MONITOOL
new tools for water quality monitoring

DGT: EQS adaptation for Nickel, Cadmium and Lead

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Report/Deliverable by

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Disclaimer

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Glossary

AA-EQS: Annual Average Environmental Quality Standard

AA-QS: Annual Average Quality Standard

AF: Assessment Factor

ASV: Anodic stripping voltammetry

BAF: Bioaccumulation Factor

BCF: Bioconcentration Factor

BLM: Biotic ligand model

BMF: Biomagnification Factor

CAS: Chemical Abstract Service

CCC: Criterion Continuous Concentration

Cd: Cadmium

CF: Concentration Factor

CWQG: Canadian Water Quality Guideline

DGT: Diffusive Gradient in Thin film

DOC: Dissolved Organic Carbon

EC10: Effect Concentration measured as 10% effect

EC50: Median Effect Concentration

EQS: Environmental Quality Standard

IP: Prediction interval

IC: Confidence Interval

HC5: Hazardous Concentration (5th percentile)

ICP-MS: Inductively coupled plasma mass spectrometry

Koc: Organic-Carbon normalised partition (or distribution) coefficient

Kow: Octanol-Water partition coefficient

Kp: Solids-water Partition (or distribution) coefficient

LC50: Lethal median Concentration

LOQ: Limit of quantification

MAC-EQS: Maximum Allowable Concentration Environmental Quality Standard

MPA: Maximum Permissible Addition

MPC: Maximum Permissible Concentration

Ni: Nickel

NOEC: No Observed Effect Concentration

OECD: Organisation for Economic Cooperation and Development

Pb: Lead

PNEC: Predicted No Effect Concentration

QS: Quality Standard

RAR: Risk Assessment Report

SPM: Suspended Particulate Matter

SSD: Species Sensitivity Distribution

TGD: Technical Guidance Document

VRAR: Voluntary Risk Assessment Report

WHAM: Windermere Humic Aqueous model

WFD: Water Framework Directive

Introduction

According to the Water Framework Directive (WFD), (Directive 2000/60/EC) (1) the Chemical Status of water bodies is assessed on the basis of the compliance for each priority substance of the measured concentration with Environmental Quality Standards (EQS). Directive 2008/105/EC (2) amended by Directive 2013/39/EU (3), established the maximum allowable concentrations (MAC-EQS) and annual average concentrations (AA-EQS) of four metals. Only mercury (Hg) has an AA-EQS that refers to biota (fish); the three others – lead (Pb), cadmium (Cd) and nickel (Ni) – have an EQS applicable to surface waters. In the case of metals in transitional and coastal water bodies, the EQS refers to the dissolved concentration, i.e. the dissolved phase of a water sample obtained by filtration through a 0.45 µm filter or any equivalent pre-treatment.

In aquatic environments, most chemical contaminants (metallic or organic) are present at trace levels, complicating the detection (and quantification) of contaminants by standardized analytical techniques. Additionally, in seawater, due to the saline matrix, using "conventional" techniques requires the implementation of "ultra-clean" sampling of high volumes of water and complex concentration/extraction and analytical steps. Beyond that, the low spatial and temporal representativeness of the results of spot sampling, especially in highly dynamic systems, has been pointed out, therefore the use of integrative matrix, such as molluscs or sediments, is preferred to monitor the chemical contamination of water bodies (OSPAR (4,5), French Chemical Contamination Monitoring Network in marine environment: ROCCH). The use of passive samplers, enabling low disturbance *in situ* sampling of trace element species and providing time-averaged concentration of contaminants during the deployment time, appears as a more reliable approach for the environment chemical monitoring (6). Since one of the primary objectives of the WFD is the assessment of the annual average concentrations of pollutants in waterbodies, the determination of time-integrated concentrations using passive samplers is a promising approach, which is less influenced by short-term fluctuations in concentrations than grab sampling (i.e., discrete spot sampling). The MONITOOL project focuses on the diffusive gradients in thin films (DGT) technique, which stands out as one of the most widely used passive sampler for metals (6). These samplers were developed, in the early 90s, by Lancaster University (7) (8), in collaboration with the UK Environment Agency.

Despite the wide application of DGTs for *in situ* measurements of metal speciation in numerous scientific studies (9), the use of DGT results in a regulatory context for chemical status assessment is not considered as yet. However, passive sampling techniques are mentioned in Directive 2013/39/EU as "novel monitoring methods showing promise for future application", and in three Technical Guidance Documents (Surface water chemical monitoring (10), Chemical monitoring of sediment and biota (11), and Biota monitoring (12)) as methods under development and evaluation that are desirable to introduce as they become available for improving the quality of the assessment. This opens the opportunity for their introduction in future directives if sufficient scientific evidence demonstrates their reliability for establishing the chemical status of water bodies.

The MONITOOL project aims to provide a robust database of dissolved and labile metal concentrations in transitional and coastal waters for adapting existing Environmental Quality Standards (EQS; 0.45 µm-filtered) for passive sampling devices (EQS_{DGT}), in order to evaluate the chemical status of marine waters under the WFD.

Scope

As DGT results cannot be directly compared to marine water AA-EQS, the general objective of this document is to propose a methodology so that DGT results can be applied in a regulatory context for waterbody quality assessment. Using a pragmatic approach applied to the context of the WFD, this methodology is based on the study of European reports, European technical and scientific guidance documents, publications of network of experts and processing of MONITOOL dataset.

For this purpose, the document is organised in two parts:

- a bibliographic part with a review of the derivation process of EQSs, a description of the differences between DGT and spot sampling based measurements, the proposed methodology for the use of DGT results in a regulatory framework, by comparing DGT results to EQS ;
- a data processing part carried out using MONITOOL datasets in order to adapt EQS $_{\text{marine water}}$ in EQS$_{\text{DGT}}$ for Cd, Ni and Pb. Moreover, another methodology is proposed, which is to predict the concentrations measured by DGT into its corresponding dissolved concentrations, so they can be directly compared to EQS$_{\text{marine water}}$.

Field of application:

In this document, EQS refers only to AA-EQS and it does not apply to MAC-EQS. DGTs measure concentrations integrated over time and therefore they are not suitable for identifying short-term fluctuations in concentrations.

This document focuses on three metals and its compounds, defined as priority substances in the WFD: Ni, Pb, and Cd.

Mercury (Hg) has not been considered in the MONITOOL project, as it requires the use of specific DGTs that are still being optimized. Indeed, the water sampling and analysis of Hg are very specific and complex, and the available AA-EQS for Hg refers to biota (fish) and not to marine water.

1. EQS derivation for priority metals

1.1. General presentation of an EQS derivation

An EQS is defined as the concentration of a particular pollutant or group of pollutants in water, sediment or biota which should not be exceeded in order to protect human health and the environment (1). A general description of an EQS derivation is presented in Figure 1.

The methodology used to derive an EQS is described in the Technical Guidance Document for deriving Environmental Quality Standard (TGD EQS) (13)**. The information presented in this section was extracted from this document.** EQSs should protect freshwater and marine ecosystems from possible adverse effects of chemicals as well as human health from exposure via drinking water or fishery product consumption. Key steps involved in deriving an EQS are presented in Figures 1 and 2.

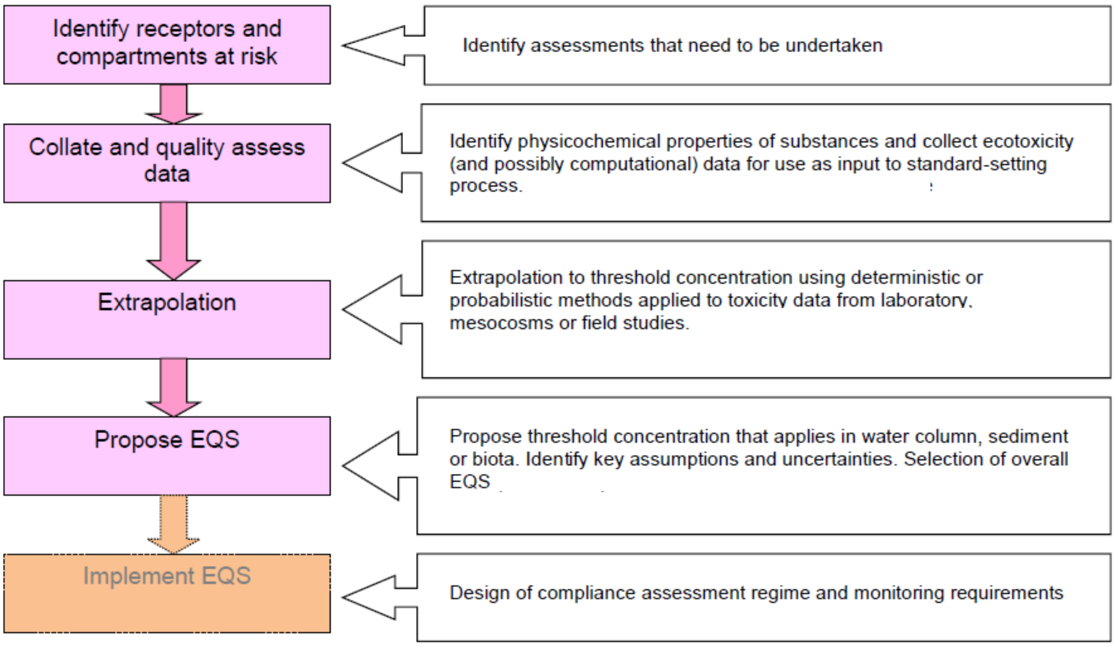


Figure 1: Key steps involved in deriving an EQS (13)

An overview of the assessments needed (or receptor needed to be considered) and the procedure to be followed for the selection of an "overall" EQS is presented below.

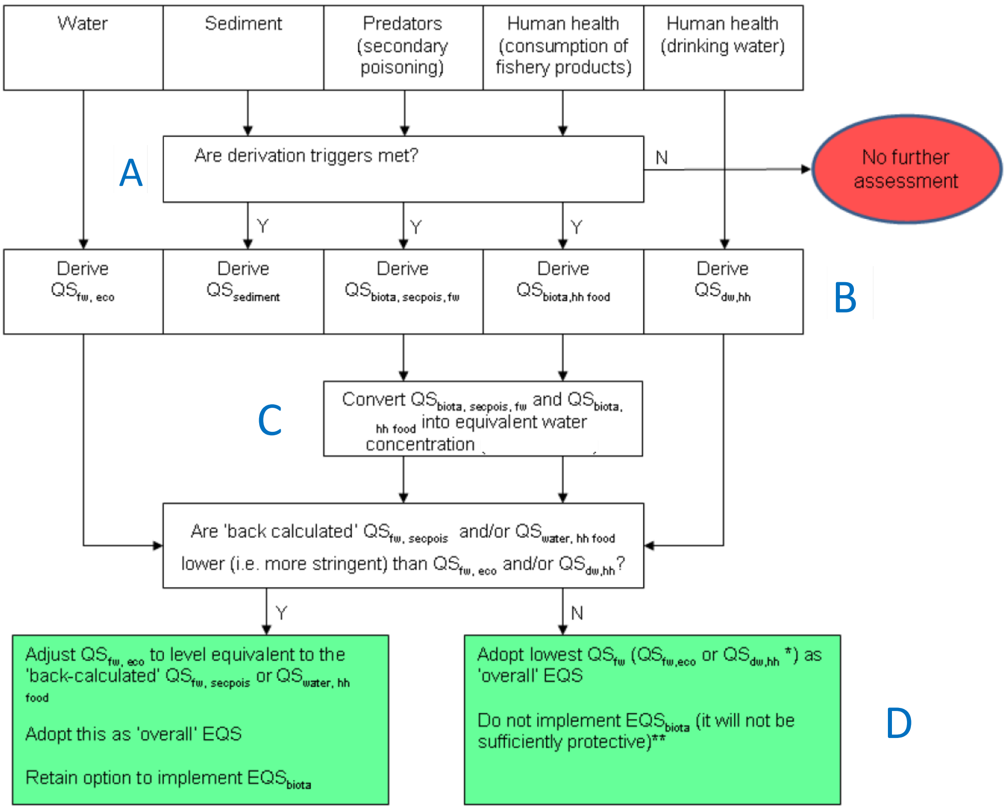


Figure 2: Overview of assessments needed and selection of an "overall" EQS (13) Y: YES; N: No; QS: Quality Standard.

A: EQSs should protect freshwater and marine ecosystems from possible adverse effects of chemicals as well as human health via drinking water or ingestion of food originating from aquatic environments. Several different types of receptor therefore need to be considered, *i.e.* the pelagic and benthic communities in freshwater, brackish or saltwater ecosystems, the top predators of these ecosystems and human health. Not all receptors need to be considered for every substance. This depends on the environmental fate and behaviour of the substance. For example, if a substance does not bioaccumulate (or does not have high intrinsic toxicity), there is no risk of secondary poisoning and so a biota standard is not required. However, where a possible risk is identified, quality standards should be derived for that receptor.

B: Quality standards are derived for each relevant compartment by assessing toxicity data from laboratory, mesocosms or field studies for a range of organisms from a number of trophic levels within the aquatic system (typically fish, algae, and invertebrates). Two ecotoxicological extrapolation methods are described in the TGD EQS for deriving Predicted No Effect Concentrations (PNECs): the deterministic approach (or **assessment factor (AF)** approach) and the probabilistic approach (or **species sensitivity distribution (SSD))**.

1. $QS_{saltwater}$ determination with assessment factor (AF) approach: the most reliable and sensitive (i.e. lowest) value is identified for acute and chronic exposition. An assessment factor (AF) is then applied to the lowest chronic data (No Observed Effect Concentration, NOEC) to derive the QS (deterministic approach). The AF accounts for uncertainty and varies depending on the amount of data available but is usually between a factor of 10 and 10,000, as recommended by the TGD EQS.

2. $QS_{saltwater}$ determination with species sensitivity distribution (SSD) approach: QS_{water} may also be derived using the species sensitivity distribution (SSD) methodology (probabilistic approach) if the minimum quantity of reliable, long-term toxicity data is available (minimum 15 NOEC data on 8 species). Depending on the available information, an AF of 1 to 5 is applied to the 5th percentile of the SSD (HC5) to derive the QS (TGD EQS).

C: To select an overall EQS, quality standards will need to be expressed in the same units (i.e. mass/volume). This means that biota standards must be 'back-calculated' to the corresponding water concentration (using BAF (Bioaccumulation Factor) or BCF (Bioconcentration Factor) -BMF (Biomagnification Factor) data). It should be noted that the conversion from a biota standard into an equivalent water concentration can introduce uncertainty, especially for highly lipophilic substances and metals.

D: Standards for water, sediment and biota are derived independently and they should all be made available for possible implementation. Where several assessments are performed, the lowest (most stringent) of the QS obtained will be selected as an overall EQS (14). An exception arises when the drinking water route results in the lowest (most stringent) QS but that waterbody is not designated as a source of drinking water.

The quantity of data available for deriving an EQS can vary. Where an EQS can be derived on the basis of a large dataset, there may be only small uncertainties in the final outcome. If, however, only a very small dataset is available, the residual uncertainties can be large. Uncertainty is accounted for by the use of assessment factors (AFs) but, clearly, there is a considerable difference in the robustness and reliability of such EQSs compared to those based on extensive data sets (13).

1.2. How have EQSs been derived for Ni, Cd and Pb?

The description on the derivation of AA-EQS in the marine compartment is describe in the following subsections for each of the three metals: Ni, Pb and Cd. A summary of the main information is given in 1.3.

Nickel (Ni)

Presentation: Nickel (Ni, CAS number 7440-02-0) is a ubiquitous metal, essential for the normal growth of many species of microorganisms, plants and vertebrates. It is introduced into the environment from natural but also human sources: chemical and physical erosion of rocks and soils, atmospheric deposition of nickel-containing particulates and discharges of industrial and municipal wastes releasing nickel into ambient waters. Ni circulates into the environment by chemical and physical processes and biological transport mechanisms of living organisms. The chemical and physical forms of nickel and its salts influence bioavailability and toxicity (15).

Harmonised classification - Annex VI of Regulation (EC) N° 1272/2008 (CLP Regulation) (16)**:**

H317: May cause an allergic skin reaction
H351: Suspected of causing cancer
H372: Causes damage to organs through prolonged or repeated exposure
H412: Harmful to aquatic life with long lasting effects

Distribution: In surface waters, Ni is present in both particulate and dissolved forms. Ni is one of the most mobile metals when released into waters, particularly in polluted waters, as complexation with dissolved organic compounds enhances Ni solubility. Ni released into soils may leach into ground waters or be leached towards surface waters. The fate of Ni in fresh waters and marine waters is affected by the pH, dissolved organic carbon (DOC), ionic strength, type and concentration of ligands, and the availability of solid surfaces for adsorption (15). In one particularly relevant study, the distribution of Ni in sediment and water in Danish coastal waters was investigated. Samples of water, suspended particulate matter, filtrate, porewater and sediments were collected simultaneously and analysed. The filtrate was sampled by filtration of water samples through 0.45 µm filter. Porewater was obtained by filtration of sediments through 0.4 µm filter. The following partition coefficients Kp were derived in Danish brackish coastal waters (15): log Kp sed (total water, mean) 4.2 $l.kg^{-1}$; log Kp (spm/filtrate, mean) 3.8 $l.kg^{-1}$; log Kp (sed/porewater, mean) 4.2 $l.kg^{-1}$.

Degradation: Ni is considered to be persistent in the environment. Biotic and abiotic degradation rates are not relevant for metals. It should be noted that organo-metallic compounds may be metabolised (the organic part) or even degraded through photolysis (12).

Bioaccumulation: Ni does not appear to biomagnify. The BCF value of 270 is used for derivation of quality standards in the EQS datasheet (17).

Aquatic environmental concentration (17) (table 1)**:**

Table 1: Nickel aquatic environmental concentration (17)

		Reference
Surface water (Data from 23 Member states). Total dissolved (µg/L)	Mean 6.71 Median 1.00	INERIS, 2009 cited in E.C. (2011)(17)

Marine water (µg/L)	Estuarine and estuarine-influenced coastal (RWC-ambient PEC)* waters: 3.34 (range 0.26 – 3.75) Open sea: 0.30 (range 0.14 – 3.75) Baltic sea: 0.79 (range 0.64 – 0.81)	Ni EU-RAR (15)

*Reasonable worst-case ambient PEC (median of the all 90th percentiles that have been derived for the different sites, rivers/catchments or regions.

Nickel Environmental Quality Standard (Ni EQS) (17): The TGD EQS (13) recommends that the PNECs derived from the existing substances regulation be adopted as QS, on the basis that the assessment and the data have undergone thorough peer review. This is the case with the Ni EU-RAR (15), so that these reliable results are used almost exclusively for the derivation of Ni QS in the present document. The aquatic effects assessment of Ni in the EU-RAR assumes that adverse effects on aquatic organisms are a consequence of exposure to the bioavailable Ni-ion, rather than the parent substances. The result of this assumption is that these effects will be similar for all Ni substances containing Ni-ion (e.g., nickel metal, nickel sulphate, nickel chloride, nickel carbonate, nickel dinitrate, etc). QS derived in this document will therefore be relevant for all inorganic Ni substances. Determining the EQS for Ni should be consistent with this approach. Therefore, data from soluble Ni salts are used in the derivation of chronic ecotoxicological NOEC and L(E)C10 values (17).

- Environmental Quality Standard (EQS) (17) (Table 2)

Table 2: Nickel Environmental Quality Standard

Proposed AA-EQS$_{\text{bioavailable}}$ for freshwater (µg/L)	**2**
Proposed AA-EQS for marine water (µg/L)	**8.6**

- Specific Quality Standard (QS) derived for Nickel (17) (Table 3)

Table 3: Specific Quality Standard (QS) derived for Nickel (17)

Protection objective / Quality Standard (QS)	Value
Pelagic community (freshwater) / AA-QS $_{\text{freshwater}}$	2 µg/L *
Pelagic community (marine water) / AA-QS $_{\text{saltwater}}$	**8.6 µg/L**
Benthic community (freshwater) /QS$_{\text{sediment freshwater}}$	No data**
Benthic community (saltwater) / QS$_{\text{sediment saltwater}}$	No data**
Mammalian predators (secondary poisoning) / Freshwater / QS$_{\text{biota secpois}}$	92 000 µg/kgbiota ww 340 µg/L
Mammalian predators (secondary poisoning) / Marine water / QS$_{\text{biota secpois}}$	184 000 µg/kgbiota ww 682 µg/L
Avian predators (secondary poisoning) / Fresh and marine water / QS$_{\text{biota secpois}}$	12 300 µg/kgbiota ww 46 µg/L
Human health via consumption of fishery products / QS$_{\text{biota hh food}}$	40 780 µg/kgbiota ww 151 µg/L
Human health via consumption of water /QS$_{\text{biota hh dw}}$	20 µg/L

*** The 2013/39/UE directive fixed the EQS freshwater at 4 µg/L.** - ** Mentioned as under development in the Ni EU-RAR (2008).

The lowest QS calculated for the different objectives of protection is adopted as the overall EQS. For Ni, AA-QS for the protection of the pelagic community (freshwater 4 µg/L and marine water 8.6 µg/L) are the lowest, and were adopted as AA-EQS. So, we will focus on the methodology used to derive the AA-$QS_{saltwater}$ to understand how the marine Ni EQS was set.

