^{-1}) per season	Simulation EQS $_{DGT}$ n°1 4600 ng.L^{-1}	Simulation EQS $_{DGT}$ n°2 3080 ng.L^{-1}	Mean per season (ng·L^{-1})	Results number	Simulation Status 8600 ng.L^{-1}
AZTI	DEBA	WS	estuary	1108	< EQS	< EQS	974	10	< EQS
AZTI	DEBA	DS	estuary	2414	< EQS	< EQS	2348	10	< EQS
AZTI	LEZO	WS	estuary	408	< EQS	< EQS	349	10	< EQS
AZTI	LEZO	DS	estuary	257	< EQS	< EQS	372	10	< EQS
AZTI	MUSEO	DS	estuary	540	< EQS	< EQS	243	10	< EQS
AZTI	MUSEO	WS	estuary	240	< EQS	< EQS	435	10	< EQS
AZTI	PRACTICOS	WS	estuary	334	< EQS	< EQS	242	10	< EQS
AZTI	PRACTICOS	DS	estuary	296	< EQS	< EQS	195	10	< EQS
CEFAS	BELFAST	WS	estuary	500	< EQS	< EQS	884	11	< EQS
CEFAS	BELFAST	DS	estuary	316	< EQS	< EQS	561	11	< EQS
CEFAS	FAL	WS	estuary	742	< EQS	< EQS	785	10	< EQS
CEFAS	FAL	DS	estuary	348	< EQS	< EQS	546	9	< EQS
CEFAS	LIVERPOOL	WS	coastal	759	< EQS	< EQS	635	3	< EQS
CEFAS	LIVERPOOL	DS	coastal				319	1	< EQS
CEFAS	X38A	DS	coastal	314	< EQS	< EQS	373	2	< EQS
CEFAS	X38A	WS	coastal	407	< EQS	< EQS	415	3	< EQS
DCU	ABW	WS	estuary	617	< EQS	< EQS	1278	3	< EQS
DCU	ABW	DS	estuary	1362	< EQS	< EQS	421	5	< EQS
DCU	M69	WS	estuary	549	< EQS	< EQS	748	2	< EQS
DCU	M70	DS	estuary	900	< EQS	< EQS	253	3	< EQS
DCU	M70	WS	estuary	588	< EQS	< EQS	745	2	< EQS
DCU	M71	DS	estuary	1444	< EQS	< EQS	231	3	< EQS
DCU	DUBLIN BAY BUOY	DS	coastal	1451	< EQS	< EQS	309	3	< EQS
DCU	DUBLIN BAY BUOY	WS	coastal	516	< EQS	< EQS	889	3	< EQS
IFREMER	FONTENELLE	WS	estuary	572	< EQS	< EQS	479	10	< EQS
IFREMER	FONTENELLE	DS	estuary	398	< EQS	< EQS	242	10	< EQS
IFREMER	TERENEZ	DS	estuary	604	< EQS	< EQS	506	10	< EQS
IFREMER	PORT EN BESSIN	WS	coastal	776	< EQS	< EQS	559	5	< EQS
IFREMER	PORT EN BESSIN	DS	coastal	679	< EQS	< EQS	584	5	< EQS
IFREMER	LAZARET_EIL	DS	coastal	286	< EQS	< EQS	193	3	< EQS
IFREMER	SAINT NAZAIRE	WS	coastal	931	< EQS	< EQS	873	5	< EQS
IFREMER	SAINT NAZAIRE	DS	coastal	1123	< EQS	< EQS	1187	5	< EQS
IFREMER	SAUMONARD	WS	coastal	554	< EQS	< EQS	263	3	< EQS
IFREMER	SAUMONARD	DS	coastal	291	< EQS	< EQS	178	5	< EQS
IFREMER	ANTIFER_BAF	WS	coastal	335	< EQS	< EQS	441	4	< EQS
IFREMER	LE CROISIC	WS	coastal	327	< EQS	< EQS	285	2	< EQS
IFREMER	SILLON DES ANGLAIS	WS	coastal	596	< EQS	< EQS	367	2	< EQS

Nickel results per season

Institute	Sampling points	Season	WBType	DGT			Dissolved concentration		
				Mean (ng·L^{-1}) per season	Simulation EQS $_{DGT}$ n°1 4600 ng.L^{-1}	Simulation EQS $_{DGT}$ n°2 3080 ng.L^{-1}	Mean per season (ng·L^{-1})	Results number	Simulation Status 8600 ng.L^{-1}
IPMA	AVEIRO	WS	estuary	621	< EQS	< EQS	823	5	< EQS
IPMA	AVEIRO	DS	estuary				605	6	< EQS
IPMA	PORTO	WS	coastal	349	< EQS	< EQS	383	2	< EQS
IPMA	PORTO	DS	coastal				236	3	< EQS
IPMA	SESIMBRA	WS	coastal	220	< EQS	< EQS	225	3	< EQS
IPMA	SESIMBRA	DS	coastal				135	3	< EQS
IPMA	TAGUS	WS	coastal	343	< EQS	< EQS	431	3	< EQS
IPMA	TAGUS	DS	coastal				220	3	< EQS
ITC	GANDO	DS	coastal	165	< EQS	< EQS	84	3	< EQS
ITC	GANDO	WS	coastal	746	< EQS	< EQS	275	3	< EQS
ITC	JINAMAR	DS	coastal	156	< EQS	< EQS	103	3	< EQS
ITC	JINAMAR	WS	coastal	177	< EQS	< EQS	249	3	< EQS
ITC	LUZ	DS	coastal	184	< EQS	< EQS	170	3	< EQS
ITC	LUZ	WS	coastal	261	< EQS	< EQS	279	3	< EQS
ITC	LUZ_WP4	DS	coastal	543	< EQS	< EQS	327	3	< EQS
ITC	TALIARTE	DS	coastal	164	< EQS	< EQS	131	3	< EQS
ITC	TALIARTE	WS	coastal	187	< EQS	< EQS	473	3	< EQS
ITC	TALIARTE_WP4	DS	coastal	498	< EQS	< EQS	224	3	< EQS
MSS-SEPA	BRAEHEAD	DS	coastal	694	< EQS	< EQS	1544	3	< EQS
MSS-SEPA	MONTROSE	DS	coastal	284	< EQS	< EQS	358	3	< EQS
MSS-SEPA	NEWHAVEN	NA	coastal	481	< EQS	< EQS	400	3	< EQS
UNICA	MOLODOGANA	DS	coastal	305	< EQS	< EQS	445	3	< EQS
UNICA	MOLODOGANA	WS	coastal	422	< EQS	< EQS	417	3	< EQS
UNICA	MOLOINCHUSA	DS	coastal	358	< EQS	< EQS	371	3	< EQS
UNICA	MOLOINCHUSA	WS	coastal	406	< EQS	< EQS	450	3	< EQS
UNICA	MOLORINASCITA	DS	coastal	578	< EQS	< EQS	579	3	< EQS
UNICA	MOLORINASCITA	WS	coastal	429	< EQS	< EQS	368	3	< EQS
UNICA	SANTELMO	DS	coastal	263	< EQS	< EQS	304	3	< EQS
UNICA	SANTELMO	WS	coastal	418	< EQS	< EQS	368	3	< EQS

1.4. Lead

The graphical representation of the annual mean concentration of lead measured in DGT and in the dissolved fraction is presented in Figure 4, with the indication of the EQS $_{marine\ water}$ and the proposed EQS $_{DGT}$ n°1 and n°2.

