Simulation of Chemical status assessment using DGT results

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Report/Deliverable by

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Disclaimer

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1. 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 labile concentration to EQS_{DGT} or predict metals dissolved concentration from their concentration in DGT and compare it to the $EQS_{marine\ water}$. 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).

2. Scope

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

The scope of this deliverable is to update the simulation of the chemical status by using the results of the 2022 campaign (additional campaign - Monitool extension).

This deliverable is a complementary work to the previous one (1,2) and it is advisable to review the previous one if better understanding of the methodological details is desired.

The aim of this work is to check the agreement of the assessment using these different approaches for the sites sampled in 2022 within MONITOOL extension, 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.

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

3.1. 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)" (3).

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 $_{marine\ water}$) (4), and proposed EQS $_{DGT}$ determined in WP6- action 1 are indicated in Table 1, with and without the Prediction interval ($PI_{95\%}$). The equation 2 used to predict the dissolved concentration from DGT result are precised in Table 2.

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

Table 1: AA-EQS $_{marine\ water}$ and proposed AA-EQS $_{DGT}$ for Cd, Pb and Ni (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 interval 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).

Table 2: Application of Equation 2 for predicting Cd, Ni and Pb dissolved concentrations from DGT results. The mean and highest predicted concentrations and the validity range are shown

	Mean predicted $[M]_{dissolved\ concentration}$ ($ng \cdot L^{-1}$)	**Highest predicted** $[M]_{dissolved\ concentration}$ (HPI 95%) ($ng \cdot L^{-1}$)	**Validity range** ($ng \cdot L^{-1}$)
Cadmium	$[Cd]_{Dissolved\ concentration} = 0.67\ [Cd]_{DGT} + 6$	$[Cd]_{Dissolved\ concentration} = 0.68\ [Cd]_{DGT} + 17$	$[Cd]_{DGT}$: [<LQ, 75]
Nickel	$[Ni]_{Dissolved\ concentration} = 0.41\ [Ni]_{DGT} + 217$	$[Ni]_{Dissolved\ concentration} = 0.44\ [Ni]_{DGT} + 645$	$[Ni]_{DGT}$: [<LQ, 2,128]
Lead	$[Pb]_{Dissolved\ concentration} = 0.77\ [Pb]_{DGT} + 72$	$[Pb]_{Dissolved\ concentration} = 0.84\ [Pb]_{DGT} + 292$	$[Pb]_{DGT}$: [<LQ, 327]

3.2. Simulation of chemical status based on MONITOOL data

For each MONITOOL site (Figure 1 and Table 3), the following simulations were performed:

- Simulation 1: Annual average dissolved concentrations of spot sampling results were compared to the $AA\text{-}EQS_{marine\ water}$.
- Simulation 2: Annual mean DGT results were compared to $(A)\text{-}EQS_{DGT}$ n°1 and n°2 (Table 1).
- Simulation 3: Predicted dissolved concentrations from DGT results (mean and highest predicted concentrations) were compared to $EQS_{marine\ water}$.
- Results of these previous simulations done within MONITOOL are presented Figure 2 (1,2).

Figure 1: MONITOOL sampling sites map

Table 3: MONITOOL sampling points, point number and WB type

Date	Institute	Number	Sampling points	WB Type
2018	AZTI	1	DEBA	estuary
2018	CEFAS	5	BELFAST	estuary
2018	CEFAS	6	FAL	estuary
2018	CEFAS	7	X38A	coastal
2018	DCU	9	DUBLIN BAY BUOY 4	coastal
2018	DCU	10	M69	estuary
2018	DCU	11	M70	estuary
2018	IFREMER	12	PORT EN BESSIN	coastal
2018	IFREMER	13	FONTENELLE	estuary
2018	IFREMER	14	SAINT NAZAIRE	coastal
2018	IFREMER	15	SAUMONARD	coastal
2018	UNICA	20	MOLODOGANA	coastal
2018	UNICA	21	MOLOINCHUSA	coastal
2018	UNICA	22	MOLORINASCITA	coastal
2018	UNICA	23	SANTELMO	coastal
2018	ITC	16	GANDO	coastal
2018	ITC	17	JINAMAR	coastal
2018	ITC	18	LUZ	coastal
2018	ITC	19	TALIARTE	coastal