- ANNUAL AVERAGE QUALITY STANDARD DERIVATION FOR MARINE WATER (AA-$QS_{MARINE\ WATER}$)

Chronic saltwater ecotoxicity data used to derive the AA-$QS_{saltwater}$ are listed in Table 4 (17):

Table 4: Summary of the “species mean” NOEC or EC10 values in µg/L (with most sensitive endpoint) for marine organisms (17)

Groupe taxonomique	Substance	Species	Effect	Endpoint / duration	Value (µg/L) (95% CI)	Analysis of conc.	Adminitration Of test response	T°C	pH	Salinity (PSU)	DOC (mg/L)	Test water
Algue	Nickel chloride	*Macrocystis* zoospores	Growth	EC10 (48h)	96.7 (93.5-100.1)	Yes	Static	15	8.0	34	Nm	Natural water
	Nickel chloride	*Champia parvula*	Reproduction	EC10 (10d)	144 (118-170)	Yes	Staic-renewal	23	8	30	1.2	Natural water
	Nickel chloride	*Skelatonema costatum*	Specific Growth Rate	EC10 (72h)	190.6 (124.4-266.0)	Yes	Static	20	8.3	30.2	1.2	Natural water (Yaquina Bay, USA)
	Nickel chloride	*Dunaliella tertiolecta*	Specific Growth Rate	EC10 (72h)	17891 (15186-20373)	Yes	Static	20	7.8	29.4	1.2	Natural water
Mollusques	Nickel chloride	*Haliotis rufescens* / Embryo	Metamorphosis	EC10 (22d)	36.4 (29.0-45.6)	Yes	Static-renewal	15	-	34	-	Natural sea water
	Nickel chloride	*Mytilus galloprovincialis* / Embryo	Development	EC10 (48h)	228 (162-238)	Yes	Static	16.1	7.9	30	1.6	Natural seawater (Shonnon Point USA)
	Nickel chloride	*Crassostrea gigas*/Embryo	Development	EC10 (48h)	430.8 (407-456)	Yes	Static	20.7	7.4	30	1.2	Natural water (Yaquina Bay, USA)
Echinodermata	Nickel nitrate	*Paracentrotus lividus*/Embryo	Development	EC10 (48h)	89 (57-121)	No	Static	18	8.0	35	Not measured	Artificial seawater
	Nickel chloride	Paracentrotus lividus/Embryo	Development	EC10 (48h)	217 (198-237)	Yes	Static	15.8-16.8		38	1.0	Natural Seawater (Mytilene, Greece)
	Nickel chloride	*Dendraster excentricus*/embryo	Development	EC10 (48h)	191 (46-280)	Yes	Static	15.4	8.1	30	1.2	Natural seawater
	Nickel chloride	*Strongylocentrot us purpuratus*/embryo	Development	EC10 (48h)	335 (307-345)	Yes	Static	15.6	8.1	30	1.2	Natural seawater
Crustacea	Soluble Nickel	*Mysidopsis bahía*/Juvenile (2d)	Reproduction	NOEC (36d)	61	Yes	Static-renewal	21	-	34	-	Natural seawater
	Nickel chloride	*Mysidopsis intii*/Juvenile (2d)	Growth	EC10 (28j)	45.2 (35.8-54.6)	Yes	Flow-through	20	-	34	-	Natural seawater
Polycaetes	Nickel chloride	*Neanthes arenaceodentata*/Juvenil	Reproduction	EC10 (90d)	22.5 (3.8-133.6)	Yes	Staticrenewal	20	7.9	29.5	<0.5	Natural seawater
Fish	Nickel chloride	*Atherinops affinis*/Larval	Survival	EC10(40d)	3,599 (2,283-5,673)	Yes	Flow-through	20	-	34	Not measured	Natural seawater
	Nickel chloride	*Cyprinodon variegatus*/Larval (<48h)	Growth	EC10 (28d)	20,760 (20,350-21,170)	Yes	Flow-through	25	-	30	Not measured	Natural seawater

The marine nickel ecotoxicity database includes 15 different organisms representing 6 different taxonomic groups (i.e., algae, crustaceans, echinoderms, molluscs, annelids, and fish) and covering a range of different life forms, feeding strategies and trophic levels. The marine Ni toxicity database includes almost entirely of data from standardized test methodology, so normally carried out under conditions of high (bio)availability. For each ecotoxicity result, the Ni form studied and the temperature, pH, salinity and DOC are reported (15).

Bioavailability: It is important to note that for the Ni $AA\text{-}QS_{saltwater}$ derivation, the "bioavailability" notion has not been considered. However, data show that metals binding to organic ligands can reduce metal toxicity to marine organisms, so an availability correction may be needed. In marine waters (coastal and open sea), hardness, pH and alkalinity do not play a role because coastal/open sea waters are characterised by high pH (typically, between 7.8 and 8.3), high salinity (35 UI) then high ionic strength. Unlike the inorganic composition of marine waters, DOC levels may vary considerably between marine waterbodies (11).

As previously mentioned, two ecotoxicological extrapolation methods are described in the TGD-EQS for deriving AA-QS: The AF approach and SSD approach.

The AF approach: The AA-QS is calculated from the lowest acute LC50 or EC50 or, preferably, from the lowest chronic EC10 or NOEC value, using assessment factors that depend on the available toxicity data (11). Given that chronic NOECs are available for >3 species, an assessment factor of 10 can be applied to the lowest EC10 or NOEC value (11). In this case the lowest EC10 value (22.5 µg/L) was reported for the polychaete, *Neanthes arenaceodentata*. The calculated AA-QS using the assessment factor approach would be 2.3 µg/L.

SSD approach: A statistical species sensitivity analysis of the chronic marine data has been performed to derive a 5th percentile Hazardous Concentration (HC5 = 17.2 µg/L). Based on the amount, type and nature of chronic data on marine organisms and remaining uncertainty, an AF of 2 was chosen in the Ni EU-RAR (15) which yielded a $PNEC_{marine}$ value of 8.6 µg Ni/L corresponding to AA-QS marine water.

The statistical approach taking into account all the available data, is preferred. Therefore, the **AA-QS marine water is proposed to be 8.6 µg/L.**

Other available thresholds (source: ETOX: Information System Ecotoxicology and Environmental Quality Targets):

- Freshwater Canadian water quality guideline (CWQG) (1987):
    - CWQG = 25 µg/L (hardness $CaCO_3$ unknow)
    - CWQG = 150 µg/L (hardness $CaCO_3$ > 180 mg/L)
    - At hardness > 60 to ≤ 180 mg/L the CWQG is calculated using this equation (Cf. calculator http://stts.ccme.ca/en/index.html?lang=en&factsheet=139): CWQG (µg/L) = e{0.76[ln(hardness)]+1.06}
- Switzerland (1994):
    - QS = 50 µg/L (Aquatic life, total dissolved)
- USA (1995):
    - Criterion Continuous Concentration (CCC, freshwater, hardness 100 mg $CaCO_3$/L, dissolved) = 52 µg/L
    - Criterion Continuous Concentration (CCC, saltwater, hardness 100 mg $CaCO_3$/L, dissolved) = 8.2 µg/L
- Australia & New-Zealand marine water quality guideline (18) :
    - 70 µg/L (statistical distribution method at 95% protection),
    - 7 µg/L (statistical distribution method at 99% protection)

Cadmium (Cd)

Presentation: Cadmium (CAS number 7440-43-9) is a naturally occurring element with an ubiquitous distribution in the environment. Cd is a non-essential metal in aquatic organisms except for a marine diatom (*Thalassiosira weissflogii*) for which it is a micronutrient at low concentrations. Cd, at least in short-term exposures, exerts its toxic effects in aquatic organisms by blocking the uptake of calcium from water. (19)

Harmonised classification. Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation) (16)

Classification: Carc.1B; Muta. 2; Repr. 2
Hazard sentences:

H330: Fatal if inhaled.
H341: Suspected of causing genetic defects <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>
H350: May cause cancer <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>
H361fd: Suspected of damaging fertility or the unborn child <state specific effect if known> <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>
H372: Causes damage to organs <or state all organs affected, if known> through prolonged or repeated exposure <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>.
H400: Very toxic to aquatic life.
H410: Very toxic to aquatic life with long lasting effects.

Distribution: The environmental fate and behaviour of Cd is dependent on abiotic conditions, such as pH, hardness, alkalinity, and natural organic matter. These factors influence the toxicity and mobility of Cd by altering the speciation or physiochemical forms of Cd in aquatic systems. Because Cd has a high affinity for negatively charged particle surfaces such as hydroxides, chlorines, carbonates, and organic matter, sorption and complexation processes could affect Cd fate in waters containing high concentrations of organic and inorganic ligands (20).

Degradation: Cd is considered to be persistent in the environment. Biotic and abiotic degradation rates are not relevant for metals. It should be noted that organo-metallic compounds may be metabolized (the organic part) or even degraded through photolysis (16).

Bioaccumulation: Highest BCFs are for primary producers and lowest for secondary consumers. Factors affecting the BCF are the water hardness, pH, Cd concentration and presence of Cd^{2+}complexing agents (20). A maximum field derived bioaccumulation factors of 623 (for whole fish) was retained.

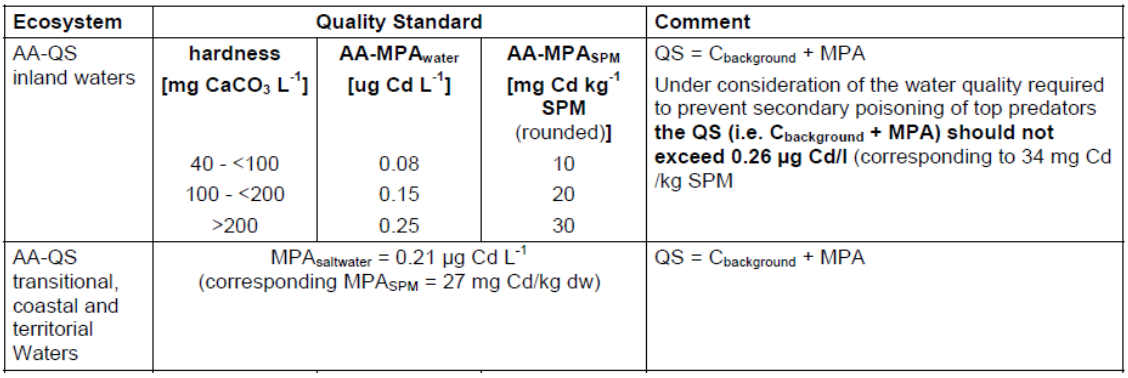
Several field studies and one laboratory experiment were found, in which the BAF (L $kgww^{-1}$) was calculated for organisms, mainly invertebrates, exposed to both contaminated water and food. BAFs range from 4 to 170 000 L kg^{-1}dw. Comparison of BAFs and BCFs of aquatic invertebrates reveals the latter to be significantly lower (20).

Aquatic environmental concentration (17)**:**

Cadmium Environmental Quality Standard (Cd EQS) (19)**:** The TGD EQS (13) recommends that the PNECs derived from the existing substances regulation be adopted as QS, on the basis that the assessment and the data have undergone thorough peer review. A European risk assessment report (RAR) is available for Cd (20). However, marine waters are not dealt with in this risk assessment and no toxicity data for marine organisms are presented. Marine effects data for Cd are provided by the Netherlands and serve for the derivation of QS referring to the pelagic communities in transitional, coastal and territorial waters (20). These data come from Appendix 2 of the report of Crommentuijn *et al*. (1997) cited in E.C.(2005) (19).

- Environmental Quality Standard (EQS) (19) (Table 5)

Table 5: Cadmium Environmental Quality Standard (19)



Ecosystem	**Quality Standard**			**Comment**
AA-QS inland waters	**hardness [mg $CaCO_3$ L^{-1}]**	**AA-MPA$_{water}$ [ug Cd L^{-1}]**	**AA-MPA$_{SPM}$ [mg Cd kg^{-1} SPM** (rounded)**]**	QS = $C_{background}$ + MPA Under consideration of the water quality required to prevent secondary poisoning of top predators **the QS (i.e. $C_{background}$ + MPA) should not exceed 0.26 µg Cd/l** (corresponding to 34 mg Cd /kg SPM
	40 - <100	0.08	10	
	100 - <200	0.15	20	
	>200	0.25	30	
AA-QS transitional, coastal and territorial Waters	MPA$_{saltwater}$ = 0.21 µg Cd L^{-1} (corresponding MPA$_{SPM}$ = 27 mg Cd/kg dw)			QS = $C_{background}$ + MPA

- Specific Quality Standard (QS) derived for Cadmium (19) (Table 6)

Table 6: Specific Quality Standards (QS) derived for Cadmium (19)

Protection objective / Quality Standard (QS)	Value
Pelagic community (freshwater) / AA-QS* $_{freshwater}$	MPA = <0.08 (class 1) µg Cd/L ** MPA = 0.08 (class 2)** MPA = 0.09 (class 3)** MPA = 0.15 (class 4)** MPA = 0.25 (class 5)** (QS = $C_{background}$ + MPA)
Pelagic community (marine water) / AA-QS* $_{saltwater}$	MPA = 0.21 µg Cd/L (QS = $C_{background}$ + MPA)
Benthic community (freshwater) /QS$_{sediment\ freshwater}$	MPA: 2.3 mg Cd/kg dw Corresponding in water: 0.018 µg/L (QS = $C_{background}$ + MPA)
Benthic community (saltwater) / QS$_{sediment\ saltwater}$	Derivation not possible (lack of data on marine benthic organisms)
Secondary poisoning) / QS$_{biota\ secpois}$ (freshwater)	0.16 mg/kg prey Corresponding to 0.26 µg/L in water and 33.8 mg/kg in SPM
Human health via consumption of fishery products / QS$_{biota\ hh\ food}$	0.1-1 mg/kg Edible parts of fish, crustaceans or cephalopods
Human health via consumption of water /QS$_{biota\ hh\ dw}$	5 µg/L

* QS = $C_{background}$ + MPA
** Class 1: < 40 mg $CaCO_3$/L; class 2: 40 to < 50 mg $CaCO_3$/L; class 3: 50 to <100 mg $CaCO_3$/L; class 4: 100 to <200 mg $CaCO_3$/L; class 5: > 200 mg $CaCO_3$/L

According to Directive 2013/39/EU: For Cadmium and its compounds (No 6) the EQS $_{freshwater}$ values vary depending on the hardness of the water as specified in five class categories (Table 6).

The lowest QS calculated for the different protection goals is adopted as the overall quality standard (EQS). In the Cd EQS datasheet, AA-QS for protection of pelagic communities (freshwater and marine waters) are the lowest and adopted as EQS. So, we will focus on the methodology used to define the AA-QS$_{\text{marine water}}$ value to understand how the Cd EQS was determined.

- Annual Average Quality Standard derivation for marine water (AA-QS$_{\text{marine water}}$)

Long-term NOECs of Cd for marine organisms are available for marine fish, crustaceans, several groups of algae (chlorophyceae, bacillariophyceae, dinophyceae, coccolithophora), shellfish, annelids, nematoda, and cyanobacteria. The species requirements for using the SSD approach is not entirely fulfilled as NOECs of insects and higher plants are not included in the database. However, the recommendation of the TGD EQS is focused on freshwater environments and insects and higher plants which are taxonomic groups that are normally not of particular relevance in saltwater or transitional waters (with the exception of higher plants in mangrove or seagrass ecosystems).

Chronic saltwater ecotoxicity data used to derive the Cd AA-QS$_{\text{saltwater}}$ are listed in Table 7 (19)**:**

Table 7: Selected NOEC data, on effects of Cd in seawater organisms, used for the calculation of the 5th percentile cut-off value of the species sensitivity distribution(17).

Taxonomic group	Organism	Endpoint	Test duration	NOEC (µg/L)
Dinophyceae	***Peridinium spec***	reproduction	4-5 weeks	0.56
Diatomeae	*Asterionella glacialis*	reproduction	4-5 weeks	1.1
	Skeletonema costatum	reproduction	4-5 weeks	34
Chlorophyceae	*Chlorella vulgaris*	chlorophyll content	7 days	39
	Dunaliella sp.	Cell number	6 days	1100
Cyanobacteria	*Synechococcus bacillaris*	reproduction	4-5 weeks	3.4
Mollusca	*Crassostrea virginica*	reproduction	9 months	5
	Mytillus eduli	growth	17 days	110
Crustacean	*Mysidopsis bahia*	mortality or immobility	28 days	1.2
	Allorchestes compressa, first instar juveniles	weight	28 days	2.1
Annelida	*Ophryotrocha labronica*	growth	30 days	200
	Capitella capitata	reproduction	25-40 days	320
Fish	*Mugil cephalus*	mortality or immobility	8 weeks	44.7
	Clupea harengus, ELS	reproduction	15 days	100
	Pleuronectes flesus, ELS	reproduction	21 days	1000
Nematoda	*Monhystera microphthalma*	mortality or immobility	13 days	500

Dinophyceae seems to be the most sensitive taxonomic group with *Peridinium spec.* NOEC = 0.56 µg/L.

The dataset used for the calculation of the HC5 covers less than the 8 different taxonomic groups normally recommended. Toxicity data on relevant marine taxonomic groups such as echinodermata, coelenterata and porifera are lacking. However, the lowest reported NOECs for saltwater organisms are in the same range as for freshwater organisms. It is therefore proposed in the EQS datasheet to use the same assessment factor as agreed by the Technical Meeting and used in the risk assessment report for the result of the SSD with freshwater data (AF = 2) (19).

MPA[1]saltwater = HC5 (0.42 µg/L) / AF (2) = 0.21 µg Cd /L

The natural background concentration estimated in the report of Crommentuijn et *al.* cited in E.U. (2005) (19) for marine waters (0.025 µg/L) is used as an example in order to illustrate the calculation of the QS. Hence, the QS for transitional, coastal and territorial waters is (19):

AA-QSsaltwater = 0.025 µg Cd /L + 0.21 µg Cd /L = 0.235 µg Cd /L

For the sake of completeness, the AF approach is also applied to the ecotoxicity dataset. Based on the amount, type and nature of chronic data on marine organisms (more of 3 taxonomic groups represented). An AF 10 is applied on the lowest ecotoxicity data *Peridinium spec.* with a NOEC at 0.56 µg/L. *So* AA-QS $_{\text{saltwater, AF methodology}}$ = 0.056 µg/L (19)**.**

The statistical approach taking into account all the available data, is preferred. Therefore, the threshold retained for Cd is 0.21 µg Cadmium /L.

It is important to note here that for the AA-QS$_{\text{saltwater}}$ derivation, the notion of “bioavailability” is not considered, neither the different environmental parameters (pH, hardness, alkalinity, and organic matter) which can impact Cd toxicity. For freshwater, different AA-EQS are proposed depending on the water hardness but not for the marine water AA-EQS. However, data show that metals binding to organic ligands can reduce metal toxicity to marine organisms, so an availability correction may be needed. In marine waters (coastal and open sea), hardness, pH and alkalinity do not play a role because coastal/open sea waters are characterised by high pH (typically, between 7.8 and 8.3), high salinity (35 UI) and high ionic strength. Unlike the inorganic composition of marine waters, DOC levels may vary considerably between marine waterbodies (13).

Other available thresholds (source: ETOX: Information System Ecotoxicology and Environmental Quality Targets):

- Canadian water quality guideline (1996):
  - CWQG = 0.09 µg/L (Freshwater, hardness: 50 mg $CaCO_3$)
  - CWQG = 0.12 µg/L (Saltwater, hardness $CaCO_3$ unspecified)
- Switzerland (1994):
  - QS = 5 µg/L (Aquatic life, total dissolved)
- Japan (1993)
  - EQS = 10 µg/L (all waters)
- USA (1999):
  - Criterion Continuous Concentration (CCC, freshwater, dissolved) = 0.25 µg/L
  - Criterion Continuous Concentration (CCC, saltwater, dissolved) = 8.8 µg/L
- Australia & New-Zealand marine water quality guideline (21):
  - 5.5 µg/L (statistical distribution method at 95% protection),
  - 0.7 µg/L (statistical distribution method at 99% protection)

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[1] Maximum Permissible Addition

Lead (Pb)

Presentation: The behaviour of Pb (CAS number 7439-92-1) in the environment depends upon its chemical form. Natural weathering processes usually turn lead and its compounds into compounds that are relatively stable and insoluble (e.g. carbonates, sulphates, sulphides and phosphates). Notable exceptions are for $PbNO_3$ and $PbCl_2$ which are very soluble (22).

Harmonised classification. Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation) (16)

Lead powder; [particle diameter < 1 mm] and lead powder; [particle diameter < 1 mm], CAS 7439-92-1.

Classification: Repr. 1A

> H360: May damage fertility or the unborn child <state specific effect if known > <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>
>
> H362: May cause harm to breast-fed children.

Degradation: Pb is considered to be persistent in the environment. Biotic and abiotic degradation rates are not relevant for metals.

Bioaccumulation: Bioconcentration of Pb in the aquatic compartment is defined as the net result of the Pb uptake, distribution and elimination in an organism due to exposure to Pb in water only. Bioaccumulation includes all routes (air, water, soil and food). BAF values are therefore considered to be ecologically more relevant than BCF values. It seems that freshwater organisms can regulate their internal Pb concentration. As a result, an inverse relationship between water concentration of Pb and the corresponding BCF/BAF is observed for both invertebrates and fish. So, BCF/BAFs cannot be interpreted without consideration of the exposure concentrations. Therefore, the RAR stated mentioned that only BAF values derived from studies with dissolved Pb concentrations between 0.18 µg/L (background concentration) and 15 µg/L (based on the 95th % of the PEC_{local} values) were retained for the assessment. Within this typical environmental concentration range, the gathered BAFs for fish ranged between 11 and 143 L/kg_{ww} (10 – 90th %) with a median value of 23 L/kg_{ww} while the BAFs for molluscs ranged between 18 and 3,850 L/kg_{ww} (median value of 675 L/kg_{ww}), for insects between 968 and 4,740 L/kg_{ww} (median value of 1,830 L/kg_{ww}) and for crustaceans between 1,583 and 11,260 L/kg_{ww} (median value of 3,440 L/kg_{ww}). There is no evidence that Pb biomagnifies in higher trophic levels of either freshwater or marine food webs (22).