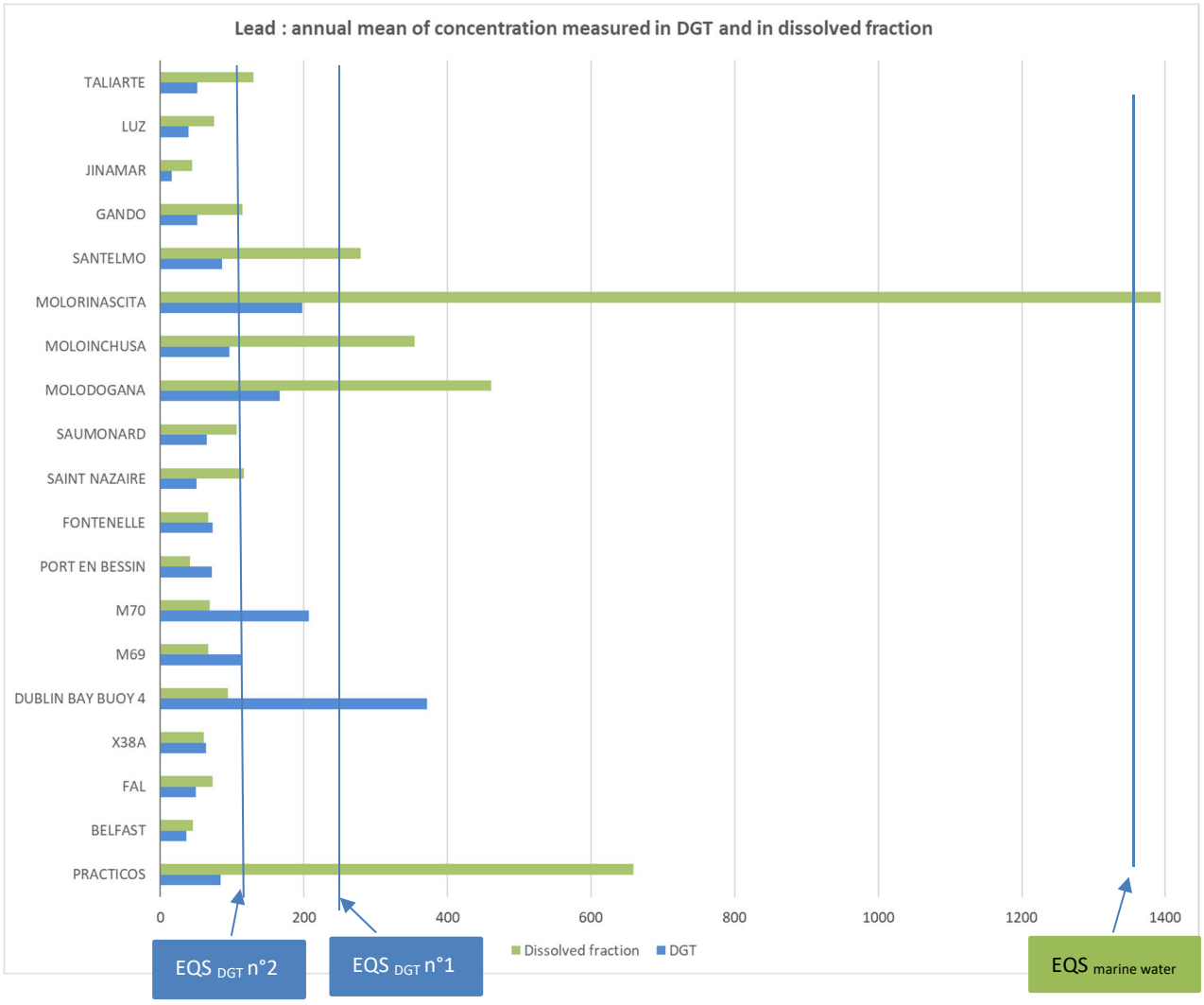

Figure 4: Lead: Annual mean concentration measured in DGT and in dissolved fraction (ng.L^{-1}) for the MONITOOL sampling points. EQS values are indicated.

The results of the three simulations of the chemical assessment for the MONITOOL sampling sites for lead are presented in Table 6.

Table 6: Simulation of the chemical assessment of MONITOOL sampling sites for Pb: annual mean of dissolved concentration compared to AA-EQS $_{marine\ water}$ and DGT results compared to proposed AA-EQS$_{DGT}$. *WB = water body. Period results = number of DGT deployments during a year. Results number = total number of measurements in discrete water samples (dissolved fraction) during the DGT deployments.*

Lead results and chemical assessment

Institute	Sampling points	WB Type	DGT				Dissolved concentration		
			Period Results	Annual Average (ng·L^{-1}) DGT	Simulation EQS $_{DGT}$ n°1 230 ng.L^{-1}	Simulation EQS $_{DGT}$ n°2 120 ng.L^{-1}	Results number	Annual average (ng·L^{-1})	Simulation Status EQS $_{marine\ water}$ 1300 ng.L^{-1}
AZTI	PRACTICOS	estuary	2	84	< EQS	< EQS	20	659	< EQS
CEFAS	BELFAST	estuary	2	36	< EQS	< EQS	21	46	< EQS
CEFAS	FAL	estuary	2	49	< EQS	< EQS	17	72	< EQS
CEFAS	X38A	coastal	2	63	< EQS	< EQS	6	60	< EQS
DCU	DUBLIN BAY BUOY 4	coastal	2	372	> EQS	> EQS	6	93	< EQS
DCU	M69	estuary	2	112	< EQS	< EQS	5	66	< EQS
DCU	M70	estuary	2	207	< EQS	> EQS	5	69	< EQS
IFREMER	PORT EN BESSIN	coastal	2	71	< EQS	< EQS	10	42	< EQS
IFREMER	FONTENELLE	estuary	2	73	< EQS	< EQS	20	67	< EQS
IFREMER	SAINT NAZAIRE	coastal	2	51	< EQS	< EQS	10	116	< EQS
IFREMER	SAUMONARD	coastal	2	65	< EQS	< EQS	7	106	< EQS
UNICA	MOLODOGANA	coastal	2	166	< EQS	> EQS	6	461	< EQS
UNICA	MOLOINCHUSA	coastal	2	96	< EQS	< EQS	6	354	< EQS
UNICA	MOLORINASCITA	coastal	2	197	< EQS	> EQS	6	1393	> EQS
UNICA	SANTELMO	coastal	2	86	< EQS	< EQS	6	279	< EQS
ITC	GANDO	coastal	2	52	< EQS	< EQS	5	114	< EQS
ITC	JINAMAR	coastal	2	16	< EQS	< EQS	6	44	< EQS
ITC	LUZ	coastal	2	39	< EQS	< EQS	6	75	< EQS
ITC	TALIARTE	coastal	2	51	< EQS	< EQS	6	129	< EQS

Among the 36 sites sampled, results for the two periods (WS and DS) were obtained in 19 sites allowing the calculation of an annual average. Out of these 19 sites, regarding the dissolved concentration of Pb, 18 presented an annual average concentration below the EQS $_{marine\ water}$, and one above (Molo Rinascita) (Table 7).

Considering the DGT results, 18 sites presented annual average below the EQS $_{DGT}$ n° 1 and 1 above (Dublin Bay Boy), and 15 sites presented annual average results below the EQS $_{DGT}$ n° 2 and 4 above (Dublin Bay Buoy, M70, Molo Dogana and Molo Rinascita).

Based on the MONITOOL DGT results, it appears more protective to select the EQS $_{DGT}$ n°2, as the DGT annual concentration of lead (weat and dry season) for Molo Rinascita appears below the EQS $_{DGT}$ n°1 and above EQS $_{DGT}$ n°2. In the case of dissolved concentrations measured in discrete water samples in Molo Rinascita, it can be noticed that there are only 6 results available, instead of the 12 results expected by the WFD for the chemical status assessment.

The results obtained for the chemical assessment of Pb are summarised in Table 7.

Table 7: Simulation of the chemical assessment of the MONITOOL sampling sites for Pb. Annual average of DGT results and spot samples (dissolved fraction) results compared to EQS values.

Simulation Pb	Number of sites		Number of sites
« Chemical status » assessment	Simulation (DGT) EQS $_{DGT}$ n°1: 0.23 µg.L^{-1}	Simulation (DGT) EQS $_{DGT}$ n°2: 0.12 µg.L^{-1}	Dissolved fraction EQS $_{marine\ water}$: 1.3 µg.L^{-1}
< EQS	18	15	18
> EQS	1	4	1
Site > EQS	Dublin Bay Buoy	Dublin Bay Buoy M70 Molo Dogana Molo Rinascita	Molo Rinascita

In order to identify potential differences between an assessment based on seasonal (wet or dry season) vs annual data, an assessment per season is presented for each sampling site in Table 8. While 19 sites presented an annual average, 26 sites presented results in dry season; and 31 sites in wet season.

Table 8: Pb- Simulation of the chemical assessment per season for each MONITOOL site using DGT and dissolved concentrations. *WB = water body.*

Lead results per season

Institute	Sampling points	Season	WB Type	DGT Mean (ng·L-1) per season	DGT Simulation EQS DGT n°1 230 ng.L^{-1}	DGT Simulation EQS DGT n°2 120 ng.L^{-1}	Dissolved concentration Results number	Dissolved concentration Mean per season (ng·L-1)	Dissolved concentration Simulation Status EQS $_{marine\ water}$ 1300 ng.L^{-1}
AZTI	DEBA	DS	estuary	10	< EQS	< EQS	9	36	< EQS
AZTI	DEBA	WS	estuary	48	< EQS	< EQS	9	39	< EQS
AZTI	LEZO	DS	estuary				10	515	< EQS
AZTI	LEZO	WS	estuary	167	< EQS	> EQS	10	335	< EQS
AZTI	MUSEO	WS	estuary	133	< EQS	> EQS	9	482	< EQS
AZTI	PRACTICOS	DS	estuary	33	< EQS	< EQS	10	1019	< EQS
AZTI	PRACTICOS	WS	estuary	135	< EQS	> EQS	10	299	< EQS
CEFAS	BELFAST	DS	estuary	29	< EQS	< EQS	11	48	< EQS
CEFAS	BELFAST	WS	estuary	43	< EQS	< EQS	10	43	< EQS
CEFAS	FAL	DS	estuary	18	< EQS	< EQS	9	91	< EQS
CEFAS	FAL	WS	estuary	81	< EQS	< EQS	8	51	< EQS
CEFAS	LIVERPOOL	WS	coastal	54	< EQS	< EQS	3	213	< EQS
CEFAS	X38A	DS	coastal	55	< EQS	< EQS	3	50	< EQS
CEFAS	X38A	WS	coastal	72	< EQS	< EQS	3	70	< EQS
DCU	ABW	DS	estuary	8046	> EQS	> EQS	5	12132	> EQS
DCU	DUBLIN BAY BUOY 4	DS	coastal	580	> EQS	> EQS	3	55	< EQS
DCU	DUBLIN BAY BUOY 4	WS	coastal	163	< EQS	> EQS	3	132	< EQS
DCU	M69	DS	estuary	128	< EQS	> EQS	3	61	< EQS
DCU	M69	WS	estuary	95	< EQS	< EQS	2	74	< EQS
DCU	M70	DS	estuary	327	> EQS	> EQS	3	74	< EQS
DCU	M70	WS	estuary	87	< EQS	< EQS	2	62	< EQS