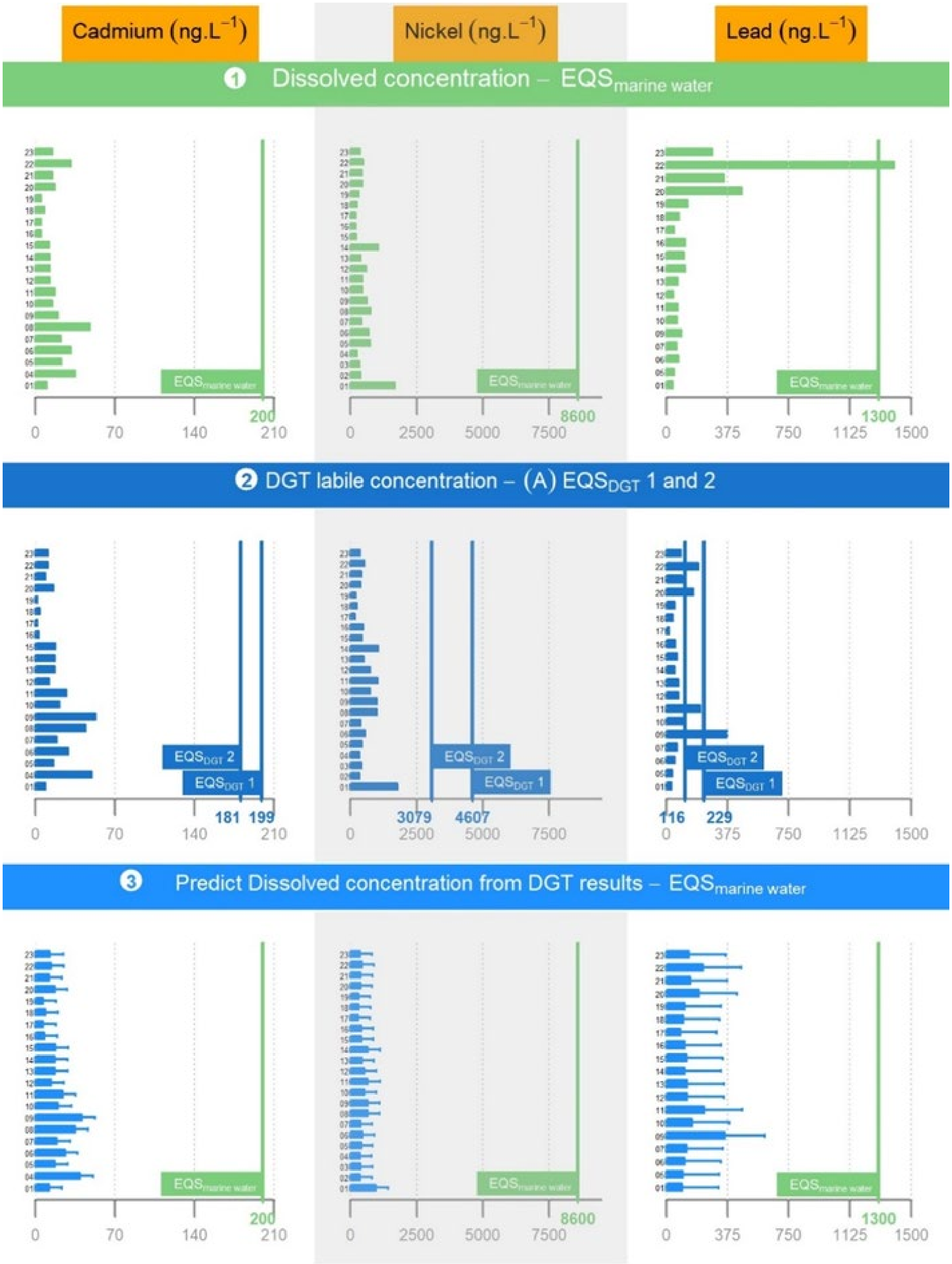

Figure 2: Simulation of “chemical status” assessment per MONITOOL site for cadmium, nickel and lead: ❶ Annual mean dissolved concentration (in green) and indication of EQS $_{marine\ water}$; ❷ Annual mean labile DGT concentration (ng·L^{-1}) (in blue) and indication of (A)-EQS $_{DGT}$ n°1 & 2; ❸ Predict dissolved concentration from DGT results (Eq. 2) and indication of EQS $_{marine\ water}$.