Aquatic environmental concentration (Table 8)**:**

Table 8: Lead aquatic environmental concentration (23)

		Reference
Surface water (Data from 23 Member states). Total dissolved (µg/L)	2 µg/L (Total, median) 1 µg/L (Dissolved, median)	INERIS, 2009 cited in E.C., 2011 (23)
Marine water (µg/L)	Europe: 0.01-0.02 µg/L The Netherlands: 0.02 µg $Pb_{dissolved}$/L North Sea: 0.02 µg $Pb_{dissolved}$/L	LDAI, 2008 cited in E.C., 2011 (23)

Lead Environmental Quality Standard (Pb EQS) (23)**:**

The TGD EQS (13) recommends that the PNECs derived from the Existing Substances Regulation be adopted as QS, on the basis that the assessment and the data have undergone thorough peer review. For Pb, a voluntary risk assessment report is available which is the starting point of the EQS factsheet. **The aquatic effects assessment of Pb in the EU-VRAR assumes that adverse effects on aquatic organisms are a consequence of exposure to the available Pb-ion, rather than the parent substances.** This means that these effects will be similar for all Pb substances containing a Pb-ion (*e.g.* Pb metal, Pb oxide, Pb tetraoxide, Pb stabiliser compounds, etc). The EQS derived in this document are relevant for all inorganic Pb substances. Therefore, data from soluble Pb salts are used in the derivation of QS (23).

- ENVIRONMENTAL QUALITY STANDARD (EQS) (23) (Table 9)

Table 9: Lead Environmental Quality Standard (23)

Proposed AA-EQSavailable for freshwater (µg/L)	**1.2**
Proposed AA-EQS for marine water (µg/L)	**1.3**

- SPECIFIC QUALITY STANDARD (QS) DERIVED FOR LEAD (23) (Table 10)

Table 10: Specific Quality Standards (QS) derived for Lead (23)

Protection objective / Quality Standard (QS)	Value
Pelagic community (freshwater) / $\text{AA-QS}_{\text{freshwater}}$	**1.2 µg/L**
Pelagic community (marine water) / $\text{AA-QS}_{\text{saltwater}}$	**1.3 µg/L**
Benthic community (freshwater) /$\text{QS}_{\text{sediment freshwater}}$	131-174 or 41 mg/kg dw (with AVS/SEM correction*)
Benthic community (saltwater) / $\text{QS}_{\text{sediment saltwater}}$	123-164 mg/kg dw
Secondary poisoning) / Mammalian predators / $\text{QS}_{\text{biota secpois}}$ (freshwater)	3.6 mg/kg $_{\text{biota ww}}$ Corresponding to 2.3 µg/L
Human health via consumption of fishery products / $\text{QS}_{\text{biota hh food}}$	Fish muscle meat: 200 µg/kg $_{\text{biota ww}}$ Crustaceans: 500 µg/kg $_{\text{biota ww}}$ Molluscs: 1000 µg/kg $_{\text{biota ww}}$ Cephalopods (excluding viscera): 1000 µg/kg $_{\text{biota ww}}$ The maximum levels of lead in fishery products intended for human consumption are imposed by Commission Regulation (EC) N.º 1881/2006
Human health via consumption of water /$\text{QS}_{\text{biota hh dw}}$	10 µg/L Directive 98/83/EC

*Simultaneously Extracted Metal/Acid Volatile Sulphide approach

- ANNUAL AVERAGE QUALITY STANDARD DERIVATION FOR MARINE WATER ($\text{AA-QS}_{\text{MARINE WATER}}$)

There is an important influence of water chemistry on the ecotoxicological effects of Pb in the aquatic environment. The most important of these are pH, hardness, and especially DOC. **However, there is strong evidence for the mitigating effects of increasing DOC concentrations on Pb toxicity**. For freshwater, $\text{AA-QS}_{\text{available}}$ is calculated with an equation taking into account DOC variations. This calculation normalises (or DOC normalisation) the measured Pb exposure in the sample into an "available" Pb exposure. The *a priori* assumption in the derivation of metal EQS is that freshwater and marine datasets should not be combined. However, as no bioavailability correction for the marine EQS is proposed and there are only 9 chronic EC10/NOEC values for marine species from five taxa (EQS Guidance specifies a minimum of 10 NOECs across eight taxa for SSD derivation), the EQS Guidance allows the freshwater and chronic datasets to be combined, unless a statistically significant difference can be observed between them. No significant difference ($p>0.05$) between mean EC10/NOEC values in the freshwater and marine datasets was detected using a t-test (equal variance) after log transformation and tests for equal variance (F-test p>0.05). As such, a marine EQS will be derived using combined freshwater and marine data (23)**.**

An overview of the geometric mean values for the most sensitive endpoints in the combined freshwater and marine datasets is given in Table 11.

Table 11: Geometric mean values of combined freshwater and marine toxicity data

Taxonomic group	**Habitat**	**Species Name**	**NOEC/EC$_{10}$ (µg Pb L^{-1} dissolved)**
Algae	FW	*Pseudokirchneriella subcapitata*	15.25
	SW	*Skeletonema costatum*	52.9
		Dunaliella tertiolecta	1231.8
Annelid (Polychaete)	SW	*Neanthes arenaceodentata*	95.9
Crustacean	FW	*Ceriodaphnia dubia*	42.2
		Hyalella azteca	8.2
Echinoderm	SW	*Strongylocentrotus purpuratus*	111.2
		Dendraster excentricus	249.8
Fish (cyprinid)	SW	*Cyprinodon variegatus*	229.6
	FW	*Pimephales promelas*	109.46
Fish (salmonid)	FW	*Salvelinus fontinalis*	39.4
Insect	FW	*Chironomus tentans*	109.0
Macrophytes	FW	*Lemna minor*	572.79
Molluscs	SW	*Crassostrea gigas*	930.8
		Mytilus galloprovincialis	51.1
		Mytilus trossulus	**9.2**
	FW	*Lymnaea stagnalis*	**1.7**
Rotifer	FW	*Brachionus calyciflorus*	89.5
		Philodina rapida	9.89
Number of taxa		**10**	
Number of EC10/NOEC		**19**	

As sufficient data is available in the combined freshwater and marine dataset (criteria for 10 NOEC/EC$_{10}$ values across a minimum of eight taxonomic groups, including specific marine taxa are met), a statistical approach (SSD) was used to derive a 5th percentile Hazardous Concentration (HC$_5$) (E.C., 2011b).

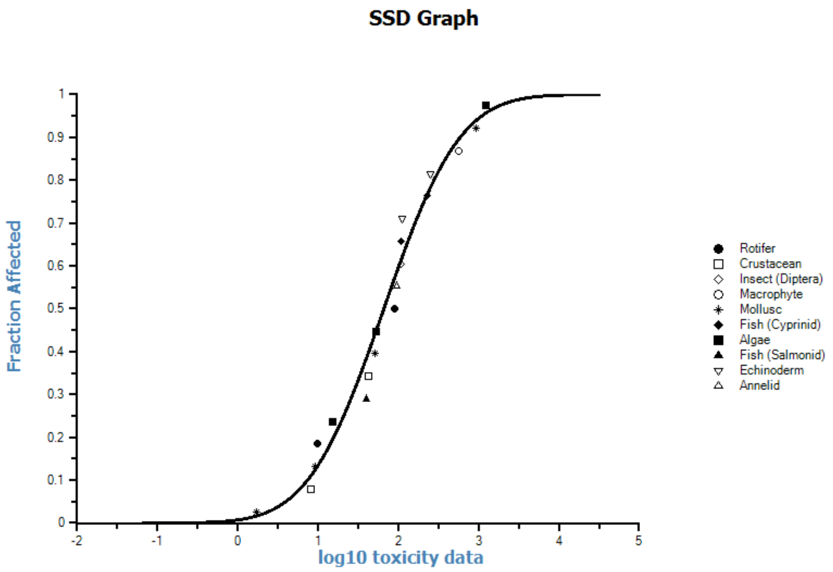


Figure 3: Species Sensitivity Distribution of the species mean NOEC or EC10 values from the combined freshwater and marine chronic Pb toxicity datasets (23)**.**

An assessment factor of 3 is applied on the HC_5 (3.79 µg/L) (Figure 3). Therefore, the AA-QS marine water is proposed to be **1.3 µg/L**.

Other available thresholds (source: ETOX: Information System Ecotoxicology and Environmental Quality Targets):

- Canadian Water Quality Guideline (Aquatic life, freshwater, 1987):
  - Hardness 0 to < 60 mg/L = 1 µg/L;
  - Hardness > 60 to < 180 mg/L = calculate using equation (*CWQG (µg/L)=* $e^{\{1.273[\ln(\underline{hardness})]-4.705\}}$);
  - Hardness >180 mg/L, the CWQG is 7 µg/L,
  - Hardness unknown, the CWQG is 1 µg/L
- Switzerland (1994):
  - Quality Standard (QZ), Aquatic life, 50 µg/L (Total dissolved)
- Germany (1994)
  - Quality Criteria, Aquatic life, fresh water, 3.4 µg/L (total)
- United Kingdom (1993)
  - Environmental quality criteria for United Kingdom, marine Waters: 25 µg/L (dissolved); freshwater: 4-20 µg/L (dissolved)
- Netherland (1999)
  - Maximum Permissible Concentration (MPC), surface water = 11 µg/L (dissolved)
- USA
  - ○ National recommended water quality criteria correction: 8.1 µg/L (dissolved, marine water) and 2.5 µg/L (dissolved, freshwater)
- Australia & New-Zealand marine water quality guideline (24) 4.4 µg/L (statistical distribution method at 95% protection).

1.3. Metals specificities and comments on EQS derivation

The TGD EQS (13) highlights the specificities of metals that make the derivation of EQS very complex. Unlike most organic substances, metals are neither created nor destroyed by biological or chemical processes; instead, they are only transformed from one chemical form into another one. Because metals are naturally occurring, many organisms have developed over time mechanisms to regulate their accumulation, elimination and storage. Moreover, some metals being essential micronutrients (e.g. Cr, Co, Cu, Fe, Mn, Mo, Ni, Se, Zn), they can limit growth, survival and reproduction of the organisms when in concentrations below their needs. In contrast, excess amounts of some of these metals and other non-essential metals and elements (e.g. As, Sb, Cd, Pb, Hg, Tl, Ag, Sn) are potentially toxic to aquatic organisms. All of this complicates the evaluation of toxicity data for inorganic metal substances.

When evaluating toxicity data to derive quality standards for metals, total metal concentrations are not usually directly related to ecotoxicological effects because many abiotic and biotic processes can modify the (bio)availability of metals, even making them unavailable for uptake. This means that the fraction available for uptake and toxicity may be a very small part of the total metal present. Due to several physicochemical processes, metals exist in different chemical forms with different (bio)availability. Thus, the (bio)availability of metals in both laboratory tests and *in situ* may be affected by several physicochemical parameters such as pH, hardness of water and DOC. For this reason, ecotoxicity data, derived for the same species and same endpoint may vary widely when artificial/natural waters or sediments are used as test media.

The WFD explicitly acknowledges the issues of (bio)availability and naturally occurring concentrations for metals. The Daughter Directive to the WFD on EQSs (2008/105/EC) (2) states in Annex I, part B.3: *Member States may, when assessing the monitoring results against the EQS, take into account: (a) natural background concentrations for metals and their compounds, if they prevent compliance with the EQS value; and (b) hardness, pH or other water quality parameters that affect the bioavailability of metals.*

Ideally, the derivation of QSs for metals requires an explicit consideration of (bio)availability using speciation models or, failing that, the use of dissolved concentrations instead of total concentrations. Natural background concentrations may also need to be considered.

The main information on EQS derivation are summarized in Table 12 for Ni, Pb and Cd: derivation method used, the most stringent standard (QS), EQS proposals made by the experts and standards laid down in the regulation (Directive 2013/39/EU (3)) for fresh and marine waters.

These three EQSs refer to dissolved concentrations (*i.e.* the dissolved phase of a water sample obtained by filtration through a 0.45 µm filter), or any equivalent pre-treatment, or, where specifically indicated, to the bioavailable concentration. Thus, for Ni and Pb, $\text{EQS}_{\text{bioavailable}}$ are defined in freshwater.

These three EQSs are derived on the basis of the most stringent QS, which is defined for the protection of the pelagic community and determined using the SSD method.

Several limits can be pointed out: only few ecotoxicological data are available on marine species for Cd, Pb and Ni and these data do not represent the 8 recommended taxonomic groups for using the SSD method (only 5 or 6). As no differences have been highlighted between fresh and marine ecotoxicity data, all data has been pooled for Pb to determine EQS. The determination of the QS for Cd is only based on the data in the BKH report (1995)(25).

It is important here to indicate that the EQS is derived either for freshwaters or saltwaters and that the cut-off value for implementing one or the other EQS is based on salinity (5 per mil based on mean annual salinity (1)). However, the main problem with these EQSs is that they are not based on the (bio)available fraction of metals. As mentioned previously, metals binding to organic ligands can reduce metal toxicity to marine organisms, so an availability correction may be needed. In marine waters (coastal and open sea), hardness, pH and alkalinity do not play a role because coastal/open sea waters are characterised by high pH (typically, between 7.8 and 8.3), high salinity (35 UI) and then high ionic strength. Very low variability of these parameters is expected in the marine environment. Unlike the inorganic composition of marine waters, DOC levels may vary considerably between marine waterbodies (13).

Table 12: Description of the main information of EQS derivation for nickel, lead and cadmium

EQS Dossier	**Nickel** **and its compounds**	**Lead** **and its compounds**	**Cadmium** **and its compounds**
CAS number	7440-02-0	7439-92-1	7440-43-9
Date of the dossier	2011 (data based on EU-RAR 2008)	2011	2005
Method used for EQS derivation	SSD *(15 different organisms representing 6 taxonomic groups- less than the 8 recommended)* + Assessment Factor: 2 But other methods have also been discussed	SSD Based on a combined freshwater and marine water dataset *(only 9 chronic EC10/NOEC values for marine species from five taxa)* + assessment Factor: 3	SSD Based on Finland's data *(less than the 8 recommended different taxonomic group)* + assessment Factor: 2
Stringent QS used for EQS derivation	QS for the protection of pelagic community (fresh and marine water)	QS for the protection of pelagic community (fresh and marine water)	QS for the protection of pelagic community (fresh and marine water)
EQS proposition *from expert datasheet*	2 µg/L freshwater 2 or 8.6 µg/l marine water	1.3 µg/L marine water	0.21 µg/L marine water
Directive 2013/39/EU AA-EQS - Inland Surface waters (freshwater) - Unit: µg/L	EQS$_{\text{bioavailable}}$ 4 µg/L	EQS$_{\text{bioavailable}}$ 1.2 µg/L	≤ 0.08 (Class 1) / 0.08 (Class 2) 0.09 (Class 3) / 0.15 (Class 4) 0.25 (Class 5)
AA-EQS - Other Surface waters (marine water) - Unit: µg/L	8.6 µg/L	1.3 µg/L	0.2 µg/L

1.4. Bioavailability and EQS

Principles of metal toxicity – availability and bioavailability (TGD EQS** (13)**)

As describe in the TGD in progress on the determination of EQS $_{\text{bioavailable}}$ for metals (3): “bioavailability may have different interpretations depending on the particular area of science, but in relation to this guidance and the use of EQS$_{\text{bioavailable}}$ under the WFD, bioavailability is considered to be a combination of the physico-chemical factors governing metal behaviour (the abiotic part) and the biological receptor – i.e. its specific pathophysiological characteristics (such as route of entry, and duration and frequency of exposure). A measure of bioavailability reflects what the organism in the water column *“experiences”* in regard to metal exposure and so is of greatest regulatory relevance. This is important, as it has long been established that measures of total dissolved metal in waters have limited relevance to potential environmental risk (*e.g.* (26,27)”.

The estimation of the bioavailable concentration of a contaminant is difficult, since it depends on the contaminant molecular structure, the environment and the exposed organisms (Figure 4). It can be estimated by a chemical measurement in the environment or through a biological response if the tested concentration induces measurable uptake or biological effects. The physico-chemical measurement of bioavailability consists of measuring the different forms of the contaminant in the environment (for example, the distribution among dissolved and particulate forms) along with a hypothesis concerning the bioavailability of all chemical forms.

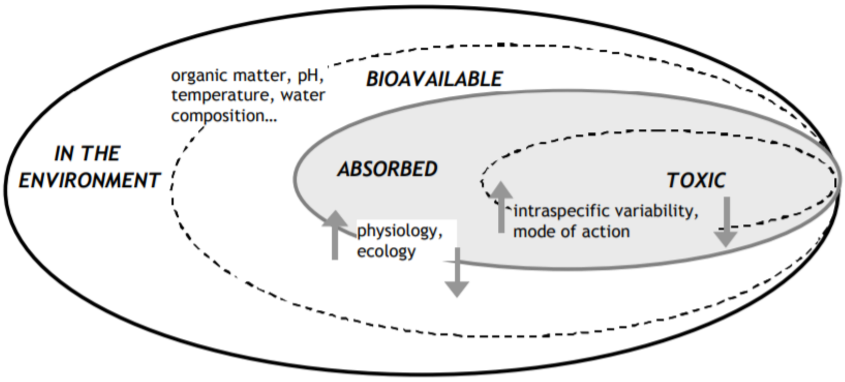


Figure 4: Schematic representation of the species of a contaminant regarding its potential **toxicity** (28,29).

The TGD EQS defined the principles of metal toxicity - availability and bioavailability (13): it pointed out the major advances in our understanding of the physiological processes that control the uptake of inorganic metals and toxicity in aquatic systems. That is, for most metals (e.g., Cd, Cu, Zn, Ni, Pb, Ag), the primary target tissues are ‘respiratory organs (gills or gill-like structures)’ at the interface between the organism and the waterbody. Bioavailable metal species (especially free metal ions) have a high affinity for binding sites at gills and gill-like surfaces (30).

Metal toxicity is strongly affected by water chemistry, through its effects on speciation and (bio)availability. The understanding of the interactions between metal species, water characteristics, and the ionoregulatory/respiratory system of aquatic organisms, has led to the development of several models linking metal bioavailability to toxicity in freshwaters (‘Biotic Ligand Model’, BLM). The potential for additional toxicity through dietary intake has also been assessed for a range of metals (Cu, Zn, Ni). The data from laboratory settings (waterborne versus diet-borne toxicity, assessment of potential for secondary poisoning), mesocosms contaminated with metals (ECI, 2008) and field exposure assessments (31–33) using metal EQSs derived from water-only exposures and EQS calculated using the application of metal bioavailability models, suggested that, **water-only exposures are also protective of exposure via the diet** at least for the metals that were investigated.

Without consideration of (bio)availability, intraspecies variability of several orders of magnitude can be seen in estimates of ecotoxicity with metals. If it is not dealt with properly, this obviously would undermine confidence in any resulting QS.

Therefore, where adequate understanding exists, it is strongly recommended to incorporate bioavailability in the derivation of QSs for metals.

2. How to foster the use of DGT in a regulatory context?

2.1. What are the differences between DGT and “dissolved concentration” measurements?

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 $\text{EQS}_{\text{marine water}}$ (AA-EQS).

The DGT technique is used to preconcentrate metals *in situ.* Specifically, the "classic" DGTs (Chelex® 100 resin) was used in MONITOOL for the measurement of the three priority metals of interest, Cd, Ni and Pb, and other metals such as Co, Cu, Fe, Mn and Zn. The DGT allows a time-integrated measurement of the concentration (as a function of immersion time and temperature) of the "labile" fraction of contaminants.

Thus, there are two major differences to consider between DGT and spot water sample results as regard the requirements set by the current directive:

- firstly, results do not represent the same sampling timescale: a time-integrated measurement *via* DGTs, representing few days, *versus* an average concentration from spot water sample;

- secondly, there is a difference in the fraction analysed: "labile" fraction in DGTs *versus* dissolved fraction in spot water samples. Different chemical forms are measured depending on the fraction considered.

What do passive samplers measure (34)**?**

Dissolved metals in solution can be found as free ions (e.g., Cu^{2+}) or as inorganic (e.g., $CuOH^+$, $CuOH_2$, etc), or organic (e.g., copper complexed with humic substances, proteins, sugars, etc.) forms (Figure 5). The diffusion of metal complexes through the DGT gel will be conditioned by the size of the metal-ligand complex (i.e., the gel's porosity limits the diffusion of large organic complexes). During migration into the diffusive gel, some complexes dissociate (depending on the affinity of the metal with the resin relative to the ligand with which it is associated) and the cation binds to the resin. These dissociating complexes are called "labile" and are measured by DGT. Generally, the major part of the accumulated metals is represented by the free ions and the inorganic forms, with a limited contribution of organic forms (i.e., only metals weakly bound to organic ligands will be accumulated. **This labile concentration is therefore generally lower than the concentration measured in water after filtration through 0.45 µm, which includes all "dissolved" species** (organic and mineral complexes, colloidal forms and particles smaller than 0.45 µm). The fraction of "labile" metal more or less largely depends on the properties of the metal cation and the nature and concentration of the ligands present in the medium.