Lead results per season

Institute	Sampling points	Season	WB Type	Mean (ng·L-1) per season	DGT Simulation EQS DGT n°1 230 ng.L^{-1}	DGT Simulation EQS DGT n°2 120 ng.L^{-1}	Dissolved concentration Results number	Mean per season (ng·L-1)	Simulation Status EQS $_{marine\ water}$ 1300 ng.L^{-1}
IFREMER	ANTIFER_BAF	WS	coastal	44	< EQS	< EQS	4	353	< EQS
IFREMER	PORT EN BESSIN	DS	coastal	39	< EQS	< EQS	5	40	< EQS
IFREMER	PORT EN BESSIN	WS	coastal	104	< EQS	< EQS	5	43	< EQS
IFREMER	FONTENELLE	DS	estuary	27	< EQS	< EQS	10	34	< EQS
IFREMER	FONTENELLE	WS	estuary	118	< EQS	< EQS	10	99	< EQS
IFREMER	LAZARET_EIL	DS	coastal	73	< EQS	< EQS	3	106	< EQS
IFREMER	LE CROISIC	WS	coastal	67	< EQS	< EQS	2	62	< EQS
IFREMER	SAINT NAZAIRE	DS	coastal	21	< EQS	< EQS	5	28	< EQS
IFREMER	SAINT NAZAIRE	WS	coastal	81	< EQS	< EQS	5	204	< EQS
IFREMER	SAUMONARD	DS	coastal	25	< EQS	< EQS	4	37	< EQS
IFREMER	SAUMONARD	WS	coastal	105	< EQS	< EQS	3	199	< EQS
IFREMER	SILLON DES ANGLAIS_	WS	coastal	229	< EQS	> EQS	2	336	< EQS
IFREMER	TERENEZ	DS	estuary	222	< EQS	> EQS	9	118	< EQS
IPMA	AVEIRO	WS	estuary	39	< EQS	< EQS	6	131	< EQS
IPMA	PORTO	WS	coastal	92	< EQS	< EQS	2	202	< EQS
IPMA	SESIMBRA	WS	coastal	58	< EQS	< EQS	3	136	< EQS
IPMA	TAGU	WS	coastal	117	< EQS	< EQS	3	139	< EQS
ITC	GANDO	DS	coastal	10	< EQS	< EQS	2	50	< EQS
ITC	GANDO	WS	coastal	93	< EQS	< EQS	3	157	< EQS
ITC	JINAMAR	DS	coastal	7	< EQS	< EQS	3	28	< EQS
ITC	JINAMAR	WS	coastal	25	< EQS	< EQS	3	60	< EQS
ITC	LUZ	DS	coastal	21	< EQS	< EQS	3	57	< EQS
ITC	LUZ_WP4	DS	coastal	78	< EQS	< EQS	3	62	< EQS
ITC	LUZ	WS	coastal	57	< EQS	< EQS	3	92	< EQS
ITC	TALIARTE	DS	coastal	46	< EQS	< EQS	3	48	< EQS
ITC	TALIARTE_WP4	DS	coastal	77	< EQS	< EQS	3	77	< EQS
ITC	TALIARTE	WS	coastal	57	< EQS	< EQS	3	210	< EQS
MSS-SEPA	BRAEHEAD	DS	coastal	46	< EQS	< EQS	3	66	< EQS
MSS-SEPA	MONTROSE	DS	coastal	89	< EQS	< EQS	3	270	< EQS
MSS-SEPA	NEWHAVEN	NA	coastal	83	< EQS	< EQS	3	76	< EQS
UNICA	MOLODOGANA	DS	coastal	142	< EQS	> EQS	3	197	< EQS
UNICA	MOLODOGANA	WS	coastal	191	< EQS	> EQS	3	724	< EQS
UNICA	MOLOINCHUSA	DS	coastal	67	< EQS	< EQS	3	208	< EQS
UNICA	MOLOINCHUSA	WS	coastal	125	< EQS	> EQS	3	500	< EQS
UNICA	MOLORINASCITA	DS	coastal	115	< EQS	< EQS	3	1358	> EQS
UNICA	MOLORINASCITA	WS	coastal	279	> EQS	> EQS	3	1429	> EQS
UNICA	SANTELMO	DS	coastal	69	< EQS	< EQS	3	150	< EQS
UNICA	SANTELMO	WS	coastal	102	< EQS	< EQS	3	408	< EQS

The Table 9 presents the results of the assessment made seasonally and with DGT labile concentration data (passive sampling). Some sites presented data above the EQS_{DGT}, while the assessment based on the dissolved concentration results (spot sampling) pointed out only 2 sites above the EQS $_{marine\ water}$: ABW (DS) and Molo Rinascita (DS and WS).

Table 9: Seasonal simulation using DGT results and EQS $_{DGT}$ n°1 and EQS $_{DGT}$ n°2. The sites presenting DGT results above the EQS $_{DGT}$ are listed.

Simulation EQS $_{DGT}$ n°1	DS	WS	Simulation EQS $_{DGT}$ n°2	DS	WS
ABW	> EQS	No data	ABW	> EQS	ND
Dublin Bay Buoy	> EQS		Dublin Bay Buoy	> EQS	> EQS
			Lezo	No data	> EQS
			Molo Dogana	> EQS	> EQS
			Molo Inchusa		> EQS
Molo Rinascita		> EQS	Molo Rinascita		> EQS
			Museo	No data	> EQS
			M69	> EQS	
M70	> EQS		M70	> EQS	
			Practicos		> EQS
			Sillon des Anglais	No data	> EQS
			St Nazaire		> EQS
			Tagus	No data	> EQS
			Terenez	> EQS	No data

For simulation with EQS $_{DGT}$ n°1, 4 sites present results above the EQS (3 with dry season's results).

For simulation with EQS $_{DGT}$ n°2, 14 sites present results above the EQS (6 with dry season's results, 10 with wet season, results).

2. Determination of predicted dissolved concentrations from DGT results and comparison to AA-EQS $_{\text{marine water}}$

Predicted dissolved metal concentrations from DGT results were calculated for the MONITOOL sampling sites for each season (WS and DS), based on the relationship described in WP6- action 1, and listed in Table 10. Then these predicted dissolved concentrations were compared to the AA-EQS $_{\text{marine water}}$.

Two simulations were done, the first one, using the equation to determine the predicted dissolved metal concentration, and a second one considering the upper limit of the confidence interval (+95%) of the predicted value, in order to maximise the dissolved concentration to be compared to the AA-EQS $_{\text{marine water}}$, and thus to be more protective.

Table 10: Equations to determine the predicted $[M]_{\text{dissolved fraction}}$ from DGT results for Cd, Ni and Pb

	Predicted $[M]_{\text{dissolved fraction}}$	**Predicted $[M]_{\text{dissolved fraction}}$ + Confidence Interval** (+95%)
Cadmium	$[Cd]_{\text{Dissolved Fraction}} = 0.67\ [Cd]_{DGT} + 6$	$[Cd]_{\text{Dissolved Fraction}} = 0.68\ [Cd]_{DGT} + 17.10$
Nickel	$[Ni]_{\text{Dissolved Fraction}} = 0.41\ [Ni]_{DGT} + 217$	$[Ni]_{\text{Dissolved Fraction}} = 0.44\ [Ni]_{DGT} + 645.36$
Lead	$[Pb]_{\text{Dissolved Fraction}} = 0.77\ [Pb]_{DGT} + 72$	$[Pb]_{\text{Dissolved Fraction}} = 0.84\ [Pb]_{DGT} + 291{,}86$

The results of these two simulations to predict the dissolved concentration from measurements in DGT per season and per MONITOOL sampling site are presented for cadmium, nickel and lead respectively in Tables 11, 12, 13. To carry out these simulations, we have considered the DGTs that have been exposed to seawater for at least 4 days. Once the predicted concentration in the dissolved fraction is calculated, it is compared to the AA-EQS $_{\text{marine water}}$ and to the real concentrations measured in discrete water samples (dissolved fraction).

The objective is to check whether the chemical status assessed on the basis of these predicted concentrations from DGT measurements are consistent with the chemical status assessed on the basis of the results from dissolved concentrations measured in discrete water samples (via spot sampling).

2.1. Cadmium

Results of the two simulations to predict the dissolved concentration of cadmium from measurements in DGT and the comparison with the AA-EQS $_{marine\ water}$ per season and per MONITOOL sampling site are presented in Table 11. A comparison between concentrations measured in discrete water samples (average of the dissolved concentrations) and predicted dissolved concentration based on DGT results (simulations 1 and 2) can be seen graphically in Figure 5.