3.3. Simulation of chemical status for sites sampled in 2022 during the additional campaign - MONITOOL extension

As part of the MONITOOL extension, a single sampling campaign was carried out in 2022 on 10 sites by the partners (Table 4). The data processing method described in section 3.1 for the simulation is therefore not applicable (no determination of annual average on the basis of data acquired during 2 campaigns). Nevertheless, the data can be compared with the EQS in order to assess whether they are compliant or not. The results for each of these sites are presented Figure 3 and details are provided Tables 5, 6 and 7 for cadmium, nickel and lead. It should be noted that the scale of the Figure 6 had to be adapted to display the highest values measured at two sites (25,31). The comparison with the EQSs are done for all the data obtained, even those presenting results outside the validity range of the models (see Amouroux et al, Report WP6- action 1- 2023).

Table 4: MONITOOL – extension – additional 2022 campaign: sampling points, point number and type

Date	Institute	Number	Sampling points	Type
2022	IFREMER	24	BASSIN-1 (B1)	closed bassin
2022	IFREMER	25	BASSIN-2 (B2)	closed bassin
2022	CEFAS	26	NEYLAND MARINA (HT)	
2022	CEFAS	27	NEYLAND MARINA (LT)	
2022	AZTI	28	HERRERA	estuary
2022	AZTI	29	LEZO	estuary
2022	UNICA	30	MOLO SABAUDO (MS)	
2022	UNICA	31	PARCO DI MOLENTARGIUS (PM)	
2022	DCU	32	DUN LAOGHAIRE HARBOUR	
2022	DCU	33	POOLBEG MARINA	

Figure 3: Comparaison to EQS per sites sampled in 2022 within additional sampling campaign (MONITOOL extension) for cadmium, nickel and lead: ❶ Measured dissolved concentration (in green) and indication of EQS $_{marine\ water}$; ❷ Labile DGT concentration (ng·L^{-1}) (in blue) and indication of (A)-EQS $_{DGT}$ n°1 & 2; ❸ Predict dissolved concentration from DGT results (Eq. 2) and indication of EQS $_{marine\ water}$.

Cadmium

Table 5: Comparison to EQS for additional sampling sites 2022- MONITOOL extension: DGT labile concentration compared to EQS $_{DGT}$ n°1 and n°2, comparison of mean measured dissolved concentration to EQS $_{marine\ water}$, comparison of predicted dissolved concentration from DGT result (Equ. 2: simulations 1 and 2)

		DGT labile concentration			Measured dissolved concentration			Predicted dissolved concentration from DGT			
Number	Sampling points	DGT (ng·L-1)	Comparison to EQS $_{DGT}$ n°1	Comparison to EQS $_{DGT}$ n°2	Nb data number	ICPMS - mean	comparison to EQS	Simulation 1	Simulation 2	Simulation 1	Simulation 2
24	BASSIN-1 (B1)	88	< EQS	< EQS	6	112	< EQS	65	77	< EQS	< EQS
25	BASSIN-2 (B2)	1077	> EQS	> EQS	6	3297	> EQS	728	749	> EQS	> EQS
26	NEYLAND MARINA (HT)	18	< EQS	< EQS	7	16	< EQS	18	29	< EQS	< EQS
27	NEYLAND MARINA (LT)	18	< EQS	< EQS	7	17	< EQS	18	29	< EQS	< EQS
28	HERRERA	18	< EQS	< EQS	14	17	< EQS	18	29	< EQS	< EQS
29	LEZO	43	< EQS	< EQS	14	47	< EQS	35	46	< EQS	< EQS
30	MOLO SABAUDO (MS)	9	< EQS	< EQS	5	6	< EQS	12	23	< EQS	< EQS
31	PARCO DI MOLENTARGIUS (PM	16	< EQS	< EQS	6	39	< EQS	17	28	< EQS	< EQS
32	DUN LAOGHAIRE HARBOUR	14	< EQS	< EQS	4	13	< EQS	15	27	< EQS	< EQS
33	POOLBEG MARINA	14	< EQS	< EQS	4	11	< EQS	15	27	< EQS	< EQS