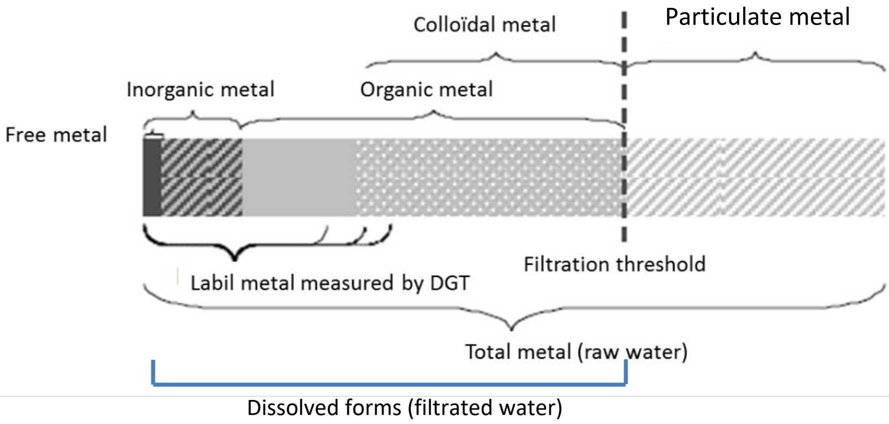


Figure 5: Schematic representation of the chemical forms measured using the DGT technique (29,34)

2.2. Expert stances and recommendations

A position paper on the use of passive sampling techniques for monitoring contaminants in the aquatic environment was written by international experts in 2015 (35) following the Norman network workshop on passive sampling (July 2013). This paper highlights the united stance of the passive sampling community experts and their will to implement concrete actions to foster the use of passive sampling techniques to support contaminant risk assessment and management, as well as for routine contaminant monitoring in aquatic systems. Among various recommendations, it underlines the need for pilot studies to gain experience and demonstrate the usefulness and relevance of passive sampling strategies compared to grab sampling, to highlight the differences between conventional monitoring and monitoring using passive sampling. It also recommends the organisation of interlaboratory exercises for passive sampling in water and, finally, the establishment of passive sampler-based assessment criteria in relation to existing EQS.

The TGD on surface water chemical monitoring, published in 2009 (10), has pointed out the need to gain experience and suggests that passive samplers could be used alongside spot sampling in order to corroborate or contradict spot sampling data. This would be an important weight of evidence for water bodies where contaminant concentrations are expected to show large temporal variation or affected by fluctuating point sources (*i.e.* transitional waters). Passive sampling is less influenced by short-term fluctuations in concentrations than spot sampling. As previously mentioned, the main issue for the recognition of DGT relates to the fraction analysed, which currently differs depending on the use of traditional "filtered water" analysis or analysis using passive samplers. Experts agree that passive samplers allow the measurement of the labile fraction of contaminants, i.e. the fraction that is primarily available to the first link in the food chain. Passive samplers thus allow us to measure a relevant fraction, which appears to be of interest with regards to the purpose of the EQS (35).

As an integrative matrix, passive sampler appears in the TDG on Biota Monitoring (12) as one that can be used as a first level tier in water as well in sediment, as a riks indicator prior the biota monitoring.

DGT is presented as an alternative, simple and inexpensive technique for the monitoring of contaminants, which measures the fraction of metals most likely to cause toxicity to organisms (36–39). It has numerous advantages and studies are increasingly showing DGT-labile metal concentrations to be the fraction that best predicts toxicity in benthic invertebrates, bivalves, amphipod in sediment (37, 38, 40–42), in plants (43), in crustacean, fish and molluscs in freshwater (Cu, Zn) (44,45), in microalgae and molluscs in marine water (Cu) (36,46)

> According to article 3 (3.3) *"Member States may opt, in relation to one or more categories of surface water, to apply an EQS for a matrix other than that specified in article 3.2, or, where relevant, for a biota taxon other than those specified in Part A of Annex I. Member States that make use of the option referred to in the first subparagraph shall apply the relevant EQS laid down in Part A of Annex I or, if none is included for the matrix or biota taxon,* ***establish an EQS that offers at least the same level of protection as the EQS*** *laid down in Part A of Annex I. Member States may use the option referred to in the first subparagraph only where the method of analysis used for the chosen matrix or biota taxon fulfils the minimum performance criteria laid down in Article 4 of Directive 2009/90/EC. "*

The use of passive samplers is mentioned in the TGD on Biota Monitoring (12), but relates mainly to passive samplers for organic contaminants. Little reference is made to passive samplers for metal contaminants (in particular DGTs), despite the fact that these samplers have been developed and used for many years, in particular for studying metal speciation. Moreover, for substances with a EQS_{biota}, passive sampling is presented as an alternative to biota monitoring (12,35); in a tiered monitoring approach. Passive samplers are used as an intermediary between water and biota, enabling the targeting of risk sites where biota sampling appears necessary (in particular fish sampling). However, in the context of marine environmental monitoring, where spot water sampling does not constitute an adapted monitoring matrix, **the use of passive samplers is also pertinent for substances with EQS $_{\text{marine water}}$.**

2.3. Methodology for using DGT results towards EQS

There are three options to use DGT results in relation to EQS:

❶ Compare DGT results to an EQS $_{\text{bioavailable}}$

This option would be the best, as the labile fraction concentrate by DGTs appears to be the one that best predicts toxicity in biota, and thus appears very close to the (bio)available fraction (to the first link of the food chain). However, as no EQS $_{\text{bioavailable}}$ is defined for Cd, Pb or Ni in marine waters, this option cannot be applied for the moment.

❷ Compare DGT results to an EQS $_{\text{DGT}}$

This option implies the adaptation of an EQS $_{\text{DGT}}$ from the EQS $_{\text{marine water}}$.

Directive 2013/39/EU (3) states that an alternative biota taxon, or matrix, may be monitored instead of the specified matrix, **as long as the EQS applied provides at least an equivalent protection level**.

This implies to establish for each metal a valid relationship between the dissolved concentration measured in spot water samples and the DGT-labile concentration measured by DGTs (Figure 6). A relationship can be defined according to the following generic equation (equation 1):

$$[M]_{\text{DGT}} = \text{slope x } [M]_{\text{Dissolved fraction}} + \text{intercept} \qquad \text{(eq.1)}$$

From equation 1, the EQS $_{\text{DGT}}$ corresponding to the EQS $_{\text{marine water}}$ value is determined, based on metal concentrations measured by both techniques and using a predictive model.

DGT results can then be compared to this EQS $_{\text{DGT}}$.

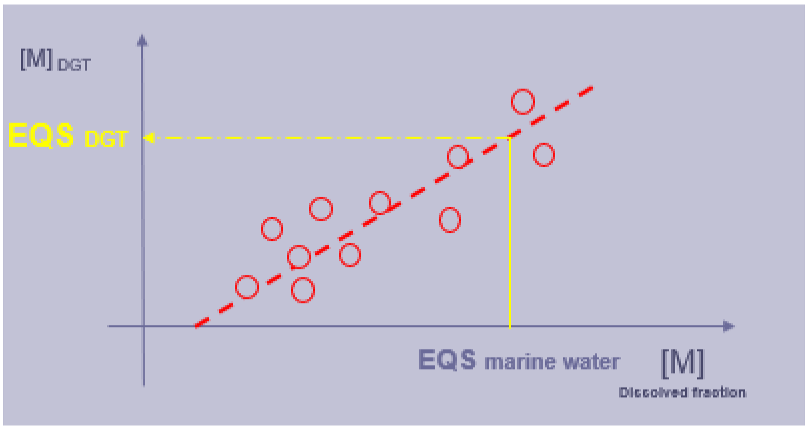


Figure 6: Illustration of the relationship [M] in DGT and in the dissolved fraction, and determination of EQS $_{\mathrm{DGT}}$
$[M]_{DGT}$= slope x [M] $_{Dissolved\ fraction}$ + intercept

❸ Compare DGT results to the EQS $_{\text{marine water}}$

This option implies to establish a valid relationship between the DGT-labile concentration measured by DGTs and the dissolved concentration measured in spot water samples, that allows the back-calculation of the dissolved concentrations from the measured DGT-labile concentrations. The relation is the inverse of the previous one (2nd possibility) and the relation can be described by equation 2:

$$[M]_{\text{Dissolved fraction}} = \text{slope} \times [M]_{\text{DGT}} + \text{intercept} \qquad \text{(eq.2)}$$

From equation 2, for each DGT result, a corresponding value is given in the dissolved fraction (Figure 7). This value can then be compared to the EQS $_{\text{marine water}}$.

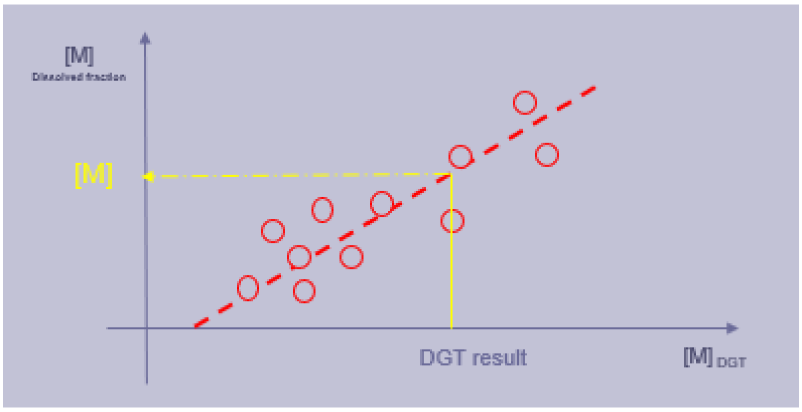


Figure 7: Illustration of the relationship [M] in the dissolved fraction and in DGT,
[M] $_{Dissolved\ fraction}$ = slope x $[M]_{DGT}$ + intercept

Whether it is the 2nd or 3rd option, it is necessary to have results, acquired in parallel, from spot water samples and DGTs. The data must be reliable, homogeneous, and with low analytical uncertainty at the required low concentration levels. The sites sampled should cover a concentration range as wide as possible (from slightly contaminated to highly contaminated sites) and, if possible, present concentrations close or higher than the EQS value. For this purpose, sites suspected to be highly contaminated with Pb, Cd or Ni were targeted as a priority.

This is why the MONITOOL partners have included port areas in their sampling sites. The data must be sufficiently numerous to allow obtaining a robust relationship.

The objective is to allow the establishment of relationships between the concentrations measured in the DGTs and the concentrations measured in the dissolved fraction (spot-sampling) by ICP-MS. For each sampling point and each season (wet season and dry season), a DGT result (average of the triplicates) and a spot-sampling result (average of the discrete samples results obtained during the DGT immersion time) were obtained. In total 36 sampling points were sampled, allowing 84 couples of data (DGT – spot sampling) for the two sampling periods.

The MONITOOL protocol is described in WP5 (not described here)(47).

The following data processing is based on the MONITOOL dataset provided by WP4 (v24). This dataset provides valid data results, after a validation process carried out by the expert laboratories in charge of the analysis. The following study of determination of EQS $_{\text{DGT}}$ in relation to EQS $_{\text{marine water}}$ is complementary to the work done in WP4, dealing with the study of the relationships between the metal concentrations measured by the different methods (i.e., DGT-labile metal concentrations and concentrations measured by ICP-MS and voltammetry in spot water samples) and the influence of environmental parameters (temperature, salinity, pH, SPM, COD...) on these relations.

Data processing:

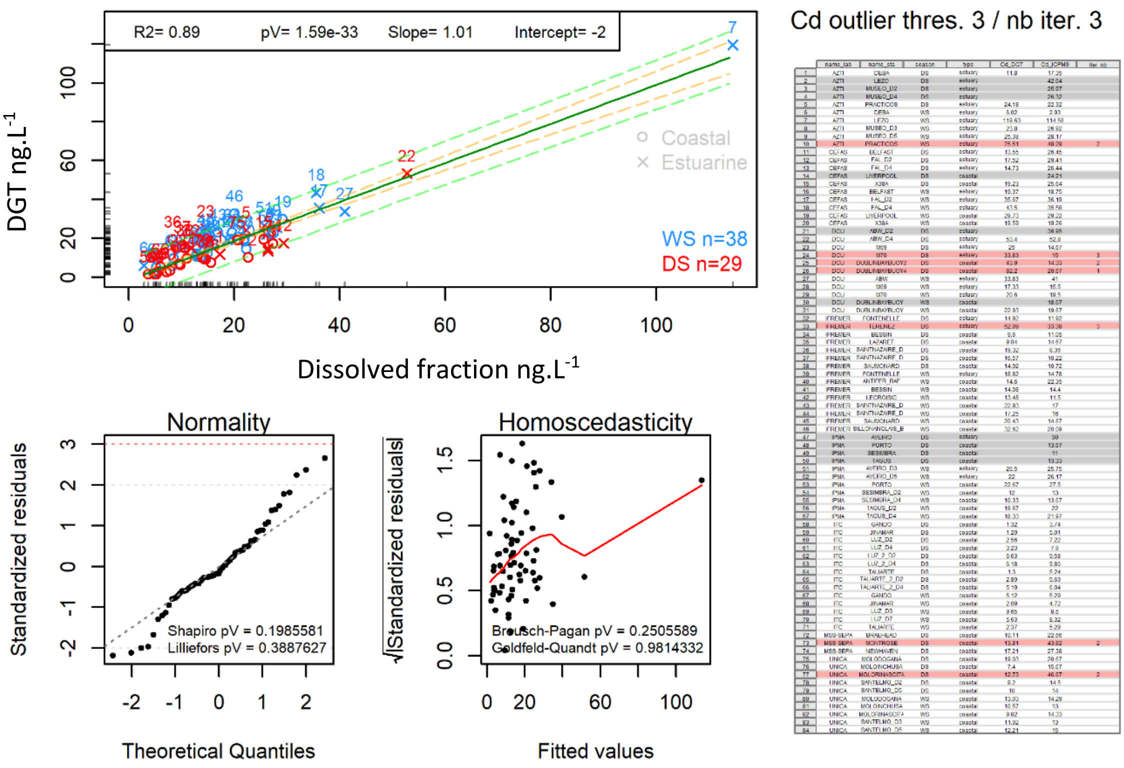
For each metal, a statistical process has been run in order to identify outliers based on the results of linear models. The objective here is to identify as outliers those samples presenting standardized residuals, from the linear model, greater than 3 (rejection of values above 99.73% of the total values assuming that their distribution follows a normal distribution).

In this way, an iterative process is carried out until no more outliers are identified: the process starts with the linear modeling of all the results, thus allowing the identification of possible outliers. A new linear model is made by removing the previously identified outliers. The new outliers are then removed and the process is repeated until all the outliers are identified. The last model without outliers is then kept and diagnosed.

The diagnosis of the model is based on a standard graphical panel with graphical and numerical outputs to judge the normality and homoscedasticity of the residuals. The description of the outputs is done in Figure 8 for illustration purpose. Although there is a consensus on these parameters for the validation of linear models, the assumption of normality of the residuals is often considered secondary; the linear model is then considered to be robust to the absence of normality of the residuals given. Nevertheless, in addition to the QQ-plot (which allows a graphical analysis of the normality of the residuals) the Shapiro-Wilk and Lilliefors (Kolmogorov-Smirnov) tests were performed to guide the validation of the model (48). The most important thing is to have a QQ-plot curve that is as linear as possible with no real residuals that stand out (no curved distributed residuals). In this case, even if the results of the normality tests mentioned above are below the validity threshold (p-value < 0.05), the normality hypothesis is accepted (except when the p-value of the tests is far from the threshold).

The homoscedasticity of the residuals was also considered thanks to the graphical output illustrating the square roots of the residuals (standardized residuals) as a function of the predicted theoretical values (fitted-values) of Y and the Breush-Pagan and Golfeld-Quandt tests. Although we have taken care to use Koenker's version (less sensitive to the lack of normality than original version), the Breush-Pagan test stay sensitive to the lack of normality. The homoscedasticity of the residuals was also tested with the Golfeld-Quandt test.

The validity of the final model for each metal was evaluated, first based on its pValue (valid if <= 0.05), and secondly on the normality and homoscedasticity of the residues (valid if >= 0.05); It should nevertheless be specified that the choice to consider two tests for each criterion offers the possibility to be more objective on the decision (each test having its limits/gaps). Thus, the validation of a model is acquired if one of the 2 tests for each criterion is valid. As mentioned above, normality can be the subject of a less clear-cut decision, also based on the graphical output (QQ-plot). In any case, it is advisable to remain vigilant on this cut-off point of statistical thresholds (i.e. p<0.05), keeping in mind the number of values taken into account, their general appearance by a visual glance (graphical output) and by relativizing the concept of "significant" (49).



Cd outlier thres. 3 / nb iter. 3

	name_lab	name_sta	season	type	Cd_DGT	Cd_ICPMS	iter_nb
1	AZTI	DEBA	DS	estuary	11.8	17.35	
2	AZTI	LEZO	DS	estuary		42.64	
3	AZTI	MUSEO_D2	DS	estuary		25.97	
4	AZTI	MUSEO_D4	DS	estuary		26.32	
5	AZTI	PRACTICOS	DS	estuary	24.18	22.32	
6	AZTI	DEBA	WS	estuary	6.02	2.93	
7	AZTI	LEZO	WS	estuary	119.63	114.58	
8	AZTI	MUSEO_D3	WS	estuary	23.8	26.92	
9	AZTI	MUSEO_D5	WS	estuary	25.38	28.17	
10	AZTI	PRACTICOS	WS	estuary	75.51	48.29	2
11	CEFAS	BELFAST	DS	estuary	13.55	26.45	
12	CEFAS	FAL_D2	DS	estuary	17.52	29.41	
13	CEFAS	FAL_D4	DS	estuary	14.73	26.44	
14	CEFAS	LIVERPOOL	DS	coastal		24.21	
15	CEFAS	X38A	DS	coastal	19.23	25.64	
16	CEFAS	BELFAST	WS	estuary	19.37	18.75	
17	CEFAS	FAL_D2	WS	estuary	35.67	36.19	
18	CEFAS	FAL_D4	WS	estuary	43.5	35.58	
19	CEFAS	LIVERPOOL	WS	coastal	29.73	29.22	
20	CEFAS	X38A	WS	coastal	19.59	19.26	
21	DCU	ABW_D2	DS	estuary		36.95	
22	DCU	ABW_D4	DS	estuary	53.4	52.8	
23	DCU	M69	DS	estuary	25	14.67	
24	DCU	M70	DS	estuary	33.83	15	3
25	DCU	DUBLINBAYBUOY2	DS	coastal	43.9	14.33	2
26	DCU	DUBLINBAYBUOY4	DS	coastal	82.2	20.67	1
27	DCU	ABW	WS	estuary	33.83	41	
28	DCU	M69	WS	estuary	17.33	15.5	
29	DCU	M70	WS	estuary	20.6	19.5	
30	DCU	DUBLINBAYBUOY	WS	coastal		18.67	
31	DCU	DUBLINBAYBUOY	WS	coastal	22.93	19.67	
32	IFREMER	FONTENELLE	DS	estuary	14.92	11.92	
33	IFREMER	TERENEZ	DS	estuary	52.09	33.38	3
34	IFREMER	BESSIN	DS	coastal	9.6	11.06	
35	IFREMER	LAZARET	DS	coastal	9.04	14.67	
36	IFREMER	SAINTNAZAIRE_D	DS	coastal	19.32	8.36	
37	IFREMER	SAINTNAZAIRE_D	DS	coastal	16.57	10.22	
38	IFREMER	SAUMONARD	DS	coastal	14.92	10.72	
39	IFREMER	FONTENELLE	WS	estuary	18.82	14.78	
40	IFREMER	ANTIFER_RAF	WS	coastal	14.6	22.35	
41	IFREMER	BESSIN	WS	coastal	14.08	14.4	
42	IFREMER	LECROISIC	WS	coastal	13.48	11.5	
43	IFREMER	SAINTNAZAIRE_D	WS	coastal	22.93	17	
44	IFREMER	SAINTNAZAIRE_D	WS	coastal	17.25	16	
45	IFREMER	SAUMONARD	WS	coastal	20.43	14.67	
46	IFREMER	SILLONANGLAIS_B	WS	coastal	32.62	20.09	
47	IPMA	AVEIRO	DS	estuary		30	
48	IPMA	PORTO	DS	coastal		13.67	
49	IPMA	SESIMBRA	DS	coastal		11	
50	IPMA	TAGUS	DS	coastal		13.33	
51	IPMA	AVEIRO_D3	WS	estuary	20.5	25.75	
52	IPMA	AVEIRO_D5	WS	estuary	22	26.17	
53	IPMA	PORTO	WS	coastal	22.67	27.5	
54	IPMA	SESIMBRA_D2	WS	coastal	12	13	
55	IPMA	SESIMBRA_D4	WS	coastal	10.33	13.67	
56	IPMA	TAGUS_D2	WS	coastal	19.67	22	
57	IPMA	TAGUS_D4	WS	coastal	18.33	21.97	
58	ITC	GANDO	DS	coastal	1.32	3.74	
59	ITC	JINAMAR	DS	coastal	1.29	5.01	
60	ITC	LUZ_D2	DS	coastal	2.56	7.22	
61	ITC	LUZ_D4	DS	coastal	3.23	7.9	
62	ITC	LUZ_2_D2	DS	coastal	5.63	9.58	
63	ITC	LUZ_2_D4	DS	coastal	6.18	9.86	
64	ITC	TALIARTE	DS	coastal	1.3	5.24	
65	ITC	TALIARTE_2_D2	DS	coastal	2.89	5.69	
66	ITC	TALIARTE_2_D4	DS	coastal	5.19	6.04	
67	ITC	GANDO	WS	coastal	5.12	5.29	
68	ITC	JINAMAR	WS	coastal	2.09	4.72	
69	ITC	LUZ_D3	WS	coastal	9.65	8.6	
70	ITC	LUZ_D7	WS	coastal	5.63	8.32	
71	ITC	TALIARTE	WS	coastal	2.37	5.29	
72	MSS-SEPA	BRAEHEAD	DS	coastal	10.11	22.66	
73	MSS-SEPA	MONTROSE	DS	coastal	13.81	43.82	2
74	MSS-SEPA	NEWHAVEN	DS	coastal	17.21	27.38	
75	UNICA	MOLODOGANA	DS	coastal	19.03	20.67	
76	UNICA	MOLOINCHUSA	DS	coastal	7.4	15.67	
77	UNICA	MOLORINASCITA	DS	coastal	12.73	46.67	2
78	UNICA	SANTELMO_D2	DS	coastal	9.2	14.5	
79	UNICA	SANTELMO_D5	DS	coastal	10	14	
80	UNICA	MOLODOGANA	WS	coastal	13.03	14.29	
81	UNICA	MOLOINCHUSA	WS	coastal	10.57	13	
82	UNICA	MOLORINASCITA	WS	coastal	9.02	14.33	
83	UNICA	SANTELMO_D3	WS	coastal	11.02	13	
84	UNICA	SANTELMO_D5	WS	coastal	12.21	15	

Figure 8: Illustration of standard output:

- Upper left chart show scatterplot DGT=f(ICPMS)* with linear model based on white results illustrated in the table on the right; the dark green line corresponds to the linear model, which is surrounded by its confidence interval CI 95(orange dashed lines), and its predictive intervalle (PI 95) (green dashed lines). **or ICPMS=f(DGT)*;
- Bottom letf chart represent QQ-plot illustrating normality of residuals with Shapiro and Lilliefors tests (normality: pV > 0.05);
- Bottom right chart represents Residuals variance plot illustrating homogeneity of residuals with Breush-Pagan and Golfeld-Quandt tests (homogeneity: pV > 0.05);
- Table on the right specifies the identity of samples with DGT and ICPMS values; background gray illustrate samples not considered because of one of DGT or ICPMS missing; background red color identify samples which are outliers; these two types of samples are not take into accompt in the regression. In some case, the number of iteraction for outliers selection are specified.