Table 11: Cd-Values of predicted concentration in the dissolved fraction (simulation 1 and simulation 2) from DGT results for the MONITOOL sampling points, and comparison to dissolved concentration values measured in discrete water samples (mean per season) and to EQS $_{marine\ water}$. Values of measured DGT concentrations are also indicated as the mean per season. *WB = water body.*

Institute	Sampling points	Season	WB Type	DGT	Dissolved concentration	Comparison to $EQS_{marine\ water}$: 0.2 µg/L	Predicted	Predicted	Comparison to $EQS_{marine\ water}$: 0.2 µg/L per season	
				Mean per season ($ng \cdot L^{-1}$)	Mean per season ($ng \cdot L^{-1}$)		[Cd] $_{dissolved\ fraction}$	[Cd] $_{dissolved\ fraction}$ + Confidence interval (+95%)		
	Sampling points	Season	WB Type	Measured	Measured	per season	Simulation 1	Simulation 2	Simulation 1	Simulation 2
AZTI	DEBA	DS	estuary	12	17	per season	14	25	< EQS	< EQS
AZTI	DEBA	WS	estuary	6	3	< EQS	10	21	< EQS	< EQS
AZTI	LEZO	DS	estuary		43	< EQS	6	17	< EQS	< EQS
AZTI	LEZO	WS	estuary	120	115	< EQS	86	99	< EQS	< EQS
AZTI	MUSEO	DS	estuary		26	< EQS	6	17	< EQS	< EQS
AZTI	MUSEO	WS	estuary	25	28	< EQS	23	34	< EQS	< EQS
AZTI	PRACTICOS	DS	estuary	24	22	< EQS	22	34	< EQS	< EQS
AZTI	PRACTICOS	WS	estuary	76	48	< EQS	57	69	< EQS	< EQS
CEFAS	BELFAST	DS	estuary	14	26	< EQS	15	26	< EQS	< EQS
CEFAS	BELFAST	WS	estuary	19	19	< EQS	19	30	< EQS	< EQS
CEFAS	FAL	DS	estuary	15	26	< EQS	16	27	< EQS	< EQS
CEFAS	FAL	WS	estuary	44	36	< EQS	35	47	< EQS	< EQS
CEFAS	LIVERPOOL	DS	coastal		24	< EQS				
CEFAS	LIVERPOOL	WS	coastal	30	29	< EQS	26	37	< EQS	< EQS
CEFAS	X38A	DS	coastal	19	26	< EQS	19	30	< EQS	< EQS
CEFAS	X38A	WS	coastal	20	19	< EQS	19	30	< EQS	< EQS
DCU	ABW	DS	estuary	53	53	< EQS	42	54	< EQS	< EQS
DCU	ABW	WS	estuary	34	41	< EQS	29	40	< EQS	< EQS
DCU	DUBLIN BAY BUOY	DS	coastal	82	21	< EQS	61	73	< EQS	< EQS
DCU	DUBLIN BAY BUOY	WS	coastal	23	20	< EQS	21	33	< EQS	< EQS
DCU	M69	DS	estuary	25	15	< EQS	23	34	< EQS	< EQS
DCU	M69	WS	estuary	17	16	< EQS	18	29	< EQS	< EQS
DCU	M70	DS	estuary	34	15	< EQS	29	40	< EQS	< EQS
DCU	M70	WS	estuary	21	20	< EQS	20	31	< EQS	< EQS
IFREMER	ANTIFER_BAF	WS	coastal	15	22	< EQS	16	27	< EQS	< EQS
IFREMER	PORT EN BESSIN	DS	coastal	10	11	< EQS	12	24	< EQS	< EQS
IFREMER	PORT EN BESSIN	WS	coastal	14	14	< EQS	15	27	< EQS	< EQS
IFREMER	FONTENELLE	DS	estuary	15	12	< EQS	16	27	< EQS	< EQS
IFREMER	FONTENELLE	WS	estuary	19	15	< EQS	19	30	< EQS	< EQS
IFREMER	LAZARET_EIL	DS	coastal	9	15	< EQS	12	23	< EQS	< EQS
IFREMER	LE CROISIC-BAF	WS	coastal	13	12	< EQS	15	26	< EQS	< EQS
IFREMER	SAINT-NAZAIRE	DS	coastal	17	10	< EQS	17	28	< EQS	< EQS
IFREMER	SAINT-NAZAIRE	WS	coastal	17	16	< EQS	18	29	< EQS	< EQS
IFREMER	SAUMONARD	DS	coastal	15	11	< EQS	16	27	< EQS	< EQS
IFREMER	SAUMONARD	WS	coastal	20	15	< EQS	20	31	< EQS	< EQS
IFREMER	SILLON DES ANGLAIS_BAF	WS	coastal	33	20	< EQS	28	39	< EQS	< EQS
IFREMER	TERENEZ-BAF	DS	estuary	52	33	< EQS	41	53	< EQS	< EQS
IPMA	AVEIRO	DS	estuary	NA	30	< EQS				
IPMA	AVEIRO	WS	estuary	22	26	< EQS	21	32	< EQS	< EQS
IPMA	PORTO	DS	coastal		14	< EQS				
IPMA	PORTO	WS	coastal	23	28	< EQS	21	33	< EQS	< EQS
IPMA	SESIMBRA	DS	coastal		11	< EQS				
IPMA	SESIMBRA	WS	coastal	10	14	< EQS	13	24	< EQS	< EQS
IPMA	TAGUS_DS	DS	coastal		13	< EQS				
IPMA	TAGUS	WS	coastal	18	22	< EQS	18	30	< EQS	< EQS

Institute	Sampling points	Season	WB Type	DGT Mean per season (ng·L^{-1})	Dissolved concentration Mean per season (ng·L^{-1})	Comparison to $EQS_{marine\ water}$: 0.2 µg/L	Predicted [Cd] $_{dissolved\ fraction}$	Predicted [Cd] $_{dissolved\ fraction}$ + Confidence interval (+95%)	Comparison to $EQS_{marine\ water}$: 0.2 µg/L per season	
	Sampling points	Season	WB Type	Measured	Measured	per season	Simulation 1	Simulation 2	Simulation 1	Simulation 2
ITC	GANDO	DS	coastal	1	4	< EQS	7	18	< EQS	< EQS
ITC	GANDO	WS	coastal	5	5	< EQS	9	21	< EQS	< EQS
ITC	JINAMAR	DS	coastal	1	5	< EQS	7	18	< EQS	< EQS
ITC	JINAMAR	WS	coastal	2	5	< EQS	7	19	< EQS	< EQS
ITC	LUZ	DS	coastal	3	8	< EQS	8	19	< EQS	< EQS
ITC	LUZ_WP4	DS	coastal	6	10	< EQS	10	21	< EQS	< EQS
ITC	LUZ	WS	coastal	6	8	< EQS	10	21	< EQS	< EQS
ITC	TALIARTE_DS	DS	coastal	1	5	< EQS	7	18	< EQS	< EQS
ITC	TALIARTE_WP4	DS	coastal	5	6	< EQS	9	21	< EQS	< EQS
ITC	TALIARTE	WS	coastal	2	5	< EQS	8	19	< EQS	< EQS
MSS-SEPA	BRAEHEAD	DS	coastal	10	23	< EQS	13	24	< EQS	< EQS
MSS-SEPA	MONTROSE	DS	coastal	14	44	< EQS	15	27	< EQS	< EQS
MSS-SEPA	NEWHAVEN	NA	coastal	17	27	< EQS	18	29	< EQS	< EQS
UNICA	MOLODOGANA	DS	coastal	19	21	< EQS	19	30	< EQS	< EQS
UNICA	MOLODOGANA	WS	coastal	13	14	< EQS	15	26	< EQS	< EQS
UNICA	MOLOINCHUSA	DS	coastal	7	16	< EQS	11	22	< EQS	< EQS
UNICA	MOLOINCHUSA	WS	coastal	11	13	< EQS	13	24	< EQS	< EQS
UNICA	MOLORINASCITA	DS	coastal	13	47	< EQS	15	26	< EQS	< EQS
UNICA	MOLORINASCITA	WS	coastal	10	14	< EQS	13	24	< EQS	< EQS
UNICA	SANTELMO	DS	coastal	10	14	< EQS	13	24	< EQS	< EQS
UNICA	SANTELMO	WS	coastal	12	15	< EQS	14	25	< EQS	< EQS