Among the 10 sampling sites, 9 sites presented a dissolved concentration of cadmium below the EQS $_{marine\ water}$ and 1 above (site n°25). Using either DGT labile concentration compared to EQS $_{DGT}$ n° 1 or 2 (Equ. 1) or predicted dissolved concentration from DGT results (Equ. 2), the same conclusion is obtained: 9 sites presented concentrations below the EQS and 1 site above (25).

Nickel

Table 6: Comparison to EQS for additional sampling sites 2022- MONITOOL extension: DGT labile concentration compared to EQS $_{DGT}$ n°1 and n°2, comparison of mean measured dissolved concentration to EQS $_{marine\ water}$, comparison of predicted dissolved concentration from DGT result (Equ. 2: simulations 1 and 2)

		DGT labile concentration			Measured dissolved concentration			Predicted dissolved concentration from DGT			
Number	Sampling points	DGT (ng·L-1)	Comparison to EQS $_{DGT}$ n°1	Comparison to EQS $_{DGT}$ n°2	Nb data number	ICPMS - mean	comparison to EQS	Simulation 1	simulation 2	Simulation 1	Simulation 2
24	BASSIN-1 (B1)	3040	< EQS	< EQS	6	2893	< EQS	1463	1983	< EQS	< EQS
25	BASSIN-2 (B2)	20189	> EQS	> EQS	6	35833	> EQS	8494	9528	< EQS	> EQS
26	NEYLAND MARINA (HT)	342	< EQS	< EQS	7	276	< EQS	357	795	< EQS	< EQS
27	NEYLAND MARINA (LT)	346	< EQS	< EQS	7	286	< EQS	359	797	< EQS	< EQS
28	HERRERA	265	< EQS	< EQS	14	299	< EQS	326	762	< EQS	< EQS
29	LEZO	280	< EQS	< EQS	14	276	< EQS	332	768	< EQS	< EQS
30	MOLO SABAUDO (MS)	465	< EQS	< EQS	5	223	< EQS	408	850	< EQS	< EQS
31	PARCO DI MOLENTARGIUS (PM)	316	< EQS	< EQS	6	937	< EQS	347	784	< EQS	< EQS
32	DUN LAOGHAIRE HARBOUR	240	< EQS	< EQS	4	207	< EQS	315	751	< EQS	< EQS
33	POOLBEG MARINA	420	< EQS	< EQS	4	330	< EQS	389	830	< EQS	< EQS

Among the 10 sampling sites, 9 sites presented a dissolved concentration of nickel below the EQS $_{marine\ water}$ and 1 above (site n°25). Using either DGT labile concentration compared to EQS $_{DGT}$ n° 1 or 2 (Equ. 1) or predicted dissolved concentration from DGT results (Equ. 2 simulation 2), the same results are obtained: 9 sites presented concentrations below the EQS and 1 site above (25). The predicted concentration from DGT result using the Equ.2 simulation 1, is just below the EQS $_{marine\ water}$. Using the Equ. 2 simulation 2 will be preferred to the simulation 1.

Lead

Table 7: Comparison to EQS for additional sampling sites 2022- MONITOOL extension: DGT labile concentration compared to EQS $_{DGT}$ n°1 and n°2, comparison of mean measured dissolved concentration to EQS $_{marine\ water}$, comparison of predicted dissolved concentration from DGT result (Equ. 2: simulations 1 and 2)