When a model is valid:

- A concentration of metal in DGT can be predicted from its concentration measured in dissolved fraction,

$[M]_{DGT} = slope \times [M]_{Dissolved\ fraction} + intercept$

- A concentration of metal in dissolved fraction can be predicted from a concentration measured in DGT (labile fraction)

$[M]_{Dissolved\ fraction} = slope \times [M]_{DGT} + intercept$

Based on these models the EQS $_{DGT}$ can then be determined. Even if the model is valid, its use is reliable within its validity range. Ideally this EQS $_{DGT}$ is determined in the validity range. If this is not the case, it could be determined in a pragmatic way as the projection of the EQS value, and to ensure that level of protection of the EQS $_{DGT}$ is the same or more than the EQS $_{marine\ water}$, it can be determined using the projection minus PI 95 (Prediction Interval 95%). In addition, the LOQ minimum corresponding to EQS/3 according to the Directive QA/QC (50) is precised.

3. Determination of EQS $_{DGT}$

3.1. Description of the MONITOOL dataset

The range of concentrations of Cd, Ni and Pb obtained by the MONITOOL strategy and sampling sites are listed in Table 13. The range of concentrations of Pb measured by spot sampling (ICP-MS) was relatively wide ([22 ; 12,132] ng.L^{-1}), but for Cd ([3 ; 115] ng.L^{-1}) and Ni ([84 ; 1,544] ng.L^{-1}) it was not possible to reach the EQS values, even though we selected *a priori* highly contaminated sites, i.e. harbour areas.

The physico-chemical parameters measured in sampling campaigns are represented in Table 14, as the average values of all sampling sites. This data shows strong disparities between sites, with a wide range of values for most parameters.

Table 13: Concentration of metals measured in dissolved fraction for Cd, Ni and Pb

Mean of concentration of metal in dissolved fraction (ICP-MS)	Mean ng.L^{-1}	Minimum ng.L^{-1}	Maximum ng.L^{-1}	Number of data
Cd	21	3	115	84
Ni	459	84	1,544	84
Pb	514	22	12,132	82

Table 14: Environmental parameters characteristics: temperature, salinity, oxygen, pH, DOC (Dissolved Organic Carbon), SPM (Suspended Particulate Matter)

Parameter – (unit)	**Minimum**	**Maximum**
Temperature - (°C)	5.7	26.3
Salinity	0.2	38.1
Oxygene - (mg.L^{-1})	5.42	11.85
pH	7.3	8.8
DOC - (µg.L^{-1})	583	4490
SPM - (mg.L^{-1})	0.45	262

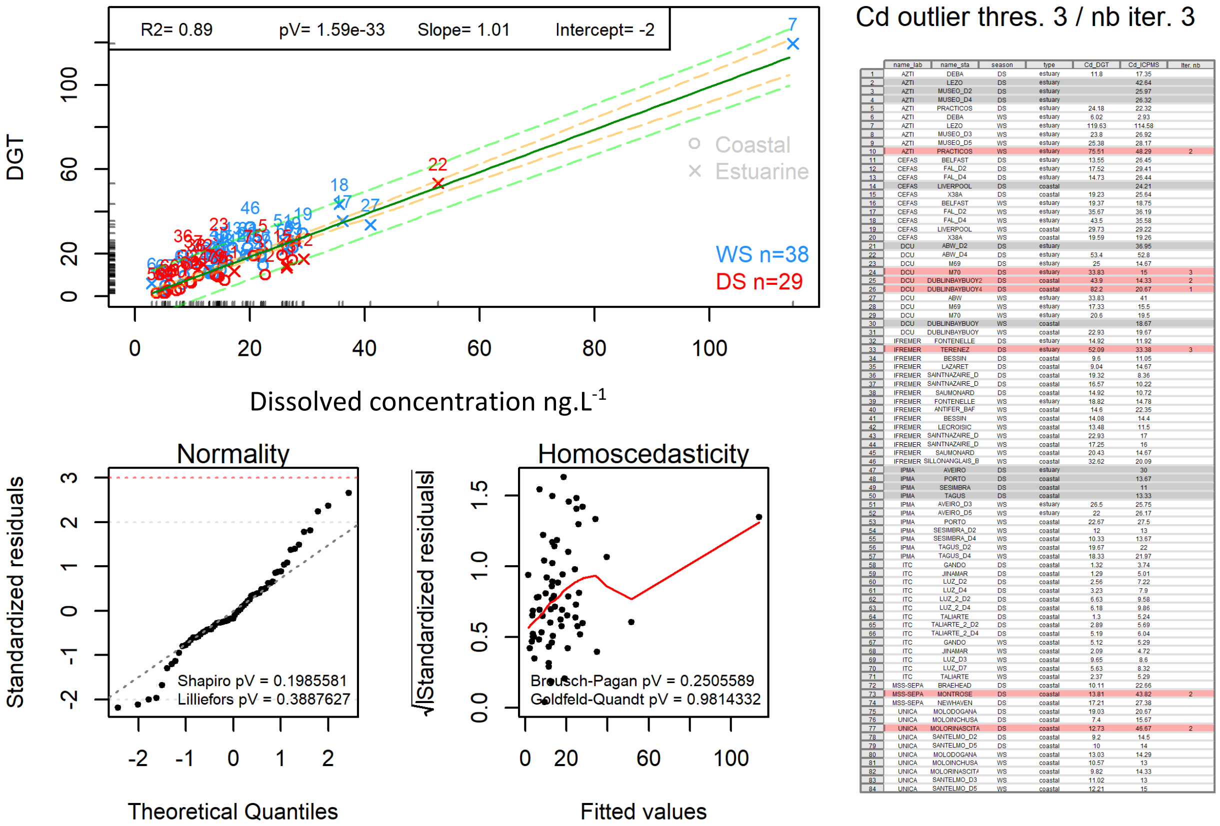
3.2. Cadmium

The graphical representation of the relationship between concentration of cadmium measured in dissolved fraction and the labile concentration measured in DGT is presented in Figure 9. The regression line is sourrounded by its prediction interval ($PI_{95\%}$), the statistical process (Fig 9 a)) and the determination of EQS $_{DGT}$ (Fig 9 b)) are presented. For cadmium, the model validation assumptions were satisfied and the relationship between DGT and dissolved fraction was significant (Fig. 9 a)), and can be described by the equation 3:

$$[Cd]_{DGT} = 1.01\ [M]_{Dissolved\ fraction} - 2 \qquad \text{(Eq. 3)}$$

Concentrations are expressed in $ng.L^{-1}$

The variability in the concentration measured in DGTs is explained at 89% by the dissolved concentrations measured by ICP-MS. From this model, a concentration of metal in DGT can be predicted from its concentration measured in dissolved fraction. Based on the MONITOOL data, the upper limit of the validity area of this model is 114 $ng.L^{-1}$, the range of validity correspond to the area in light green (Figure 9 (b)). Even choosing highly contaminated sites (mainly harbour areas), the highest concentration measured in MONITOOL reached half of the EQS value. Beyond this limit, this model is not verified.



	name_lab	name_sta	season	type	Cd_DGT	Cd_ICPMS	Iter. nb
1	AZTI	DEBA	DS	estuary	11.8	17.35	
2	AZTI	LEZO	DS	estuary		42.64	
3	AZTI	MUSEO_D2	DS	estuary		25.97	
4	AZTI	MUSEO_D4	DS	estuary		26.32	
5	AZTI	PRACTICOS	DS	estuary	24.18	22.32	
6	AZTI	DEBA	WS	estuary	6.02	2.93	
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12	CEFAS	FAL_D2	DS	estuary	17.52	29.41	
13	CEFAS	FAL_D4	DS	estuary	14.73	26.44	
14	CEFAS	LIVERPOOL	DS	coastal		24.21	
15	CEFAS	X38A	DS	coastal	19.23	25.64	
16	CEFAS	BELFAST	WS	estuary	19.37	18.75	
17	CEFAS	FAL_D2	WS	estuary	35.67	36.19	
18	CEFAS	FAL_D4	WS	estuary	43.5	35.58	
19	CEFAS	LIVERPOOL	WS	coastal	29.73	29.22	
20	CEFAS	X38A	WS	coastal	19.59	19.26	
21	DCU	ABW_D2	DS	estuary		36.95	
22	DCU	ABW_D4	DS	estuary	53.4	52.8	
23	DCU	M69	DS	estuary	25	14.67	
24	DCU	M70	DS	estuary	33.83	15	3
25	DCU	DUBLINBAYBUOY2	DS	coastal	43.9	14.33	2
26	DCU	DUBLINBAYBUOY4	DS	coastal	82.2	20.67	1
27	DCU	ABW	WS	estuary	33.83	41	
28	DCU	M69	WS	estuary	17.33	15.5	
29	DCU	M70	WS	estuary	20.6	19.5	
30	DCU	DUBLINBAYBUOY	WS	coastal		18.67	
31	DCU	DUBLINBAYBUOY	WS	coastal	22.93	19.67	
32	IFREMER	FONTENELLE	DS	estuary	14.92	11.92	
33	IFREMER	TERENEZ	DS	estuary	52.09	33.38	3
34	IFREMER	BESSIN	DS	coastal	9.6	11.05	
35	IFREMER	LAZARET	DS	coastal	9.04	14.67	
36	IFREMER	SAINTNAZAIRE_D	DS	coastal	19.32	8.36	
37	IFREMER	SAINTNAZAIRE_D	DS	coastal	16.57	10.22	
38	IFREMER	SAUMONARD	DS	coastal	14.92	10.72	
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46	IFREMER	SILLONANGLAIS_B	WS	coastal	32.62	20.09	
47	IPMA	AVEIRO	DS	estuary		30	
48	IPMA	PORTO	DS	coastal		13.67	
49	IPMA	SESIMBRA	DS	coastal		11	
50	IPMA	TAGUS	DS	coastal		13.33	
51	IPMA	AVEIRO_D3	WS	estuary	26.5	25.75	
52	IPMA	AVEIRO_D5	WS	estuary	22	26.17	
53	IPMA	PORTO	WS	coastal	22.67	27.5	
54	IPMA	SESIMBRA_D2	WS	coastal	12	13	
55	IPMA	SESIMBRA_D4	WS	coastal	10.33	13.67	
56	IPMA	TAGUS_D2	WS	coastal	19.67	22	
57	IPMA	TAGUS_D4	WS	coastal	18.33	21.97	
58	ITC	GANDO	DS	coastal	1.32	3.74	
59	ITC	JINAMAR	DS	coastal	1.29	5.01	
60	ITC	LUZ_D2	DS	coastal	2.56	7.22	
61	ITC	LUZ_D4	DS	coastal	3.23	7.9	
62	ITC	LUZ_2_D2	DS	coastal	6.63	9.58	
63	ITC	LUZ_2_D4	DS	coastal	6.18	9.86	
64	ITC	TALIARTE	DS	coastal	1.3	5.24	
65	ITC	TALIARTE_2_D2	DS	coastal	2.89	5.69	
66	ITC	TALIARTE_2_D4	DS	coastal	5.19	6.04	
67	ITC	GANDO	WS	coastal	5.12	5.29	
68	ITC	JINAMAR	WS	coastal	2.09	4.72	
69	ITC	LUZ_D3	WS	coastal	9.65	8.6	
70	ITC	LUZ_D7	WS	coastal	5.63	8.32	
71	ITC	TALIARTE	WS	coastal	2.37	5.29	
72	MSS-SEPA	BRAEHEAD	DS	coastal	10.11	22.66	
73	MSS-SEPA	MONTROSE	DS	coastal	13.81	43.82	2
74	MSS-SEPA	NEWHAVEN	DS	coastal	17.21	27.38	
75	UNICA	MOLODOGANA	DS	coastal	19.03	20.67	
76	UNICA	MOLOINCHUSA	DS	coastal	7.4	15.67	
77	UNICA	MOLORINASCITA	DS	coastal	12.73	46.67	2
78	UNICA	SANTELMO_D2	DS	coastal	9.2	14.5	
79	UNICA	SANTELMO_D5	DS	coastal	10	14	
80	UNICA	MOLODOGANA	WS	coastal	13.03	14.29	
81	UNICA	MOLOINCHUSA	WS	coastal	10.57	13	
82	UNICA	MOLORINASCITA	WS	coastal	9.82	14.33	
83	UNICA	SANTELMO_D3	WS	coastal	11.02	13	
84	UNICA	SANTELMO_D5	WS	coastal	12.21	15	

Figure 9 a): Cadmium: Relationship between dissolved concentration and DGT labile concentration - Statistical process. The dark green line corresponds to the linear model, which is surrounded by its confidence interval CI 95 (orange dashed lines), and its prediction interval (PI 95) (green dashed lines).

The Figure 9 b) shows the relationship between the measured concentrations in the dissolved fraction and the predicted concentration in the DGT. The EQS $_{\text{marine water}}$ is outside the range of validity of the model. In a pragmatic approach based on this relationship, the EQS $_{\text{DGT}}$ is predicted from the projection of the EQS $_{\text{marine water}}$ value (200 ng.L^{-1}) on the ordinate axis: the predicted EQS $_{\text{DGT}}$ is **199 ng.L^{-1}** , and the predictive interval: [181; 218] ng. L^{-1}. In order to be more protective, the low value of the prediction interval: 181 ng.L^{-1} can be selected as a proposed EQS $_{\text{DGT.}}$ According to the model, for a concentration of 200 ng. L^{-1} in the dissolved fraction, the concentration in the DGT will be between 181 and 218 ng. L^{-1} in 95% of the cases.

The two proposed EQS $_{\text{DGT}}$ expressed in µg.L^{-1} (as done in regulation) are presented in Table 15 .

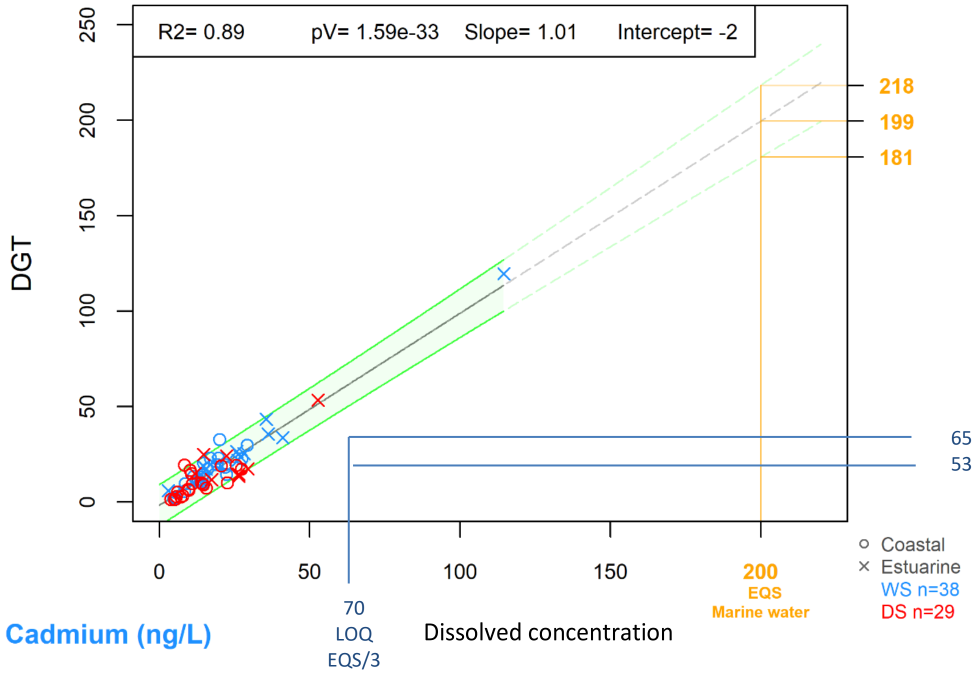


Figure 9 b): Cadmium: Relationship between dissolved concentration and DGT labile fraction - determination of EQS $_{\text{DGT}}$ (b) – the regression line (black line) is surrounded by its prediction interval (PI 95) in green line in the range of validity (area in light green).

Table 15*:* Proposed EQS $_{\text{DGT}}$ for cadmium and LOQ minimum (EQS/3)

EQS $_{\text{Marine water}}$ (µg.L^{-1})	EQS $_{\text{DGT}}$ n°1 (µg.L^{-1}) Linear Model Regression	EQS $_{\text{DGT}}$ n°2 (µg.L^{-1}) Linear Model Regression minus low prediction interval (PI 95%)
0.2	0.20	0.18

LOQ: EQS $_{\text{Marine water/3}}$ (µg.L^{-1})	LOQ EQS $_{\text{DGT}}$ n°1 /3 (µg.L^{-1}) Linear Model Regression	LOQ EQS $_{\text{DGT}}$ n°2/3 (µg.L^{-1}) Linear Model Regression minus low prediction interval (PI 95%)
0.07	0.07	0.05

3.3. Nickel

The graphical representation of the relationship between concentration of nickel measured on dissolved fraction and the labile concentration measured in DGT is presented in Figure 10. The regression line is surrounded by its prediction interval ($PI_{95\%}$), the statistical process (Fig 10 a)) and the determination of EQS $_{DGT}$ (Fig 10 b)) are presented. For nickel, the model validation assumptions were partially satisfied but the relationship between DGT and dissolved concentrations measured by ICP-MS was significant. The model validation criteria were met (p-Values, homoscedasticity, …) except for residue normality, which does not necessarily present a rebuttal aspect to the invalidation of the model (cf Data processing). The relationship between DGT and ICP-MS measurements for Ni is described by the equation 4:

$$[Ni]_{DGT} = 0.51\ [Ni]_{Dissolved\ fraction} + 261 \qquad \text{(Eq. 4)}$$

Concentrations are expressed in ng.L^{-1}

The variability of concentrations measured in DGT is explained at 30% by the dissolved concentrations measured by ICP-MS. From this model, a concentration of metal in DGT can be predicted from its concentration measured in the dissolved fraction. Based on the MONITOOL data, the upper limit of the validity area of this model is 1,544 ng.L^{-1}; the range of validity correspond to the area in light green (Figure 10 (b)). Even choosing highly contaminated sites (mainly harbour areas), the highest concentration measured in MONITOOL is far below the value of the EQS (8,600 ng.L^{-1}). Beyond this limit, this model is not verified.