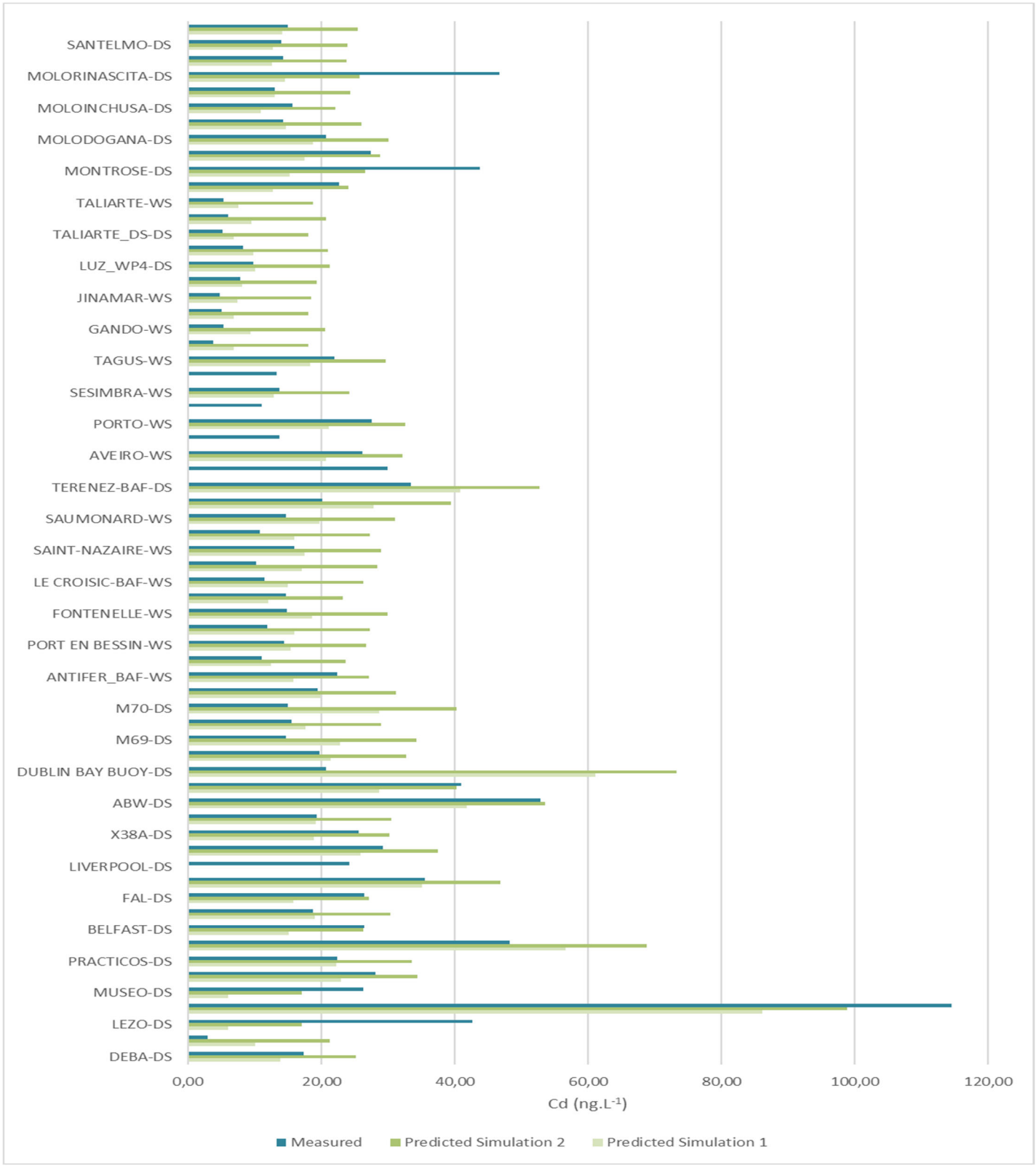

Figure 5: Cadmium concentration (ng.L-1) in marine water (dissolved concentration) for each MONITOOL sampling site and season: measured and predicted from DGT results (simulations 1 and 2).

In the case of cadmium, all the sets of data "sampling site – season" for measured Cd (dissolved fraction in spot water samples) presented an average below the EQS $_{marine\ water}$, as well as for the predicted concentrations in dissolved fraction determined from DGT results (simulations 1 and 2). The two assessment methods are therefore consistent.

The graphical approach (Figure 5) shows on one hand that whatever the site, the season and the simulation approach, the results are much lower than the EQS $_{marine\ water}$ (0.2 µg.L^{-1}). In most cases, the concentration predicted by simulation 2 is very often higher than the measured concentration.

2.2. Nickel

Results of the two simulations to predict the dissolved concentration of nickel from measurements in DGT and the comparison with the AA-EQS $_{marine\ water}$ per season and per MONITOOL sampling site are presented in Table 12. A comparison between concentrations measured in discrete water samples (average of the dissolved concentrations) and predicted dissolved concentration based on DGT results (simulations 1 and 2) can be seen graphically in Figure 6.

Table 12: Ni-values of predicted concentration in the dissolved fraction (simulation 1 and simulation 2) from DGT results for the MONITOOL sampling points, and comparison to dissolved concentration values measured in discrete water samples (mean per season) and to EQS $_{marine\ water}$. Values of measured DGT concentrations are also indicated as the mean per season. *WB = water body.*

Institute	Sampling points	Season	WB Type	DGT results Mean per season ($ng \cdot L^{-1}$) Measured	Dissolved concentration Mean per season ($ng \cdot L^{-1}$) Measured	Comparison to $EQS_{marine\ water}$: 8.6 µg/L per season	Predicted $[Ni]_{dissolved\ fraction}$ Simulation 1	Predicted $[Ni]_{dissolved\ fraction}$ + Confidence interval (+95%) Simulation 2	Comparison to $EQS_{marine\ water}$: 8.6 µg/L per season Simulation 1	Simulation 2
AZTI	DEBA	WS	estuary	1108	974	< EQS	671	1132	< EQS	< EQS
AZTI	DEBA	DS	estuary	2414	2348	< EQS	1207	1705	< EQS	< EQS
AZTI	LEZO	WS	estuary	408	349	< EQS	384	825	< EQS	< EQS
AZTI	LEZO	DS	estuary	257	372	< EQS	322	758	< EQS	< EQS
AZTI	MUSEO	DS	estuary	540	243	< EQS	438	883	< EQS	< EQS
AZTI	MUSEO	WS	estuary	240	435	< EQS	315	751	< EQS	< EQS
AZTI	PRACTICOS	WS	estuary	334	242	< EQS	354	792	< EQS	< EQS
AZTI	PRACTICOS	DS	estuary	296	195	< EQS	338	775	< EQS	< EQS
CEFAS	BELFAST	WS	estuary	500	884	< EQS	422	865	< EQS	< EQS
CEFAS	BELFAST	DS	estuary	316	561	< EQS	347	784	< EQS	< EQS
CEFAS	FAL	WS	estuary	742	785	< EQS	521	971	< EQS	< EQS
CEFAS	FAL	DS	estuary	348	546	< EQS	360	798	< EQS	< EQS
CEFAS	LIVERPOOL	WS	coastal	759	635	< EQS	528	979	< EQS	< EQS
CEFAS	LIVERPOOL	DS	coastal		319	< EQS				
CEFAS	X38A	DS	coastal	314	373	< EQS	346	783	< EQS	< EQS
CEFAS	X38A	WS	coastal	407	415	< EQS	384	824	< EQS	< EQS
DCU	ABW	WS	estuary	617	1278	< EQS	470	916	< EQS	< EQS
DCU	ABW	DS	estuary	1362	421	< EQS	775	1243	< EQS	< EQS
DCU	M69	WS	estuary	549	748	< EQS	442	887	< EQS	< EQS
DCU	M69	DS	estuary	900	253	< EQS	586	1041	< EQS	< EQS
DCU	M70	WS	estuary	588	745	< EQS	458	904	< EQS	< EQS
DCU	M70	DS	estuary	1444	231	< EQS	809	1279	< EQS	< EQS
DCU	DUBLIN BAY BUOY	DS	coastal	1451	309	< EQS	812	1282	< EQS	< EQS
DCU	DUBLIN BAY BUOY	WS	coastal	516	889	< EQS	429	872	< EQS	< EQS
IFREMER	FONTENELLE	WS	estuary	572	479	< EQS	451	896	< EQS	< EQS
IFREMER	FONTENELLE	DS	estuary	398	242	< EQS	380	820	< EQS	< EQS
IFREMER	TERENEZ_BAF	DS	estuary	604	506	< EQS	465	911	< EQS	< EQS
IFREMER	PORT EN BESSIN	WS	coastal	776	559	< EQS	535	986	< EQS	< EQS
IFREMER	PORT EN BESSIN	DS	coastal	679	584	< EQS	496	944	< EQS	< EQS
IFREMER	LAZARET_EIL	DS	coastal	286	193	< EQS	334	771	< EQS	< EQS
IFREMER	SAINT-NAZAIRE	WS	coastal	931	873	< EQS	599	1054	< EQS	< EQS
IFREMER	SAINT-NAZAIRE	DS	coastal	1123	1187	< EQS	678	1139	< EQS	< EQS
IFREMER	SAUMONARD	WS	coastal	554	263	< EQS	444	889	< EQS	< EQS
IFREMER	SAUMONARD	DS	coastal	291	178	< EQS	336	773	< EQS	< EQS
IFREMER	ANTIFER_BAF	WS	coastal	335	441	< EQS	354	792	< EQS	< EQS
IFREMER	LE_CROISIC-BAF	WS	coastal	327	285	< EQS	351	789	< EQS	< EQS
IFREMER	SILLON_DES_ANGLAIS_B	WS	coastal	596	367	< EQS	461	907	< EQS	< EQS
IPMA	AVEIRO	WS	estuary	621	823	< EQS	471	918	< EQS	< EQS
IPMA	AVEIRO	DS	estuary		605	< EQS				
IPMA	PORTO	WS	coastal	349	383	< EQS	360	798	< EQS	< EQS
IPMA	PORTO	DS	coastal		236	< EQS				
IPMA	SESIMBRA	WS	coastal	220	225	< EQS	307	742	< EQS	< EQS
IPMA	SESIMBRA	DS	coastal		135	< EQS				
IPMA	TAGUS	WS	coastal	343	431	< EQS	358	796	< EQS	< EQS
IPMA	TAGUS	DS	coastal		220	< EQS				

Institute	Sampling points	Season	WB Type	DGT results Mean per season ($ng \cdot L^{-1}$) Measured	Dissolved concentration Mean per season ($ng \cdot L^{-1}$) Measured	Comparison to $EQS_{marine\ water}$: 8.6 µg/L per season	Predicted [Ni] dissolved fraction Simulation 1	Predicted [Ni] dissolved fraction + Confidence interval (+95%) Simulation 2	Comparison to $EQS_{marine\ water}$: 8.6 µg/L per season Simulation 1	Comparison to $EQS_{marine\ water}$: 8.6 µg/L per season Simulation 2
ITC	GANDO	DS	coastal	165	84	< EQS	284	718	< EQS	< EQS
ITC	GANDO	WS	coastal	746	275	< EQS	523	973	< EQS	< EQS
ITC	JINAMAR	DS	coastal	156	103	< EQS	281	714	< EQS	< EQS
ITC	JINAMAR	WS	coastal	177	249	< EQS	290	723	< EQS	< EQS
ITC	LUZ	DS	coastal	184	170	< EQS	293	726	< EQS	< EQS
ITC	LUZ	WS	coastal	261	279	< EQS	324	760	< EQS	< EQS
ITC	LUZ_WP4	DS	coastal	543	327	< EQS	440	884	< EQS	< EQS
ITC	TALIARTE	DS	coastal	164	131	< EQS	284	717	< EQS	< EQS
ITC	TALIARTE	WS	coastal	187	473	< EQS	294	727	< EQS	< EQS
ITC	TALIARTE_WP4	DS	coastal	498	224	< EQS	421	864	< EQS	< EQS
MSS-SEPA	BRAEHEAD	DS	coastal	694	1544	< EQS	501	950	< EQS	< EQS
MSS-SEPA	MONTROSE	DS	coastal	284	358	< EQS	333	770	< EQS	< EQS
MSS-SEPA	NEWHAVEN	NA	coastal	481	400	< EQS	414	857	< EQS	< EQS
UNICA	MOLODOGANA	DS	coastal	305	445	< EQS	342	779	< EQS	< EQS
UNICA	MOLODOGANA	WS	coastal	422	417	< EQS	390	831	< EQS	< EQS
UNICA	MOLOINCHUSA	DS	coastal	358	371	< EQS	364	802	< EQS	< EQS
UNICA	MOLOINCHUSA	WS	coastal	406	450	< EQS	383	823	< EQS	< EQS
UNICA	MOLORINASCITA	DS	coastal	578	579	< EQS	454	899	< EQS	< EQS
UNICA	MOLORINASCITA	WS	coastal	429	368	< EQS	393	834	< EQS	< EQS
UNICA	SANTELMO	DS	coastal	263	304	< EQS	325	761	< EQS	< EQS
UNICA	SANTELMO	WS	coastal	418	368	< EQS	388	829	< EQS	< EQS