		DGT labile concentration			Measured dissolved concentration			Predicted dissolved concentration from DGT			
Number	Sampling points	DGT (ng·L-1)	Comparison to EQS $_{DGT}$ n°1	Comparison to EQS $_{DGT}$ n°2	Nb data number	ICPMS - mean	comparison to EQS	Simulation 1	Simulation 2	Simulation 1	Simulation 2
24	BASSIN-1 (B1)	41	< EQS	< EQS	6	91	< EQS	104	326	< EQS	< EQS
25	BASSIN-2 (B2)	142	< EQS	> EQS	6	2750	> EQS	181	411	< EQS	< EQS
26	NEYLAND MARINA (HT)	25	< EQS	< EQS	6	15	< EQS	91	313	< EQS	< EQS
27	NEYLAND MARINA (LT)	20	< EQS	< EQS	7	22	< EQS	87	309	< EQS	< EQS
28	HERRERA	39	< EQS	< EQS	14	68	< EQS	102	325	< EQS	< EQS
29	LEZO	85	< EQS	< EQS	13	123	< EQS	137	363	< EQS	< EQS
30	MOLO SABAUDO (MS)	148	< EQS	> EQS	5	136	< EQS	186	416	< EQS	< EQS
31	PARCO DI MOLENTARGIUS (PM)	2950	> EQS	> EQS	6	7688	> EQS	2344	2770	> EQS	> EQS
32	DUN LAOGHAIRE HARBOUR	31	< EQS	< EQS	4	30	< EQS	96	318	< EQS	< EQS
33	POOLBEG MARINA	58	< EQS	< EQS	4	60	< EQS	117	341	< EQS	< EQS

Among the 10 sampling sites, 8 sites presented a dissolved concentration of lead below the EQS $_{marine\ water}$ and 2 above (sites n°25 and 31). Using DGT labile concentration compared to EQS $_{DGT}$: only one site (n°31) is above the EQS $_{DGT}$ n°1, and 3 sites (N°25, 30 and 31) are above applying EQS $_{DGT}$ N°2. In such case, using EQS DGT n° 2 is at least as protective as comparing dissolved concentration to EQS $_{marine\ water}$.

When using the predicted concentration from DGT result using the Equ.2 simulations 1 and 2, only one site (n°31) is above the EQS $_{marine\ water}$. The predicted concentrations for the site 25 using simulation 1 or 2 are below the EQS $_{marine\ water}$.

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 the results obtained on the dissolved concentration and on the DGT results.

This deliverable aims to complete the previous deliverable (1,2) for additional sites sampled in 2022 within MONITOOL extension. These sites were chosen in order to reach high concentrations near or above the $EQS_{marine\ water}$ for cadmium, nickel and lead.

Two sites (25, 31) presented measured dissolved concentrations above $EQS_{marine\ water}$ for at least one of these three metals. Same conclusions were obtained comparing DGT labile concentrations to EQS_{DGT} for cadmium (EQS_{DGT} n°1 and n°2), for nickel (EQS_{DGT} n°1 and n°2) and for lead using EQS_{DGT} n°2. Using equation 2 to predict dissolved concentration from DGT result, the same conclusion was obtained comparing predicted concentration to EQS for cadmium (simulations 1 and 2), for nickel using simulation 2, while for lead a difference was observed for one site (25) (predicted concentration is below the EQS, while the measured dissolved concentration is above the $EQS_{marine\ water}$).

The results of the assessments based on the two methodologies proposed in MONITOOL are very similar to the assessment based on the comparison of dissolved concentration measurements with the $EQS_{marine\ water}$. On the basis of the elements presented, using the EQS_{DGT} n°2 and the predicted dissolved concentration using simulation 2 appears to be more protective.

Bibliography

1. Amouroux I, Guesdon S. Simulation of Chemical status assessment using DGT results. MONITOOL project. Technical deliverables. WP6. Action 3. 2021.

2. Amouroux, et al. A new approach to using Diffusive Gradient in Thin-films (DGT) labile concentration for Water Framework Directive chemical status assessment: adaptation of Environmental Quality Standard to DGT for cadmium, nickel and lead. Environ Sci Eur [Internet]. 2023 Apr 29 [cited 2023 Jul 11];35(1):29. Available from: https://enveurope.springeropen.com/articles/10.1186/s12302-023-00733-4.

3. COMMISSION DIRECTIVE 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status. 2009.

4. U.E. Directive 2013/39/EU of the European Parliament and of the council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Official journal of the European Union. 24.8.2013. L 226/1. 2013.