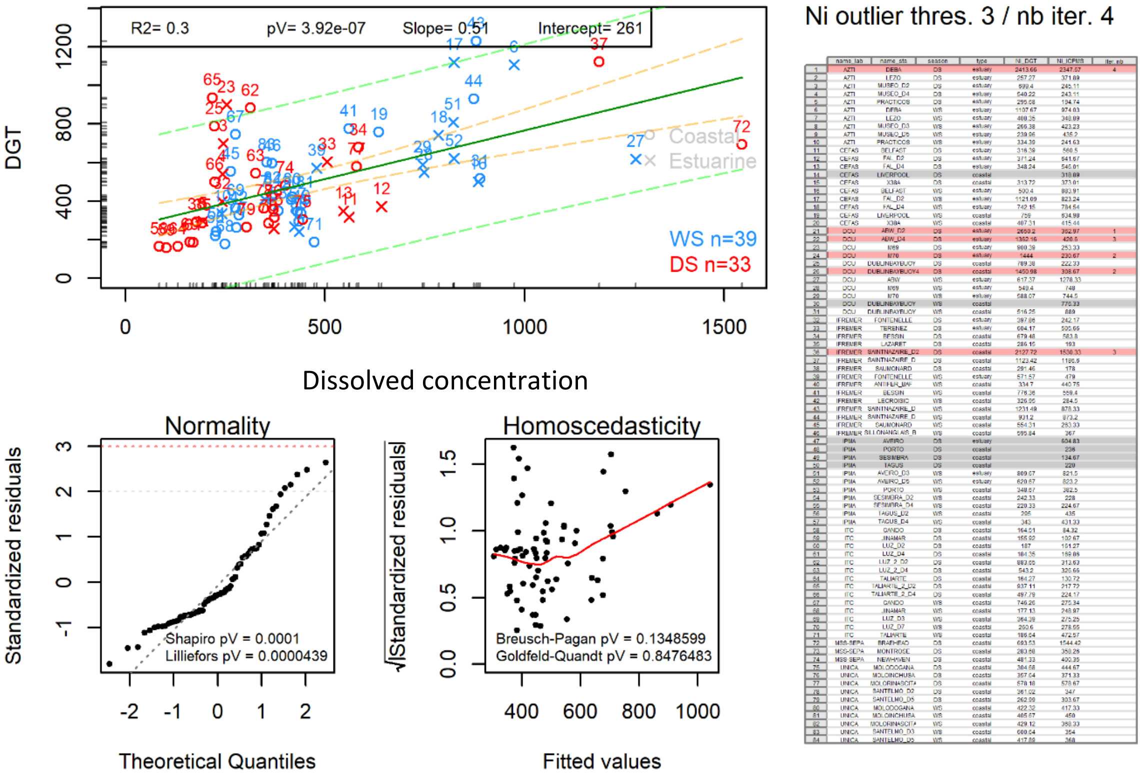


Figure 10 a): Nickel: Relationship between dissolved concentration and DGT labile concentration - Statistical process. The dark green line corresponds to the linear model, which is surrounded by its confidence interval CI 95 (orange dashed lines), and its prediction interval (PI 95) (green dashed lines).

The Figure 10 b) shows the relationship between the measured concentrations in the dissolved fraction and the predicted concentration in the DGT. The EQS $_{\text{marine water}}$ is outside the range of validity of the model. In a pragmatic approach based on this relationship, the EQS $_{\text{DGT}}$ is predicted from the projection of the EQS $_{\text{marine water}}$ value (8,600 ng.L^{-1}) on the ordinate axis: the predicted EQS $_{\text{DGT}}$ is **4,607 ng.L^{-1}** , and the predictive interval: [3,079; 6,135 ng.L^{-1}]. In order to be more protective, the low value of the prediction interval: 3,079 ng.L^{-1} can be selected as a proposed EQS $_{\text{DGT.}}$ According to the model, for a concentration of 8,600 ng. L^{-1} in the dissolved fraction, 95% of the DGT results will be between 3,079 and 6,135 ng.L^{-1} .

The two proposed EQS $_{\text{DGT}}$ expressed in µg.L^{-1} as done in regulation (2013/39/CE) are presented in Table 16).

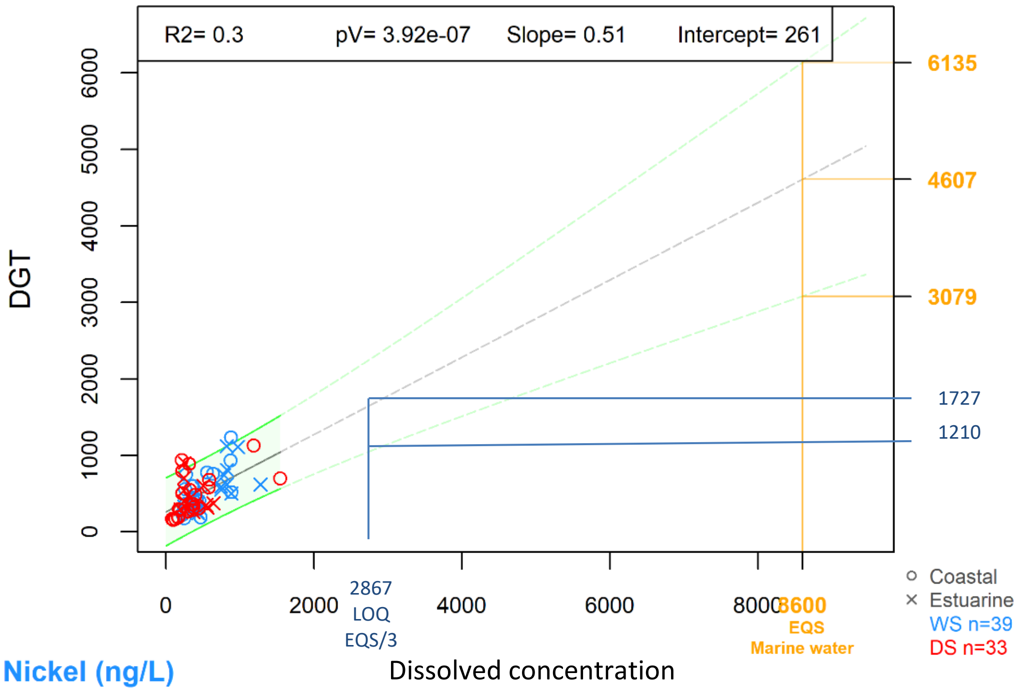


Figure 10 b): Nickel: Relationship between dissolved concentration and DGT labile concentration - determination of EQS $_{\text{DGT}}$ – the regression line (black line) is surrounded by its prediction interval (PI 95) in green line in the range of validity (area in light green).

Table 16*:* Proposed EQS $_{DGT}$ for nickel and LOQ minimum (EQS/3)

EQS $_{Marine\ water}$ (µg.L^{-1})	EQS $_{DGT}$ n°1 (µg.L^{-1}) Linear Model Regression	EQS $_{DGT}$ n°2 (µg.L^{-1}) Linear Model Regression minus low prediction interval (PI 95%)
8.6	4.60	3.08

LOQ: EQS $_{Marine\ water/3}$ (µg.L^{-1})	LOQ: EQS $_{DGT}$ n°1/3 (µg.L^{-1}) Linear Model Regression	LOQ: EQS $_{DGT}$ n°2/3 (µg.L^{-1}) Linear Model Regression minus low prediction interval (PI 95%)
2.87	1.7	1.2

3.4. Lead

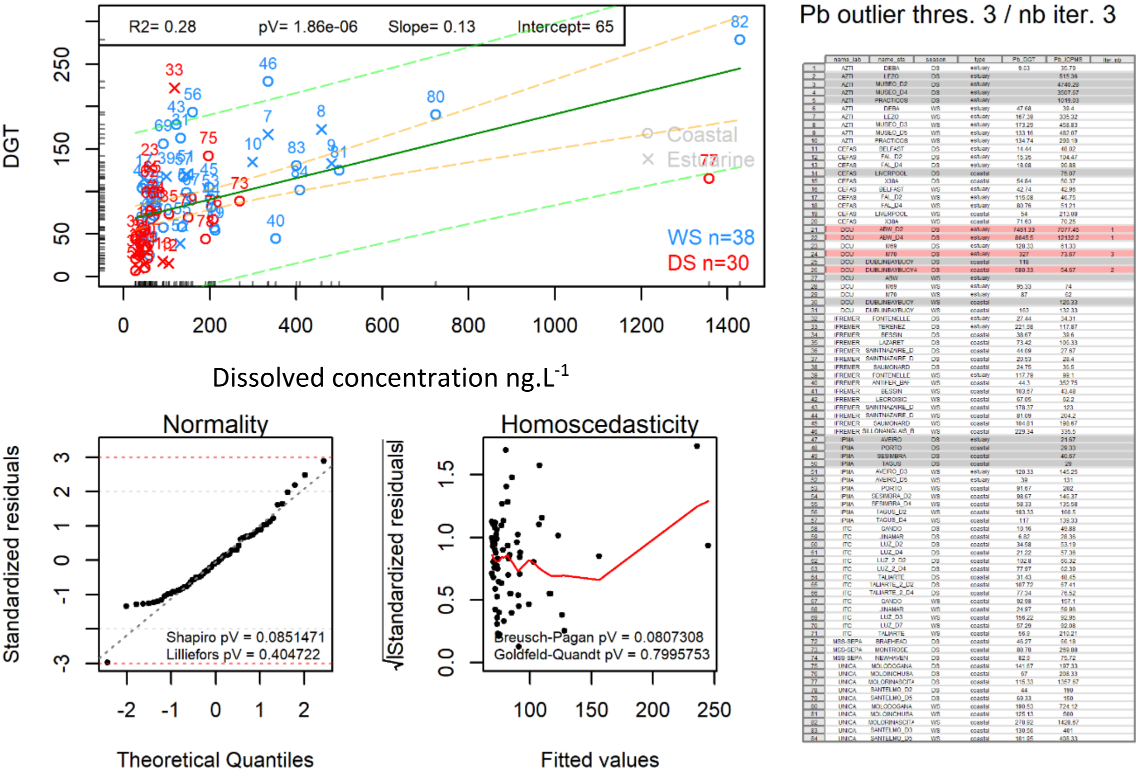
The graphical representation of the relationship between lead concentrations measured in dissolved fraction and the labile concentrations measured in DGT is presented in Figure 11. The regression line is surrounded by its prediction interval ($PI_{95\%}$); the statistical process (Fig 11 a)) and the determination of EQS $_{DGT}$ (Fig 11 b)) are presented. For lead, the model validation assumptions were satisfied and the relationship between DGT and ICP-MS were significant.

The relationship between DGT and ICP-MS measurements for lead is described by equation 5:

$$[Pb]_{DGT} = 0.13\ [Pb]_{\text{Dissolved fraction}} + 65 \qquad \text{(Eq. 5)}$$

Concentrations are expressed in ng.L^{-1}

The variability in concentrations measured in DGT is explained at 28% by the dissolved concentrations measured by ICP-MS. From this model, a concentration of metal in DGT can be predicted from its concentration measured in dissolved fraction. Based on the MONITOOL data, the upper limit of the validity area of this model is 1,428 ng.L^{-1}, which is above the EQS value (1,300 ng.L^{-1}).



Pb outlier thres. 3 / nb iter. 3

	name_lab	name_sta	season	type	Pb_DGT	Pb_ICPMS	iter_nb
1	AZTI	DEBA	DS	estuary	9.53	35.79	
2	AZTI	LEZO	DS	estuary		515.36	
3	AZTI	MUSEO_D2	DS	estuary		4740.28	
4	AZTI	MUSEO_D4	DS	estuary		3507.67	
5	AZTI	PRACTICOS	DS	estuary		1019.03	
6	AZTI	DEBA	WS	estuary	47.68	30.4	
7	AZTI	LEZO	WS	estuary	167.39	335.32	
8	AZTI	MUSEO_D3	WS	estuary	173.29	458.83	
9	AZTI	MUSEO_D5	WS	estuary	133.16	482.07	
10	AZTI	PRACTICOS	WS	estuary	134.74	299.19	
11	CEFAS	BELFAST	DS	estuary	14.44	48.02	
12	CEFAS	FAL_D2	DS	estuary	15.35	104.47	
13	CEFAS	FAL_D4	DS	estuary	18.08	90.88	
14	CEFAS	LIVERPOOL	DS	coastal		75.07	
15	CEFAS	X38A	DS	coastal	54.84	50.37	
16	CEFAS	BELFAST	WS	estuary	42.74	42.96	
17	CEFAS	FAL_D2	WS	estuary	115.08	46.75	
18	CEFAS	FAL_D4	WS	estuary	80.76	51.21	
19	CEFAS	LIVERPOOL	WS	coastal	54	213.08	
20	CEFAS	X38A	WS	coastal	71.63	70.25	
21	DCU	ABW_D2	DS	estuary	7461.33	7077.45	1
22	DCU	ABW_D4	DS	estuary	8045.5	12132.2	1
23	DCU	M69	DS	estuary	128.33	61.33	
24	DCU	M70	DS	estuary	327	73.67	3
25	DCU	DUBLINBAYBUOY	DS	coastal	118		
26	DCU	DUBLINBAYBUOY4	DS	coastal	580.33	54.67	2
27	DCU	ABW	WS	estuary			
28	DCU	M69	WS	estuary	95.33	74	
29	DCU	M70	WS	estuary	87	62	
30	DCU	DUBLINBAYBUOY	WS	coastal		126.33	
31	DCU	DUBLINBAYBUOY	WS	coastal	163	132.33	
32	IFREMER	FONTENELLE	DS	estuary	27.44	34.31	
33	IFREMER	TERENEZ	DS	estuary	221.98	117.87	
34	IFREMER	BESSIN	DS	coastal	38.67	39.6	
35	IFREMER	LAZARET	DS	coastal	73.42	106.33	
36	IFREMER	SAINTNAZAIRE_D	DS	coastal	44.09	27.67	
37	IFREMER	SAINTNAZAIRE_D	DS	coastal	20.53	28.4	
38	IFREMER	SAUMONARD	DS	coastal	24.75	36.5	
39	IFREMER	FONTENELLE	WS	estuary	117.79	99.1	
40	IFREMER	ANTIFER_BAF	WS	coastal	44.3	352.75	
41	IFREMER	BESSIN	WS	coastal	103.67	43.48	
42	IFREMER	LECROISIC	WS	coastal	67.05	52.2	
43	IFREMER	SAINTNAZAIRE_D	WS	coastal	178.37	123	
44	IFREMER	SAINTNAZAIRE_D	WS	coastal	81.09	204.2	
45	IFREMER	SAUMONARD	WS	coastal	104.81	198.67	
46	IFREMER	SILLONANGLAIS_B	WS	coastal	229.34	335.5	
47	IPMA	AVEIRO	DS	estuary		21.67	
48	IPMA	PORTO	DS	coastal		29.33	
49	IPMA	SESIMBRA	DS	coastal		40.67	
50	IPMA	TAGUS	DS	coastal		29	
51	IPMA	AVEIRO_D3	WS	estuary	120.33	145.25	
52	IPMA	AVEIRO_D5	WS	estuary	39	131	
53	IPMA	PORTO	WS	coastal	91.67	202	
54	IPMA	SESIMBRA_D2	WS	coastal	98.67	146.37	
55	IPMA	SESIMBRA_D4	WS	coastal	58.33	135.58	
56	IPMA	TAGUS_D2	WS	coastal	193.33	160.5	
57	IPMA	TAGUS_D4	WS	coastal	117	139.33	
58	ITC	GANDO	DS	coastal	10.16	49.88	
59	ITC	JINAMAR	DS	coastal	6.82	28.36	
60	ITC	LUZ_D2	DS	coastal	34.58	53.19	
61	ITC	LUZ_D4	DS	coastal	21.22	57.36	
62	ITC	LUZ_2_D2	DS	coastal	102.8	60.32	
63	ITC	LUZ_2_D4	DS	coastal	77.97	62.39	
64	ITC	TALIARTE	DS	coastal	31.43	48.45	
65	ITC	TALIARTE_2_D2	DS	coastal	107.72	67.41	
66	ITC	TALIARTE_2_D4	DS	coastal	77.34	76.52	
67	ITC	GANDO	WS	coastal	92.98	157.1	
68	ITC	JINAMAR	WS	coastal	24.97	58.96	
69	ITC	LUZ_D3	WS	coastal	156.22	92.95	
70	ITC	LUZ_D7	WS	coastal	57.29	92.08	
71	ITC	TALIARTE	WS	coastal	56.9	210.21	
72	MSS-SEPA	BRAEHEAD	DS	coastal	46.27	66.18	
73	MSS-SEPA	MONTROSE	DS	coastal	88.78	269.88	
74	MSS-SEPA	NEWHAVEN	DS	coastal	82.9	75.72	
75	UNICA	MOLODOGANA	DS	coastal	141.67	197.33	
76	UNICA	MOLOINCHUSA	DS	coastal	67	208.33	
77	UNICA	MOLORINASCITA	DS	coastal	115.33	1357.67	
78	UNICA	SANTELMO_D2	DS	coastal	44	190	
79	UNICA	SANTELMO_D5	DS	coastal	69.33	150	
80	UNICA	MOLODOGANA	WS	coastal	190.53	724.12	
81	UNICA	MOLOINCHUSA	WS	coastal	125.13	500	
82	UNICA	MOLORINASCITA	WS	coastal	270.92	1428.67	
83	UNICA	SANTELMO_D3	WS	coastal	130.56	401	
84	UNICA	SANTELMO_D5	WS	coastal	101.95	408.33	

Figure 11 a): Lead: Relationship between dissolved concentration and DGT labile concentration - Statistical process. The dark green line corresponds to the linear model, which is surrounded by its confidence interval CI 95 (orange dashed lines), and its prediction interval (PI 95) (green dashed lines).

The Figure 11 b) shows the relationship between the measured concentrations in the dissolved fraction and the predicted concentrations in the DGT.

The EQS $_{\text{marine water}}$ is in the range of validity of the model. Based on this relationship, the EQS $_{\text{DGT}}$ is predicted from the projection of the EQS $_{\text{marine water}}$ value (1,300 ng.L^{-1}) on the ordinate axis: the predicted EQS $_{\text{DGT}}$ is **229 ng.L^{-1}** , and the predictive interval: [116 ; 342 ng. L^{-1}]. According to the model, for a concentration of 1,300 ng. L^{-1} in the dissolved fraction, 95 % of the DGT results would be between 116 and 342 ng. L^{-1}.
As for cadmium and nickel another EQS DGT could be proposed as the low value of the predictive interval: 116 ng. L^{-1}.

The two proposed EQS $_{\text{DGT}}$ expressed in µg.L^{-1} as done in regulation 2013/39/CE are presented in the Table 17.

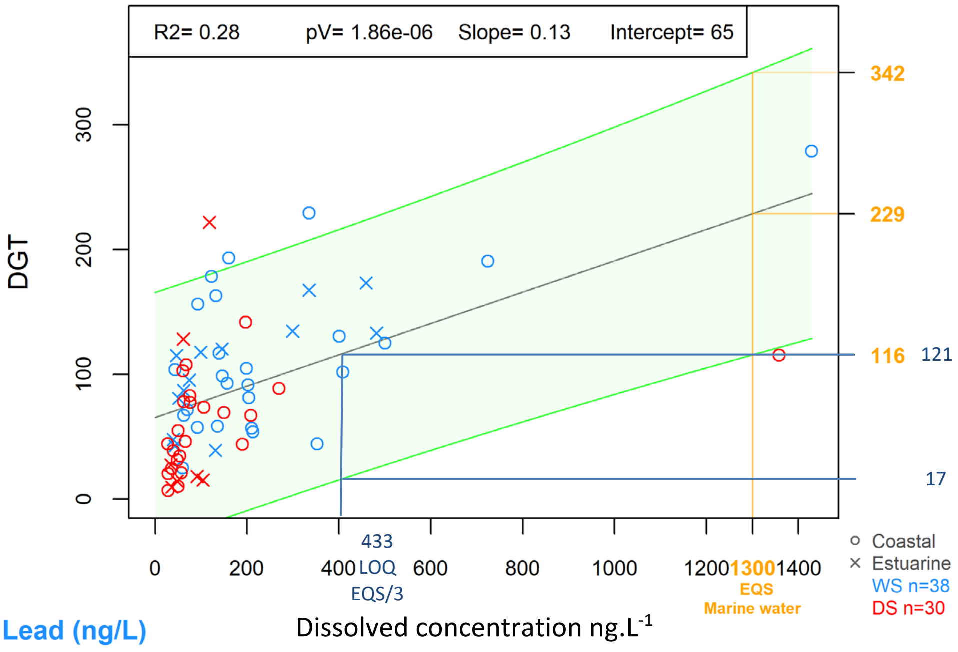


Figure 11 b): Lead: Relationship between dissolved concentration and DGT labile concentration - determination of EQS $_{\text{DGT}}$ – the regression line (black line) is sourrounded by its prediction interval (PI 95) in green line in the range of validity (area in light green).