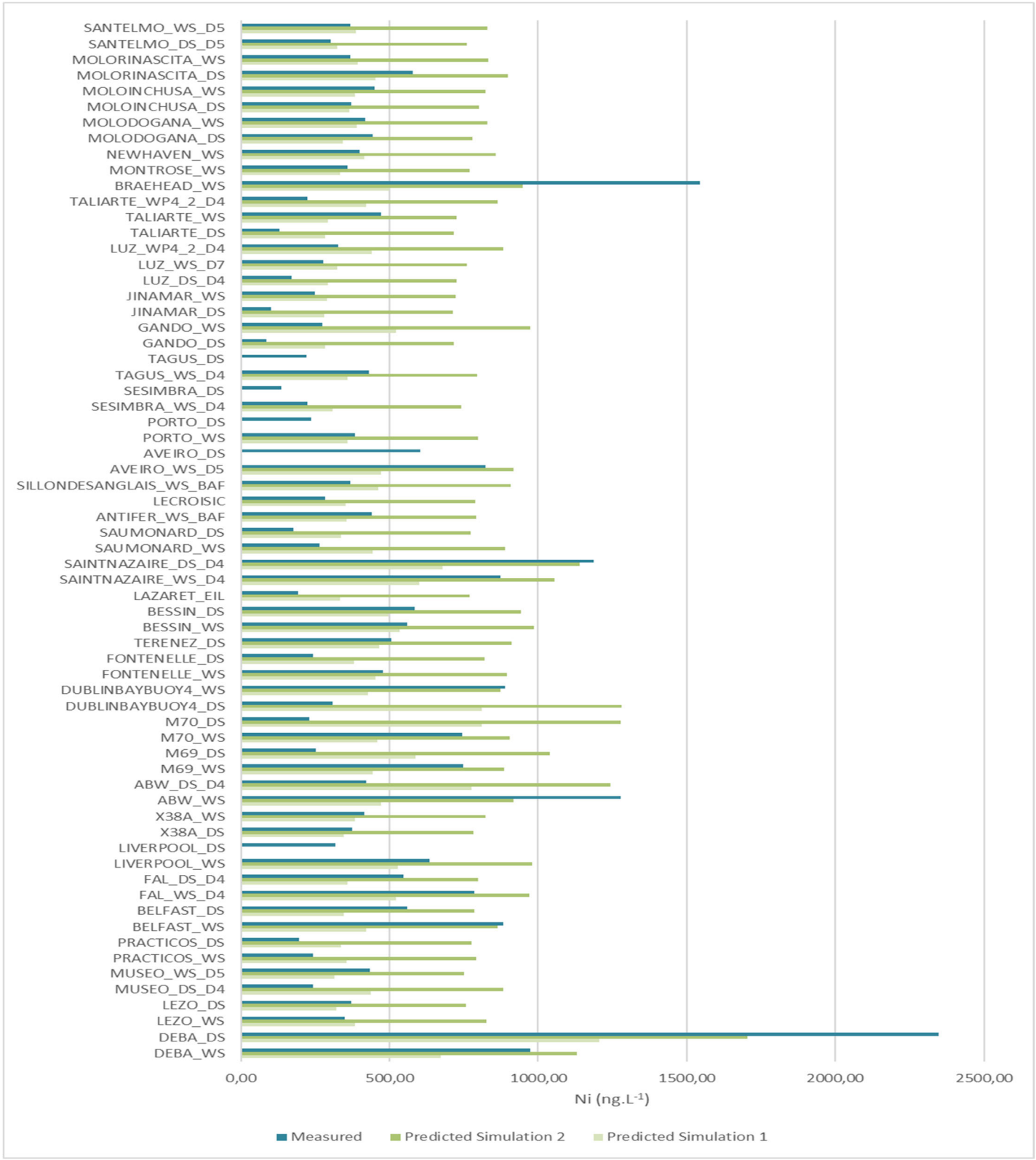

Figure 6: Nickel concentration (ng.L^{-1}) in marine water (dissolved concentration) for each MONITOOL sampling site and season: measured and predicted from DGT results (simulations 1 and 2).

In the case of nickel, all the sets of data “sampling site – season” for measured Ni (dissolved fraction in spot water samples) presented an average below the EQS $_{marine\ water}$, as well as for the predicted concentrations in dissolved fraction determined from DGT results (simulations 1 and 2). The two assessment methods are therefore consistent.

The graphical approach (Figure 6) shows on one hand that whatever the site, the season and the simulation approach, the results are much lower than the EQS $_{marine\ water}$ (8600 ng.L-1). In most cases (55/61 sites), the concentration predicted by simulation 2 is very often higher than the measured concentration. Only in 5 sites, the measured concentration is higher than the predicted concentration (simulation 2).

2.3. Lead

Results of the two simulations to predict the dissolved concentration of lead from measurements in DGT and the comparison with the AA-EQS $_{marine\ water}$ per season and per MONITOOL sampling site are presented in Table 13. A comparison between concentrations measured in discrete water samples (average of the dissolved concentrations) and predicted dissolved concentration based on DGT results (simulations 1 and 2) can be seen graphically in Figure 7 A and B (zoom for average concentration below 1600 ng. L^{-1})

Table 13: Pb-values of predicted concentration in the dissolved fraction (simulation 1 and simulation 2) from DGT results for the MONITOOL sampling points, and comparison to dissolved concentration values measured in discrete water samples (mean per season) and to EQS $_{marine\ water}$. Values of measured DGT concentrations are also indicated as the mean per season *WB = water body.*

Institute	Sampling points	Season	WB Type	DGT results Mean per season ($ng \cdot L^{-1}$) Measured	Dissolved concentration Mean per season ($ng \cdot L^{-1}$) Measured	Comparison to $EQS_{marine\ water}$: 1.3 µg/L per season	Predicted [Pb] $_{dissolved\ fraction}$ Simulation 1	Predicted [Pb] $_{dissolved\ fraction}$ + Confidence interval (+95%) Simulation 2	Comparison to $EQS_{marine\ water}$: 1.3 µg/L per season Simulation 1	Comparison to $EQS_{marine\ water}$: 1.3 µg/L per season Simulation 2
AZTI	DEBA	DS	estuary	10	36	< EQS	79	300	< EQS	< EQS
AZTI	DEBA	WS	estuary	48	39	< EQS	109	332	< EQS	< EQS
AZTI	LEZO	DS	estuary		515	< EQS				
AZTI	LEZO	WS	estuary	167	335	< EQS	201	432	< EQS	< EQS
AZTI	MUSEO	DS	estuary		3508	> EQS				
AZTI	MUSEO	WS	estuary	133	482	< EQS	175	404	< EQS	< EQS
AZTI	PRACTICOS	DS	estuary	33	1019	< EQS	98	320	< EQS	< EQS
AZTI	PRACTICOS	WS	estuary	135	299	< EQS	176	405	< EQS	< EQS
CEFAS	BELFAST	DS	estuary	29	48	< EQS	94	316	< EQS	< EQS
CEFAS	BELFAST	WS	estuary	43	43	< EQS	105	328	< EQS	< EQS
CEFAS	FAL	DS	estuary	18	91	< EQS	86	307	< EQS	< EQS
CEFAS	FAL	WS	estuary	81	51	< EQS	134	360	< EQS	< EQS
CEFAS	LIVERPOOL	WS	coastal	54	213	< EQS	114	337	< EQS	< EQS
CEFAS	X38A	DS	coastal	55	50	< EQS	114	338	< EQS	< EQS
CEFAS	X38A	WS	coastal	72	70	< EQS	127	352	< EQS	< EQS
DCU	ABW	DS	estuary	8046	12132	> EQS	6267	7050	> EQS	> EQS
DCU	DUBLIN BAY BUOY	DS	coastal	580	55	< EQS	519	779	< EQS	< EQS
DCU	DUBLIN BAY BUOY	WS	coastal	163	132	< EQS	198	429	< EQS	< EQS
DCU	M69	DS	estuary	128	61	< EQS	171	400	< EQS	< EQS
DCU	M69	WS	estuary	95	74	< EQS	145	372	< EQS	< EQS
DCU	M70	DS	estuary	327	74	< EQS	324	567	< EQS	< EQS
DCU	M70	WS	estuary	87	62	< EQS	139	365	< EQS	< EQS
IFREMER	ANTIFER_BAF	WS	coastal	44	353	< EQS	106	329	< EQS	< EQS
IFREMER	FONTENELLE	DS	estuary	27	34	< EQS	93	315	< EQS	< EQS
IFREMER	FONTENELLE	WS	estuary	118	99	< EQS	163	391	< EQS	< EQS
IFREMER	LAZARET_EIL	DS	coastal	73	106	< EQS	129	354	< EQS	< EQS
IFREMER	LECROISIC	WS	coastal	67	62	< EQS	124	348	< EQS	< EQS
IFREMER	Port en BESSIN	DS	coastal	39	40	< EQS	102	324	< EQS	< EQS
IFREMER	Port en BESSIN	WS	coastal	104	43	< EQS	152	379	< EQS	< EQS
IFREMER	SAINT NAZAIRE	DS	coastal	21	28	< EQS	88	309	< EQS	< EQS
IFREMER	SAINT NAZAIRE	WS	coastal	81	204	< EQS	134	360	< EQS	< EQS
IFREMER	SAUMONARD	DS	coastal	25	37	< EQS	91	313	< EQS	< EQS
IFREMER	SAUMONARD	WS	coastal	105	199	< EQS	153	380	< EQS	< EQS
IFREMER	SILLON DES ANGLAIS	WS	coastal	229	336	< EQS	249	485	< EQS	< EQS
IFREMER	TERENEZ	DS	estuary	222	118	< EQS	243	478	< EQS	< EQS
IPMA	AVEIRO	WS	estuary	39	131	< EQS	102	325	< EQS	< EQS
IPMA	PORTO	WS	coastal	92	202	< EQS	143	369	< EQS	< EQS
IPMA	SESIMBRA	WS	coastal	58	136	< EQS	117	341	< EQS	< EQS
IPMA	TAGUS	WS	coastal	117	139	< EQS	162	390	< EQS	< EQS