Table 17*:* Proposed EQS $_{\text{DGT}}$ for lead and LOQ minimum (EQS/3)

EQS $_{\text{Marine water}}$ (µg.L^{-1})	EQS $_{\text{DGT}}$ n°1 (µg.L^{-1}) Linear Model Regression	EQS $_{\text{DGT}}$ n°2 (µg.L^{-1}) Linear Model Regression minus low prediction interval (PI 95%)
1.3	0.23	0.12

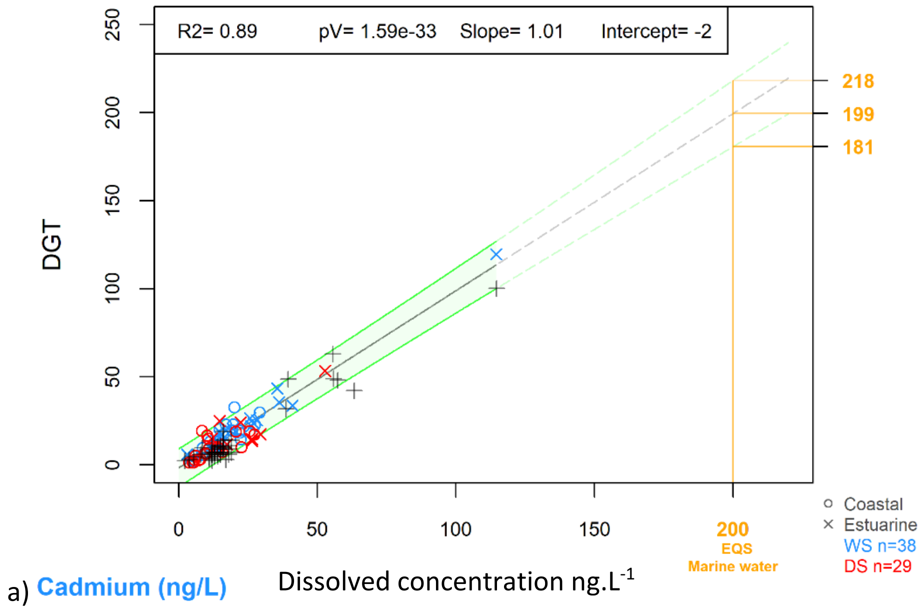
LOQ EQS $_{\text{Marine water/3}}$ ($\mu g.L^{-1}$)	LOQ: EQS $_{\text{DGT}}$ n°1/3 ($\mu g.L^{-1}$) Linear Model Regression	LOQ: EQS $_{\text{DGT}}$ n°2/3 ($\mu g.L^{-1}$) Linear Model Regression minus low prediction interval (PI 95%)
0.4	0.12	0.02

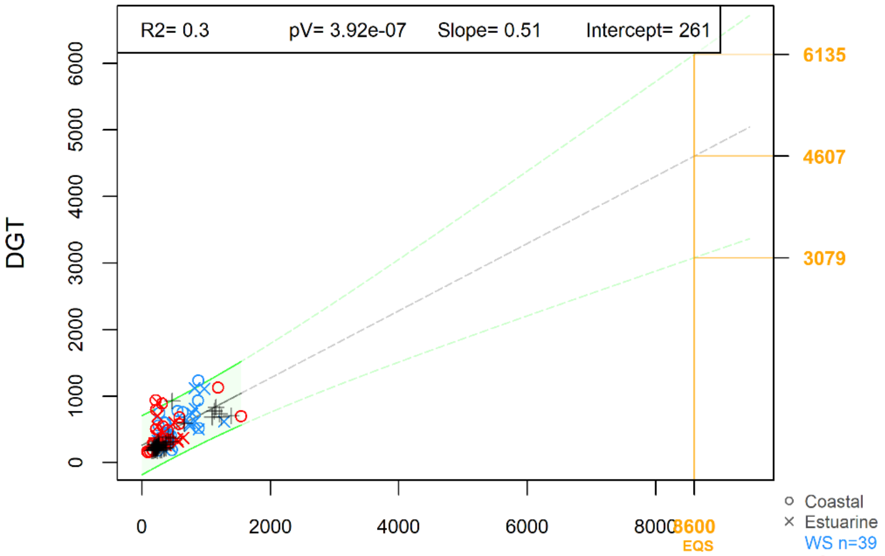
3.5. Verification

To check for the reliability and the relevance of these prediction models, additional data (DGT - ICPMS) acquired through other projects lead by Ifremer (unpublished data: RINBIO 2011, TOUCAN) on DGT vs dissolved concentration were integrated. Graphs with those additional data (black cross) are presented in Figure 12 a) for Cd, b) for Nickel and c) for Pb.

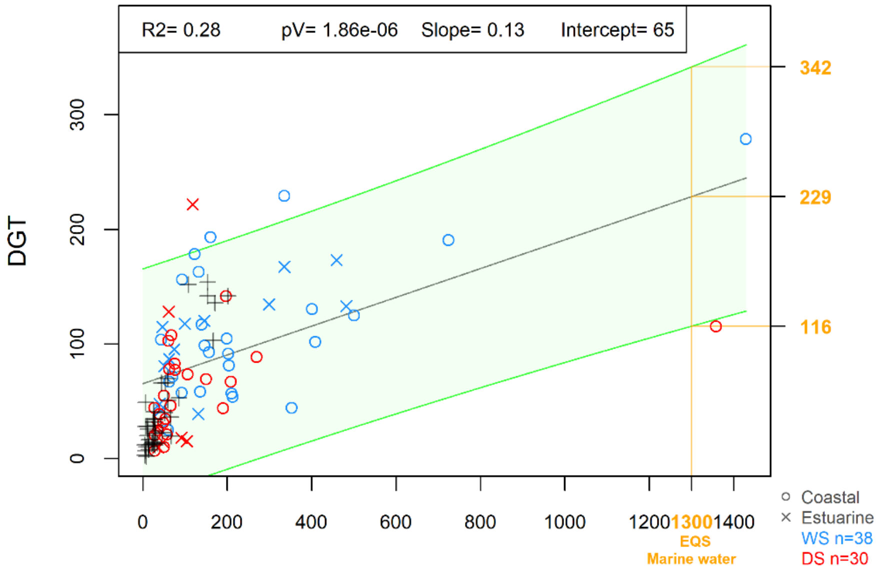
All the data fitted the regression line and its prediction interval at 95% (IP 95), except 1 result for cadmium and 3 results for lead.

However, as there were no additional data close to the EQS values for Cd and Ni, the validity of the relationship at the EQS level could not be verified.





b) **Nickel (ng/L)**



c) **Lead (ng/L)**

Figure 12: Prediction model verification with additional Ifremer data a) Cd ; b) Ni ; c) Pb.

It can be pointed out that while the variability in concentrations measured in DGT is explained at 89 % by dissolved concentrations for cadmium, this proportion falls down to around 30% for nickel and lead. Hence, the variability in DGT concentrations for nickel and lead is not only explained by their concentration in the dissolved fraction. For lead, the predictive interval at the EQS value is quite wide (around 50%), and despite the fact that the predictive model is valid, it doesn't explain all the variability. The WP4 of the MONITOOL project investigated the possible influence of environmental parameters on the relationships between concentration in DGT labile fraction vs in the dissolved fraction.

As no significant influence was shown for any of the environmental parameters measured (temperature, salinity...), the relationship is applicable whatever the characteristics of the waters considered in coastal zone or estuaries (cf Environmental parameters characteristics Tab.14).

For lead, the distribution of the data in Figure 13c suggests a different relationship depending on the concentration level. Hypotheses are that either other parameters may influence the relationship.

As the choice of data modelling tool can impact on the quality of the model, a comparison of linear models (classical linear regression and quantile regression) was carried out (Annex 1). The objective was to report on the adequacy of this classical linear model with the objective of determining EQS $_{\mathrm{DGT}}$ based on the acquired data.

The comparison of the methods on the initial data shows that the results of both methods (slopes of median of quantile regression and linear regression) are very similar. Nevertheless, the quality of the classical linear model with these initial data is not satisfactory and suggests that outliers exist. The use of quantile regression also allows to account for the presence of extreme values and a lack of homogeneity of the datasets in some parts of the range of values. These considerations then confirm that there are outliers (statistical outliers impacting the modelling) in the dataset.

The comparison of the two types of regression with the selected data (outliers removed from the initial dataset) for classical linear regression and the initial data (data provided by the WP5, after validation process by expert laboratories) for quantile regression shows a good similarity for some metals such as cadmium (or copper). Nevertheless, for lead and even nickel (and zinc), significant differences in slope are observed and justify the removal of outliers that can probably be explained by the hypotheses of deviations raised in the previous paragraph (of biological, environmental and/or methodological nature).

The results of the comparison of the two methods on the selected data (without the statistical outliers) show a very good adequacy with the slopes of classical linear regression close or even identical to median slopes of quantile regression: 1.01 vs 1.07 for Cd, 0.51 vs 0.55 for Ni, 0.13 vs 0.16 for Pb; results (EQ$_{\mathrm{S\ DGT}}$) are very close (Cd: 199 vs 212 ng/L; Ni: 4607 vs 4732 ng/L; Pb: 229 vs 210 ng/L). In addition, quantile regression is generally not used to predict values as linear regression model is. Thus, this confirms the choice of the statistical approach chosen.

4. Predicting [M] in dissolved fraction from its concentration in DGT

In order to compare DGT results to EQS $_{\mathrm{marine\ water,}}$ concentrations measured in DGT have to be converted into dissolved concentrations. In this section, the question is to study whether it is possible to predict concentrations of Cd, Ni or Pb in the dissolved fraction from their concentrations in DGT labile concentration.

The data processing described in chapter 4 is applied this time for the inverse relation, Equation 2.

The graphical representation of the relationship between concentrations of cadmium, nickel and lead measured in the dissolved fraction and their concentrations in DGT are presented respectively in Figures 14, 15 and 16. The regression line is surrounded by its prediction interval (PI$_{95\%}$), and the confidence interval (IC).

4.1. Cadmium

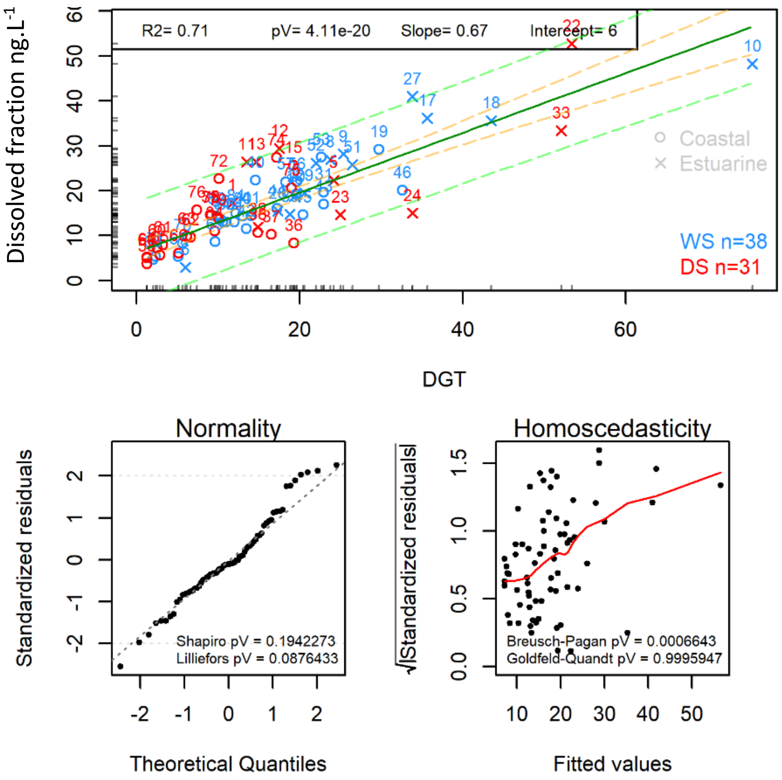
For cadmium, the model validation assumptions were satisfied and the relationship between dissolved concentration and DGT labile fraction concentrations was significant (Figure 13).

The relationship between dissolved concentration and DGT labile fraction for cadmium can thus be described by Equation 6:

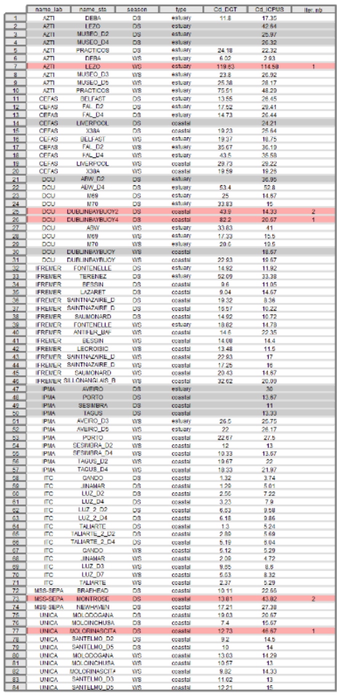
$$[Cd]_{\text{Dissolved Fraction}} = 0.67 \times [Cd]_{\text{DGT}} + 6 \qquad \text{(Eq.6)}$$

Concentrations are expressed in $ng.L^{-1}$

The variability in concentrations measured in DGT is explained at 71% by the dissolved concentrations. From this model, cadmium concentrations in the dissolved fraction can be predicted from its concentration measured in DGT. Based on the MONITOOL data, the upper limit of the validity area of this model is 75.5 $ng.L^{-1}$, which is below the $EQS_{\text{marine water}}$ (200 $ng.L^{-1}$).



Cd outlier thres. 3 / nb iter. 2



	name_lab	name_sta	season	type	Cd_DGT	Cd_ICPMS	iter. nb
1	AZTI	DEBA	DS	estuary	11.8	17.35	
2	AZTI	LEZO	DS	estuary		42.64	
3	AZTI	MUSEO_D2	DS	estuary		25.97	
4	AZTI	MUSEO_D4	DS	estuary		26.32	
5	AZTI	PRACTICOS	DS	estuary	24.18	22.32	
6	AZTI	DEBA	WS	estuary	6.02	2.93	
7	AZTI	LEZO	WS	estuary	119.63	114.58	1
8	AZTI	MUSEO_D3	WS	estuary	23.8	26.92	
9	AZTI	MUSEO_D5	WS	estuary	25.38	28.17	
10	AZTI	PRACTICOS	WS	estuary	75.51	48.29	
11	CEFAS	BELFAST	DS	estuary	13.55	26.45	
12	CEFAS	FAL_D2	DS	estuary	17.52	29.41	
13	CEFAS	FAL_D4	DS	estuary	14.73	26.44	
14	CEFAS	LIVERPOOL	DS	coastal		24.21	
15	CEFAS	X38A	DS	coastal	19.23	25.64	
16	CEFAS	BELFAST	WS	estuary	19.37	18.75	
17	CEFAS	FAL_D2	WS	estuary	35.67	36.19	
18	CEFAS	FAL_D4	WS	estuary	43.5	35.58	
19	CEFAS	LIVERPOOL	WS	coastal	29.73	29.22	
20	CEFAS	X38A	WS	coastal	19.59	19.26	
21	DCU	ABW_D2	DS	estuary		36.95	
22	DCU	ABW_D4	DS	estuary	53.4	52.8	
23	DCU	M69	DS	estuary	25	14.67	
24	DCU	M70	DS	estuary	33.83	15	
25	DCU	DUBLINBAYBUOY2	DS	coastal	43.9	14.33	2
26	DCU	DUBLINBAYBUOY4	DS	coastal	82.2	20.67	1
27	DCU	ABW	WS	estuary	33.83	41	
28	DCU	M69	WS	estuary	17.33	15.5	
29	DCU	M70	WS	estuary	20.6	19.5	
30	DCU	DUBLINBAYBUOY	WS	coastal		18.67	
31	DCU	DUBLINBAYBUOY	WS	coastal	22.93	19.67	
32	IFREMER	FONTENELLE	DS	estuary	14.92	11.92	
33	IFREMER	TERENEZ	DS	estuary	52.09	33.38	
34	IFREMER	BESSIN	DS	coastal	9.6	11.05	
35	IFREMER	LAZARET	DS	coastal	9.04	14.67	
36	IFREMER	SAINTNAZAIRE_D	DS	coastal	19.32	8.36	
37	IFREMER	SAINTNAZAIRE_D	DS	coastal	16.57	10.22	
38	IFREMER	SAUMONARD	DS	coastal	14.92	10.72	
39	IFREMER	FONTENELLE	WS	estuary	18.82	14.78	
40	IFREMER	ANTIFER_BAF	WS	coastal	14.6	22.35	
41	IFREMER	BESSIN	WS	coastal	14.08	14.4	
42	IFREMER	LECROISIC	WS	coastal	13.48	11.5	
43	IFREMER	SAINTNAZAIRE_D	WS	coastal	22.93	17	
44	IFREMER	SAINTNAZAIRE_D	WS	coastal	17.25	16	
45	IFREMER	SAUMONARD	WS	coastal	20.43	14.67	
46	IFREMER	SILLONANGLAIS_B	WS	coastal	32.62	20.09	
47	IPMA	AVEIRO	DS	estuary		30	
48	IPMA	PORTO	DS	coastal		13.67	
49	IPMA	SESIMBRA	DS	coastal		11	
50	IPMA	TAGUS	DS	coastal		13.33	
51	IPMA	AVEIRO_D3	WS	estuary	26.5	25.75	
52	IPMA	AVEIRO_D5	WS	estuary	22	26.17	
53	IPMA	PORTO	WS	coastal	22.67	27.5	
54	IPMA	SESIMBRA_D2	WS	coastal	12	13	
55	IPMA	SESIMBRA_D4	WS	coastal	10.33	13.67	
56	IPMA	TAGUS_D2	WS	coastal	19.67	22	
57	IPMA	TAGUS_D4	WS	coastal	18.33	21.97	
58	ITC	GANDO	DS	coastal	1.32	3.74	
59	ITC	JINAMAR	DS	coastal	1.29	5.01	
60	ITC	LUZ_D2	DS	coastal	2.56	7.22	
61	ITC	LUZ_D4	DS	coastal	3.23	7.9	
62	ITC	LUZ_2_D2	DS	coastal	6.53	9.58	
63	ITC	LUZ_2_D4	DS	coastal	6.18	9.86	
64	ITC	TALIARTE	DS	coastal	1.3	5.24	
65	ITC	TALIARTE_2_D2	DS	coastal	2.89	5.69	
66	ITC	TALIARTE_2_D4	DS	coastal	5.19	6.04	
67	ITC	GANDO	WS	coastal	5.12	5.29	
68	ITC	JINAMAR	WS	coastal	2.09	4.72	
69	ITC	LUZ_D3	WS	coastal	9.65	8.6	
70	ITC	LUZ_D7	WS	coastal	5.53	8.32	
71	ITC	TALIARTE	WS	coastal	2.37	5.29	
72	MSS-SEPA	BRAEHEAD	DS	coastal	10.11	22.66	
73	MSS-SEPA	MONTROSE	DS	coastal	13.81	43.82	2
74	MSS-SEPA	NEWHAVEN	DS	coastal	17.21	27.38	
75	UNICA	MOLODOGANA	DS	coastal	19.03	20.67	
76	UNICA	MOLOINCHUSA	DS	coastal	7.4	15.67	
77	UNICA	MOLORINASCITA	DS	coastal	12.73	46.67	1
78	UNICA	SANTELMO_D2	DS	coastal	9.2	14.5	
79	UNICA	SANTELMO_D5	DS	coastal	10	14	
80	UNICA	MOLODOGANA	WS	coastal	13.03	14.29	
81	UNICA	MOLOINCHUSA	WS	coastal	10.57	13	
82	UNICA	MOLORINASCITA	WS	coastal	9.82	14.33	
83	UNICA	SANTELMO_D3	WS	coastal	11.02	13	
84	UNICA	SANTELMO_D5	WS	coastal	12.21	15	

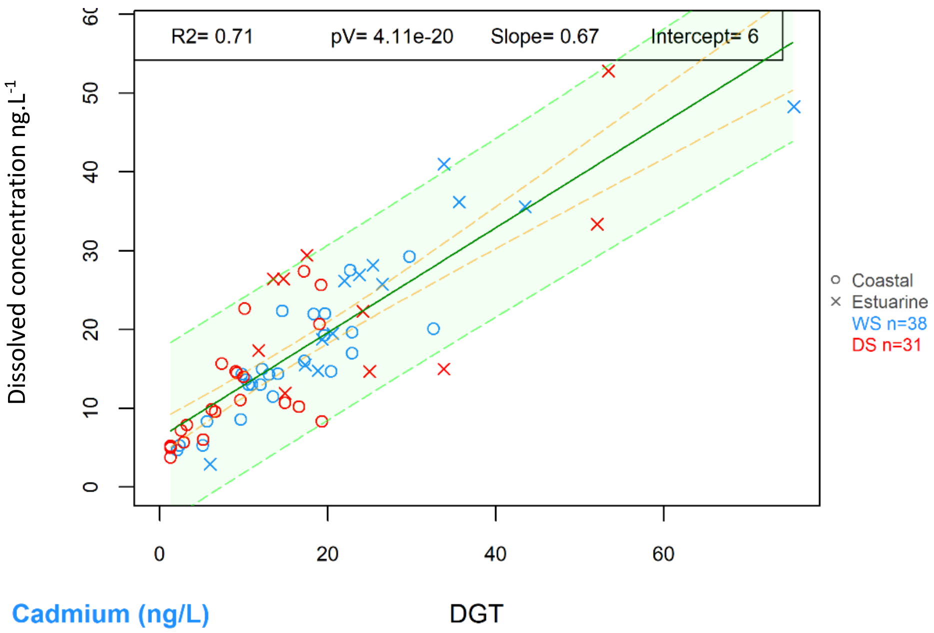


Figure 13: Cadmium: Relationship between concentrations measured in DGT labile concentration and in dissolved concentration - Statistical approach

4.2. Nickel

For nickel, the model validation assumptions were satisfied, and the relationship between dissolved concentrations and DGT labile concentrations was significant (Figure 14).

The relationship between dissolved concentration and DGT labile concentration for nickel can thus be described by Equation 7:

$$[Ni]_{\text{Dissolved Fraction}} = 0.41 \text{ x } [Ni]_{\text{DGT}} + 217 \qquad \text{(Eq. 7)}$$

Concentrations are expressed in ng.L^{-1}

The variability in concentrations measured in DGT is explained at 31% by the dissolved concentrations. From this model, nickel concentrations in the dissolved fraction can be predicted from its concentration measured in DGT labile concentration. Based on the MONITOOL data, the upper limit of the validity area of this model is 2,128 ng.L^{-1}, which is below the EQS$_{\text{marine water}}$ (8,600 ng.L^{-1}).