Institute	Sampling points	Season	WB Type	DGT results Mean per season ($ng \cdot L^{-1}$) Measured	Dissolved concentration Mean per season ($ng \cdot L^{-1}$) Measured	Comparison to $EQS_{marine\ water}$: 1.3 µg/L per season	Predicted [Pb] dissolved fraction Simulation 1	Predicted [Pb] dissolved fraction + Confidence interval (+95%) Simulation 2	Comparison to $EQS_{marine\ water}$: 1.3 µg/L per season Simulation 1	Comparison to $EQS_{marine\ water}$: 1.3 µg/L per season Simulation 2
ITC	GANDO	DS	coastal	10	50	< EQS	80	300	< EQS	< EQS
ITC	GANDO	WS	coastal	93	157	< EQS	144	370	< EQS	< EQS
ITC	JINAMAR	DS	coastal	7	28	< EQS	77	298	< EQS	< EQS
ITC	JINAMAR	WS	coastal	25	60	< EQS	91	313	< EQS	< EQS
ITC	LUZ	DS	coastal	21	57	< EQS	88	310	< EQS	< EQS
ITC	LUZ	WS	coastal	57	92	< EQS	116	340	< EQS	< EQS
ITC	LUZ_WP4	DS	coastal	78	62	< EQS	132	357	< EQS	< EQS
ITC	TALIARTE	DS	coastal	46	48	< EQS	107	330	< EQS	< EQS
ITC	TALIARTE	WS	coastal	57	210	< EQS	116	340	< EQS	< EQS
ITC	TALIARTE_WP4	DS	coastal	77	77	< EQS	132	357	< EQS	< EQS
MSS-SEPA	BRAEHEAD	DS	coastal	46	66	< EQS	108	331	< EQS	< EQS
MSS-SEPA	MONTROSE	DS	coastal	89	270	< EQS	140	366	< EQS	< EQS
MSS-SEPA	NEWHAVEN	NA	coastal	83	76	< EQS	136	361	< EQS	< EQS
UNICA	MOLODOGANA	DS	coastal	142	197	< EQS	181	411	< EQS	< EQS
UNICA	MOLODOGANA	WS	coastal	191	724	< EQS	219	452	< EQS	< EQS
UNICA	MOLOINCHUSA	DS	coastal	67	208	< EQS	124	348	< EQS	< EQS
UNICA	MOLOINCHUSA	WS	coastal	125	500	< EQS	168	397	< EQS	< EQS
UNICA	MOLORINASCITA	DS	coastal	115	1358	> EQS	161	389	< EQS	< EQS
UNICA	MOLORINASCITA	WS	coastal	279	1429	> EQS	287	526	< EQS	< EQS
UNICA	SANTELMO	DS	coastal	69	150	< EQS	125	350	< EQS	< EQS
UNICA	SANTELMO	WS	coastal	102	408	< EQS	151	377	< EQS	< EQS

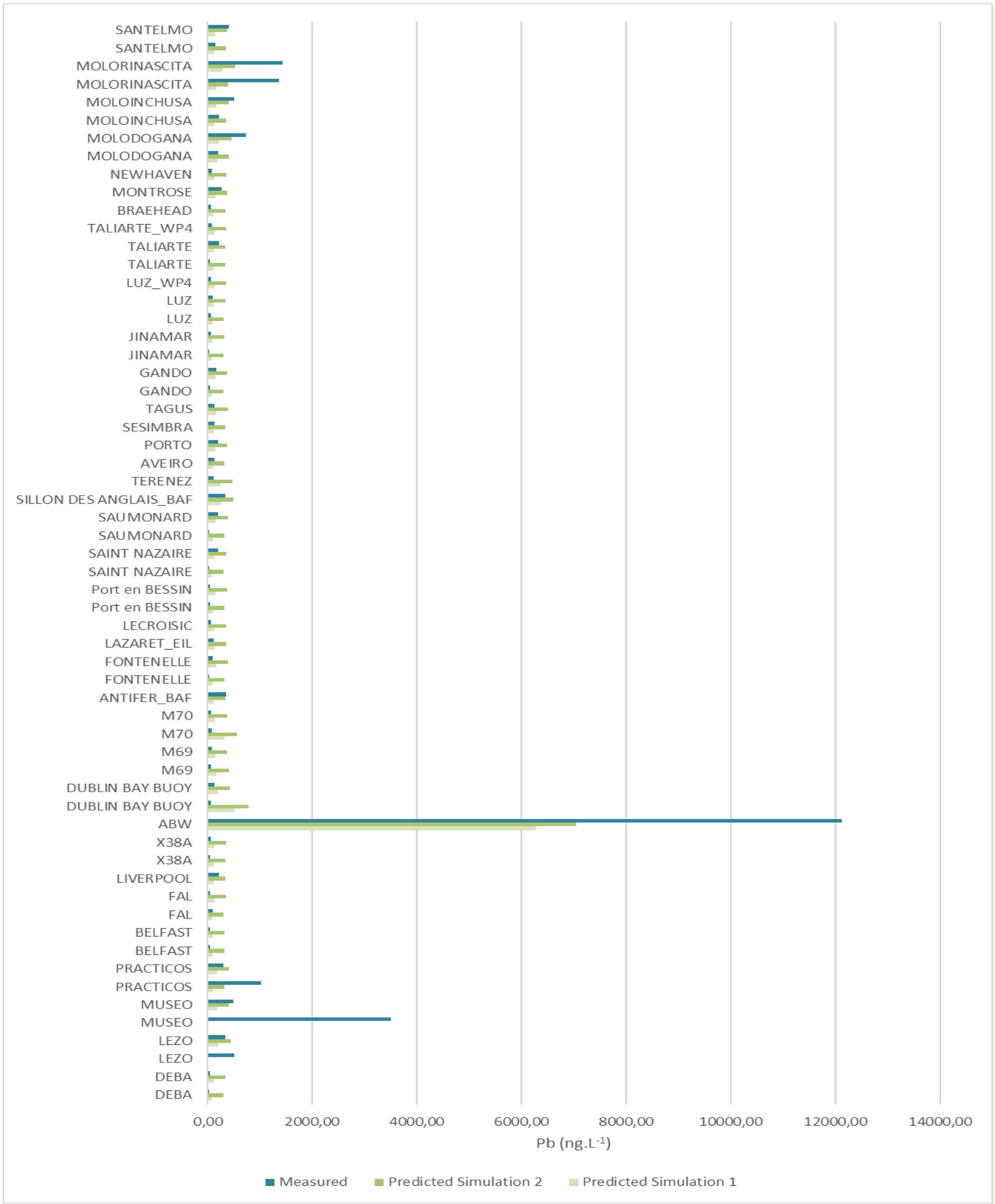

Figure 7: A - Lead concentration (ng.L^{-1}) in marine water (dissolved concentration) for each MONITOOL sampling site and season: measured and predicted from DGT results (simulations 1 and 2).

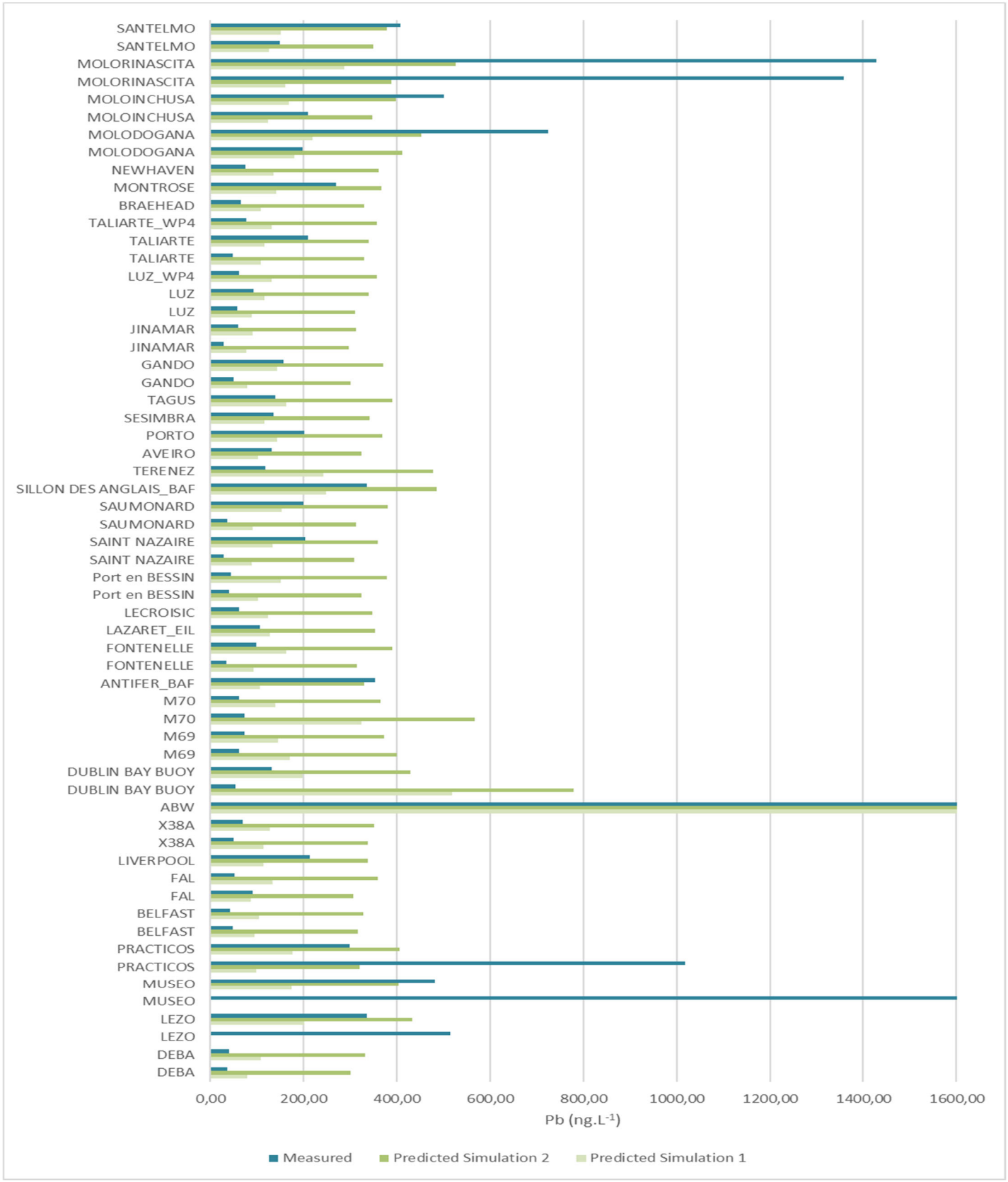

Figure 7: B – Zoom for results below 1600 ng.L^{-1} (EQS $_{\text{marine water}}$ = 1300 ng.L^{-1})

In the case of lead, among the 58 sets of data "sampling site – season", measured Pb (dissolved concentration in spot water samples) 55 presented an average below the EQS $_{marine\ water}$ and 3 above (in ABW DS, MOLO RINASCITA WS and MOLO RINASCITA DS). The concentration measured in dissolved fraction in Molo Rinascita is close to the EQS value (1300 ng.L-1): 1357 ng.L^{-1} in DS and 1428 ng.L^{-1} in WS. *(Note that Museo DS nor Lezo DS are not considered here as no DGT results are available for these sites)*.

From the predicted concentrations in the dissolved fraction determined from DGT results (simulations 1 and 2), only ABW presented a result above the EQS $_{marine\ water}$ (by both simulations). Molo Rinascita presented results much below the EQS $_{marine\ water}$.

The graphical approach (Figure 3) makes it possible to visualize and compare concentration measured in the dissolved fraction and in the predicted concentration (simulations 1 and 2). For most of the sites – season (49 among 58), the predicted concentration determined by simulation 2 is very often higher than the measured concentration.

Conclusion

In the framework of the MONITOOL project, it was planned to simulate the "chemical status" for each of the sampled sites for cadmium, nickel and lead, in order to compare and verify the conformity of the assessment results based on i) the results obtained on the water spot samples (analysis on the dissolved fraction) and ii) on the DGT results.

These simulations are not "regulatory" chemical status assessment per se, as they do not correspond to what is formally expected by the WFD as MONITOOL has not produced data on spot water samples on a monthly basis during one year. The data are processed as closely as possible to what is expected by regulation: annual average results compared to EQS.

36 sites were sampled within the MONITOOL project, targeting sites suspected of having very high levels of contamination (harbours, estuaries). The aim was to reach if possible and even exceed the EQS $_{\text{marine water}}$ values, but the results obtained are far from the EQS values even in supposedly highly contaminated sites except for one site for lead (considering an annual average of concentration in dissolved fraction).

The simulation of the chemical status assessment of each MONITOOL site was performed for each metal: Cd, Ni and Pb on the basis on the two approaches for using DGT results in a regulatory framework:

- Compare DGT results to proposed EQS $_{\text{DGT}}$ (Table 1);

- Predict the concentration in the dissolved fraction from its concentration in DGT (Table 10), and compare this predicted concentration with EQS $_{\text{marine water}}$.

Concerning the first option, the annual mean concentration (wet and dry seasons) measured in the dissolved fraction (spot-sampling) was compared to the AA-EQS $_{\text{marine mater}}$, and the mean (results of wet and dry seasons) concentration measured in DGT was compared to the AA-EQS $_{\text{DGT}}$ n°1 and AA-EQS $_{\text{DGT}}$ n°2. The objective was to assess the consistency of both assessments, based on the metal dissolved concentrations, and based on DGTs metal concentrations. For cadmium and nickel, all the annual mean concentrations measured in water samples are much lower than the AA-EQS $_{\text{marine water}}$ value and all the mean DGT concentrations are lower than the simulated EQS$_{\text{DGT.}}$ Both assessments gave the same chemical status independently of applying the dissolved fraction compared to the EQS $_{\text{marine water}}$ or the DGT results compared to the proposed EQS $_{\text{DGT}}$. However, for lead, among the 19 sites for which an annual average can be calculated, a difference is observed at one MONITOOL site: Molo Rinascita. In this site, the annual mean concentration in the dissolved fraction (average of 6 values instead of 12 expected by the WFD) is above the EQS $_{\text{marine water,}}$ while the DGT average value is lower than the EQS $_{\text{DGT}}$ n°1. But the opposite occurs in Dublin Bay Buoy that shows an annual average dissolved concentration of Pb below the EQS $_{\text{marine water,}}$ while the DGT average value is higher than the EQS $_{\text{DGT}}$ n°1. Using the EQS $_{\text{DGT}}$ n°2, 4 sites show a result higher than the EQS $_{\text{DGT:}}$ Dublin Bay Buoy, M70, Molo Rinascita and Molo Dogana.

In terms of comparison, the decision to choose either the EQS $_{\text{DGT}}$ n°1 or EQS $_{\text{DGT}}$ n°2 depends on the willingness to be more or less protective for the environment.

Concerning the second approach, the predicted metal dissolved concentrations (using the high confidence interval) calculated with DGT results, can be compared to the EQS $_{\text{marine water}}$. This process has been applied by season, to identify if there were some differences depending on the period (wet and dry season) of sampling. The assessment is consistent between predicted and measured concentration for Cd and Ni. However, in ABW

site, the lead concentration is above the EQS $_{marine\ water}$ using both, measured or predicted Pb values, while a difference in the assessment is observed for Molo Rinascita (above the EQS $_{marine\ water}$ with measured Pb concentration, below the EQS $_{marine\ water}$ with predicted Pb concentration); the assessment is compliant at 97% for Pb.

Following these simulations, both approaches (i.e. use of EQS $_{DGT}$ n°1 or n°2, or prediction of concentration in dissolved fraction from DGT results) could be used in a regularitory context for the chemical assessment using DGT results.

As highlighted in the WP6-action 1 report, the MONITOOL dataset demonstrates that even in suspected high contaminated sites, the concentration in marine water was far below the EQS $_{marine\ water}$ for Cd and Ni and in general for Pb, raising the question of the relevance of EQS $_{marine\ water}$ values. Maybe an update of those EQS should be done as the dossier are quite old (2005-2011 depending on the metal considered). It would be necessary to include more ecotoxicological results for marine species, and it should be considered the bioavailable fraction in the EQS derivation.

In addition to the adaptation of the EQS $_{DGT}$, or to the determination of predicted dissolved concentrations from DGT results, other information must be specified in order to use DGTs in a regulatory context in a homogeneous way at the European level. A complementary project could be carried out to specify the operational strategy: frequency and period of deployment of the DGT relative to different types of water bodies (coastal, estuaries). Furthermore, in order to verify the absence of toxicity at EQS $_{DGT}$ values for marine species, ecotoxicological tests could be carried out. These ecotoxicological tests should be carried out in parallel with measurements of metals concentration in the dissolved and labile fractions (by DGTs), so that this project would provide ecotoxicological data on marine species, related to the DGT labile fraction, which is very close to the (bio)available fraction. Those data are currently lacking for the marine environment.

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