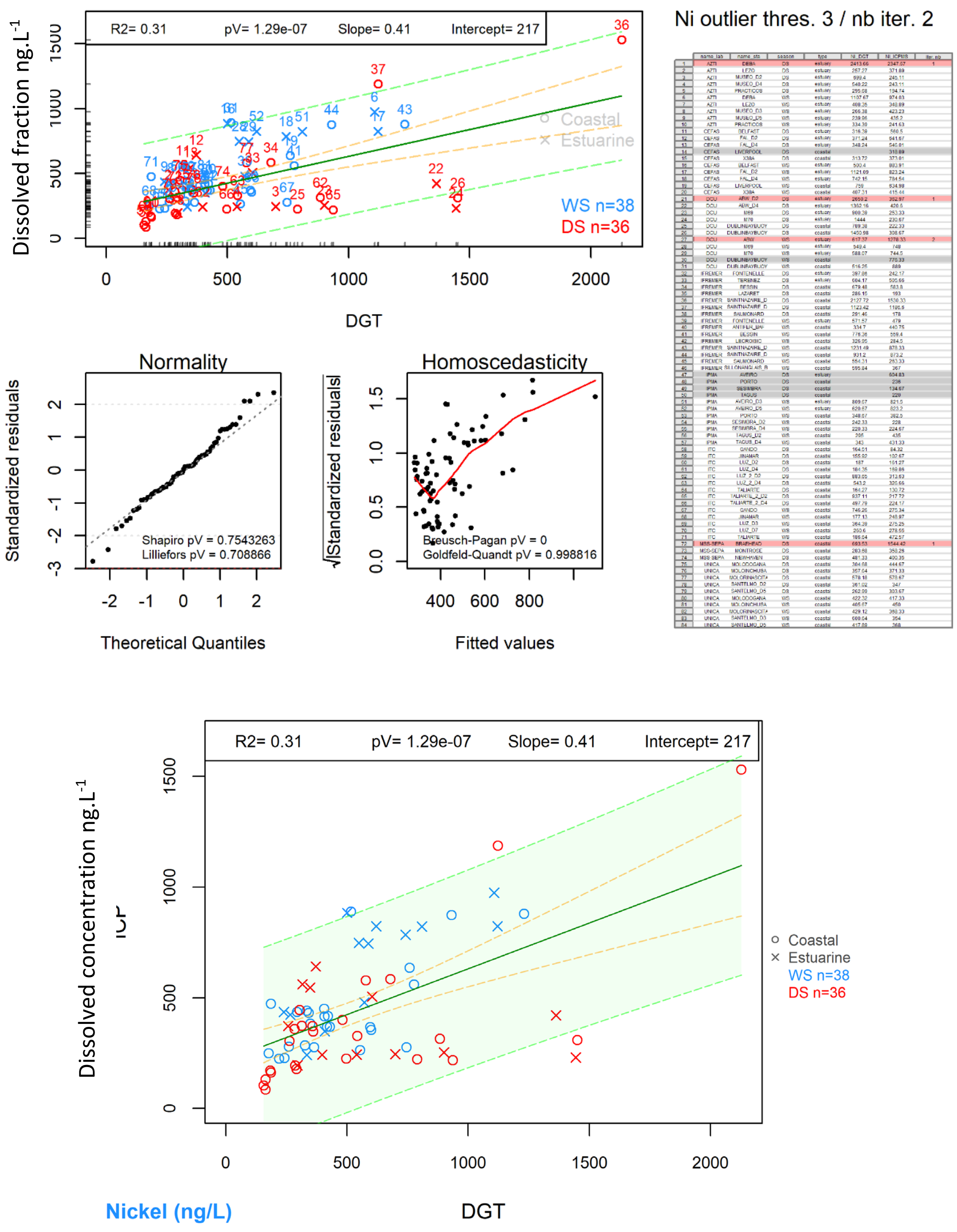


Figure 14: Nickel: Relationship between concentrations measured in DGT labile fraction and in dissolved fraction - Statistical approach

4.3. Lead

For lead, the model validation assumptions were partially satisfied, but the relationship between dissolved concentrations and DGT labile concentrations was significant (Figure 15). The model validation criteria were met (p-Values, homoscedasticity, …) except for residue normality, which does not necessarily present a rebuttal aspect to the invalidation of the model (cf Data processing).

The relationship between dissolved concentration and DGT for lead can thus be described by Equation 8:

$$[Pb]_{\text{Dissolved Fraction}} = 0.77 \times [Pb]_{\text{DGT}} + 72 \qquad \text{(Eq. 8)}$$

Concentrations are expressed in ng.L^{-1}

The variability in concentrations measured in DGT is explained at 14% by the dissolved concentrations. From this model, lead concentrations in the dissolved fraction can be predicted from its concentration measured in DGT labile fraction. Based on the MONITOOL data, the upper limit of the validity area of this model is 327 ng.L^{-1}, which is below the EQS$_{\text{marine water}}$ (1,300 ng.L^{-1}).

This model is valid, but it should be improved as the model only explain 14 % of the variability. A specific attention could be payed to lead, in order to improve the characterisation of the relationship.

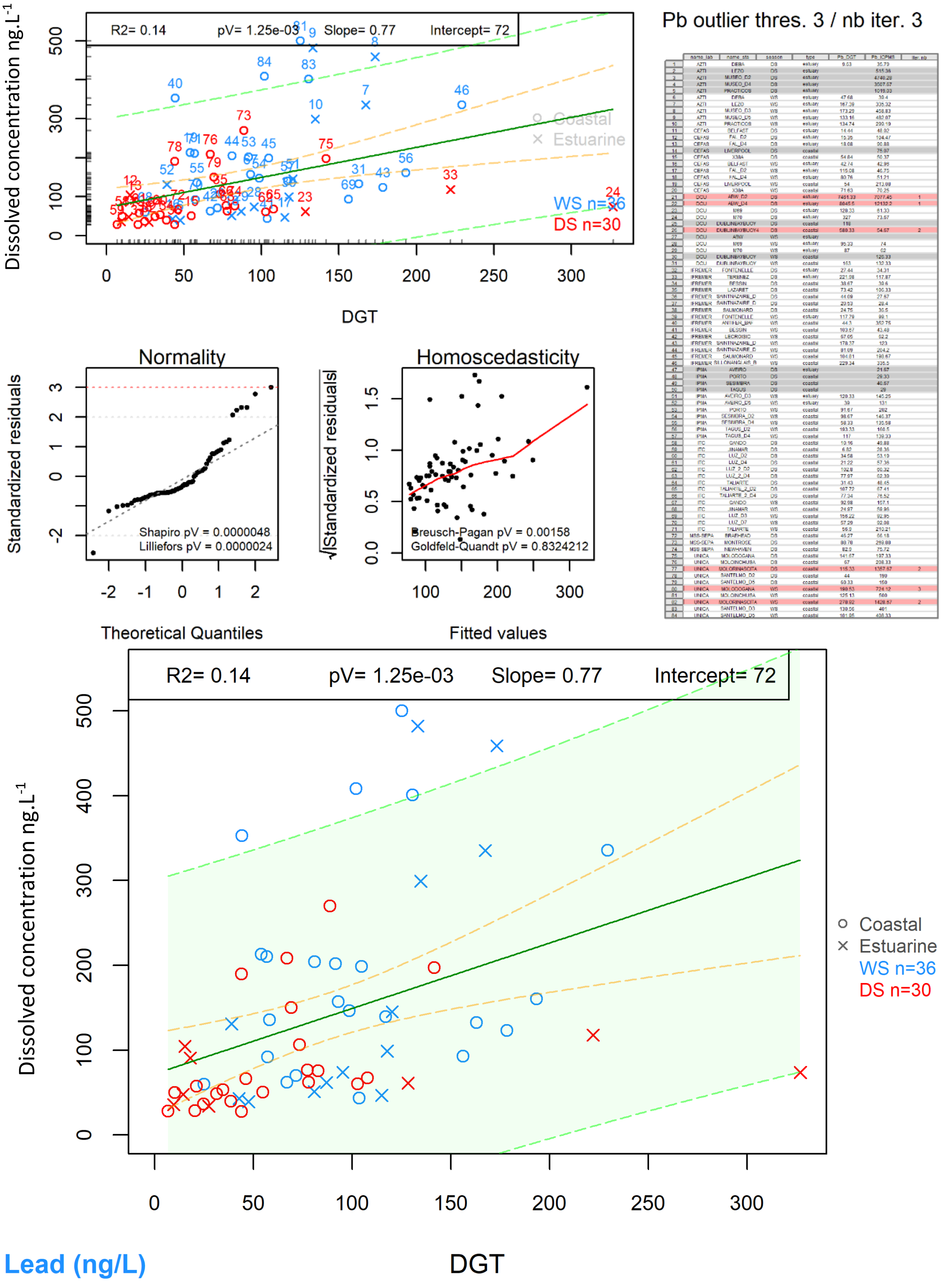


Figure 15: Lead: Relationship between concentrations measured in DGT labile fraction and in dissolved fraction - Statistical approach

5. Discussion & Conclusion

The WP6 aims to provide a methodology to determine an EQS_{DGT} adapted from $EQS_{marine\ water}$ for Ni, Pb and Cd, so that DGT results can be used in a regulatory context for marine waterbodies quality assessment. This methodology is based on a pragmatic approach applied to the context of the WFD, and in accordance with the regulation and the Technical Guidance Documents.

This document highlights: i) the difficulty of determining EQS for metals, ii) the fact that $EQS_{marine\ water}$ are based on data mainly acquired in freshwater (SSD method), and iii) particularly that $EQS_{marine\ water}$ are determined for the dissolved fraction, whereas these thresholds should be determined for the most pertinent fraction, i.e. the (bio)available fraction.

Despite the fact that: i) DGT presents a lot of advantages for monitoring, and ii) the labile fraction analysed by DGT is considered as the most potentially bioavailable fraction for the first link of the trophic chain, the fraction most likely to incur toxicity in organisms (42), and hence the most relevant for measuring and for protection purposes; it is not yet integrated into monitoring networks, since its results cannot be compared directly to $EQS_{marine\ water}$ for Cd, Ni and Pb. Two major differences are pointed out:

- DGT gives an integrated measure over the immersion time, whereas the regulation expects an average of concentrations measured in monthly spot water samples,
- Particularly a difference in the fraction analysed: labile fraction analysed by DGT vs. dissolved fraction in spot water samples. The labile fraction is described as being lower than the dissolved fraction. Comparing DGT and EQS may not therefore be as protective as comparing a result acquired with filtered water to EQS. Nonetheless, the fraction measured by DGT (labile fraction) appears more relevant and closer (at least equal to or higher than) to the bioavailable fraction.

In order to use DGT results in a regulatory context for waterbody quality assessment, three options are identified: i) compare DGT results to $EQS_{bioavailable}$, ii) compare DGT results to EQS_{DGT}, which is adapted from $EQS_{marine\ water}$, and iii) compare DGT results to $EQS_{marine\ water}$ after their conversion into dissolved metal concentrations.

As no $EQS_{(bio)available}$ are defined in marine waters for Cd, Ni and Pb, only the two other options have been explored.

The data process has been carried out on the basis of the MONITOOL dataset (WP4). A characterisation of the relationship between the metal concentrations measured in DGT and the dissolved metal concentrations measured in spot samples (ICP-MS), collected during the DGT immersion time, has been done for each metal using a linear model regression. Through a statistical process it has been possible to validate the model and to propose an EQS_{DGT} for Cd, Ni and Pb. In a pragmatic approach, the EQS_{DGT} for Cd, Ni has been determined by extrapolation, as MONITOOL results are all under the $EQS_{marine\ water}$ values. A characterisation of the inverse relationship has also been realised for Cd, Ni and Pb. All these results are presented in Table 18.

These relationships allow converting metals concentrations measured in DGTs to their concentration in the dissolved fraction, and inversely in the validated range of concentrations.

It should be noted that the applicability of linear models is the most interesting approach since the MONITOOL data come from several project partners that sampled very different sites (estuarine, coastal) in 8 countries. These sites have very different physico-chemical characteristics: salinity [0.2-38.1 UI], temperature [5.7-26.3°C], SPM [0.4 – 262.1 $mg.L^{-1}$] …. These models thus appear very reliable and it could be interesting in the future to test the relevance of these models with freshwater data. In addition, within the WP4 of the project, the exploration and the influence of environmental parameters on the relationship between DGT and ICPMS results was investigated.

To support policymakers in choosing the most appropriate EQS $_{\text{DGT}}$, whether or not to include the predictive interval (PI $_{95\%}$) or the use of the inverse relationship, the WP6-Action3 report presents the simulation of the chemical status assessment using the two proposed EQS $_{\text{DGT}}$ for each metal (Cd, Ni, Pb) and using the prediction of dissolved metal concentrations from DGT results.

What about the determination of EQS $_{\text{DGT}}$ outside the range of validity of the model?

For Cd and Ni, the proposed EQS $_{\text{DGT}}$ have been determined upon the higher limit of validity of the model. In this case, it has been considered the EQS n°2 ($[M]_{\text{DGT}}$ value minus the low PI95%), in order to be more protective.

It should be reminded that this is a pragmatic approach, which appears to be consistent and in conformity with the methodology used to convert thresholds from one matrix to another (Bioaccumulation Factor, Bioconcentration factor) in the TGD EQS (13). The MONITOOL data allowed calculating concentration factors (CF) and determining EQS_{DGT} using equation 9:

$$\text{EQS}_{\text{DGT}} = \text{EQS}_{\text{marine water}} \times \text{CF}_{\text{DGT}}\ [\mu\text{g.L}^{-1}] \qquad \text{(Eq. 9)}$$

$$\text{with} \quad \text{CF}_{\text{DGT}} = \frac{C_{DGT}}{C_{dissolved\ fraction}}$$

Results are presented in Annex 2. This approach was not selected because it appears to be less precise than the use of linear regression model results (48,49), although the modelling of results outside the range of model definition is statistically questionable. The dataset acquired by MONITOOL partners allows a much accurate and refined approach allowing the consideration of the intercept in addition to the slope, which is more or less important according to the metal under study. In addition, the proposed EQS $_{\text{DGT}}$ based on the linear regression model results is more protective than the thresholds that would have been determined using the CF, as their values are lower (Appendix 2).

Nevertheless, in order to confirm these relationships and the relevance of the proposed EQS $_{\text{DGT}}$ as much as possible, a complementary laboratory study could be carried out. Its aim should be to acquire data (DGT – ICPMS) on concentration levels of Pb, Cd and Ni close to the marine water EQS value to check the validity of the relationship up to the EQS value. In addition, ecotoxicity tests should be carried out on the seawater samples to verify the absence of toxicity of these samples.

MONITOOL data highlights the need to determine EQS $_{\text{bioavailable}}$ in marine water

The results obtained in the framework of this project highlight the fact that, even when targeting highly contaminated areas (harbour areas), it can be very difficult to reach the EQS $_{\text{marine water}}$ values. The EQS $_{\text{marine water}}$ value was exceeded at only one sampling point (for one sampling period), and for only one of the three metals (Pb). This raises question about the relevance of the EQS $_{\text{marine water}}$ 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. Therefore we recommend to carried out these actions in order to refine the EQS $_{\text{marine water}}$ and to start deriving a QS $_{\text{marine water}}$ on the bioavailable fraction. Furthermore, it should be also highlighted the fact that as the AA-QS for protection of pelagic communities are the lowest and adopted as EQS $_{\text{marine water}}$ for cadmium, nickel and lead, thus the determination of AA-QS $_{\text{marine water}}$ on the most bioavailable fraction (= labile fraction) would allow the determination of EQS $_{\text{(bio)available)}}$ for priority metals (Cd, Ni, Pb). This should be performed on the basis of new experimental tests in the laboratory, allowing both the acquisition of effects data (ecotoxicological results on marine species) and metal concentration measurements in DGT and the dissolved concentration in marine waters. Determination of this bioavailable threshold would be an ambitious project and of interest to both scientists and public policymakers in the context of the WFD, Marine Strategy Framework Directive (MSFD), Regional Sea Conventions (OSPAR, etc.) and in impact studies such as the assessment of industrial metal discharges.

Table 18: (Regression line) How to convert [M] measured in DGT to [M] measured in dissolved fraction and vice versa, validity range and proposed EQS $_{\text{DGT}}$ for Cd, Ni and Pb.

Metal	**Relationship DGT – Dissolved fraction and vice versa ng.L^{-1}**	**Validity range ng.L^{-1}**	**Proposed EQS $_{\text{DGT}}$**
	How to convert $[M]_{\text{dissolved fraction}}$ to $[M]_{\text{DGT}}$?		
Cd	*Prediction:* $[Cd]_{\text{DGT}} = 1.01\,[Cd]_{\text{Dissolved fraction}} - 2$	$[Cd]_{\text{Dissolved fraction}}$ [<LQ; 114]	n°1: 0.20 µg.L^{-1}
	Prediction – IC 95: $[Cd]_{\text{DGT}} = 0.98\,[Cd]_{\text{Dissolved fraction}} - 12$		n°2: 0.18 µg.L^{-1}
	Prediction + IC 95: $[Cd]_{\text{DGT}} = 1.03\,[Cd]_{\text{Dissolved fraction}} + 9$		
Ni	*Prediction:* $[Ni]_{\text{DGT}} = 0.51\,[Ni]_{\text{Dissolved fraction}} + 261$	$[Ni]_{\text{Dissolved fraction}}$ [<LQ; 1,544]	n°1: 4.60 µg.L^{-1}
	Prediction – IC 95: $[Ni]_{\text{DGT}} = 0.48\,[Ni]_{\text{Dissolved fraction}} - 166$		n°2: 3.08 µg.L^{-1}
	Prediction + IC 95: $[Ni]_{\text{DGT}} = 0.53\,[Ni]_{\text{Dissolved fraction}} + 689$		
Pb	*Prediction:* $[Pb]_{\text{DGT}} = 0.13\,[Pb]_{\text{ICP-MS}} + 65$	$[Pb]_{\text{Dissolved fraction}}$ [<LQ; 1,428]	n°1: 0.23 µg.L^{-1}
	Prediction – IC 95: $[Pb]_{\text{DGT}} = 0.11\,[Pb]_{\text{Dissolved fraction}} - 31$		n°2: 0.12 µg.L^{-1}
	Prediction + IC 95: $[Pb]_{\text{DGT}} = 0.13\,[Pb]_{\text{Dissolved fraction}} + 162$		
	How to convert $[M]_{\text{DGT}}$ to $[M]_{\text{dissolved fraction}}$?		
Cd	$[Cd]_{\text{Dissolved Fraction}} = 0.67 \times [Cd]_{\text{DGT}} + 6$	$[Cd]_{\text{DGT}}$ [<LQ; 75.5]	
	Prediction – IC 95: $[Cd]_{\text{Dissolved fraction}} = 0.65\,[M]_{\text{DGT}} - 4$		
	Prediction + IC 95: $[Cd]_{\text{Dissolved fraction}} = 0.68\,[M]_{\text{DGT}} + 17$		
Ni	$[Ni]_{\text{Dissolved Fraction}} = 0.41 \times [Ni]_{\text{DGT}} + 217$	$[Ni]_{\text{DGT}}$ [<LQ; 2,128]	
	Prediction – IC 95: $[Ni]_{\text{Dissolved fraction}} = 0.39\,[Ni]_{\text{DGT}} - 211$		
	Prediction + IC 95: $[Ni]_{\text{Dissolved fraction}} = 0.44\,[Ni]_{\text{DGT}} + 645$		
Pb	$[Pb]_{\text{Dissolved Fraction}} = 0.77 \times [Pb]_{\text{DGT}} + 72$	$[Pb]_{\text{DGT}}$ [<LQ; 327]	
	Prediction – IC 95: $[Pb]_{\text{Dissolved fraction}} = 0.70\,[Pb]_{\text{DGT}} - 147$		
	Prediction + IC 95: $[Pb]_{\text{Dissolved fraction}} = 0.84\,[Pb]_{\text{DGT}} + 292$		

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Annex 1: Comparison of linear regression vs quantile regression for the relation DGT=f(ICP)

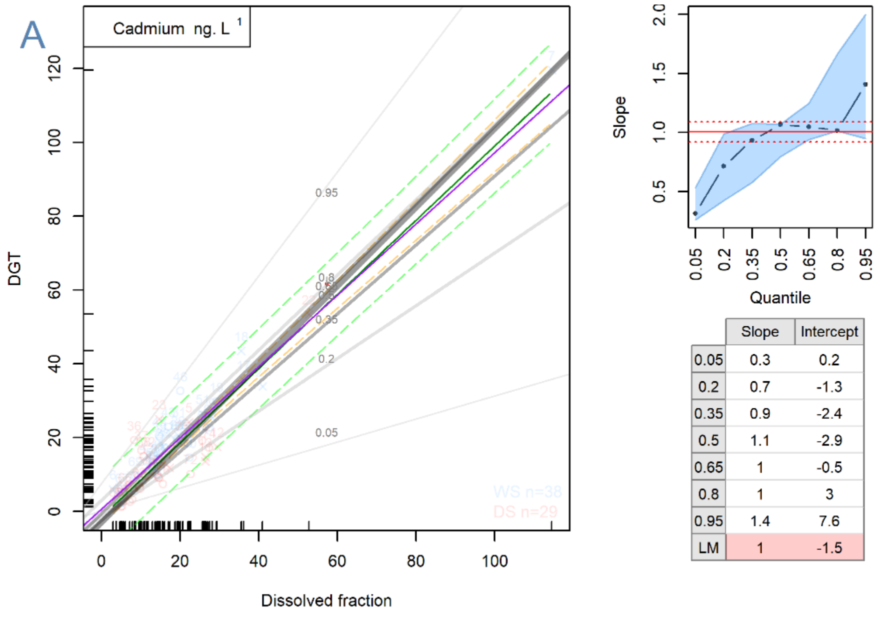
This appendix aims to visualize the differences between two modelling approaches (linear regression and quantile regression) to model the relationship DGT=f(ICP). The results of this WP6 work using the classical linear model on the selected results (statistical outliers removed) are compared with (1) those of the quantile regression based on all the available results (with the identified outliers) and (2) those of the quantile regression based on the selected results (outliers removed).

For this purpose, the same graphical output is used to view the results (Figure 2). It is based on:

— on the left: a scatter plot illustrating the results of the DGT/ICP value pairs (cross and circle of very light blue and red colours), as well as the lines associated with the linear regression (in green the linear regression line with its prediction interval in dotted line and its confidence interval in orange). In addition, the quantile regression lines (with either all the values or only the selected values – excluding outliers) are also illustrated for quantiles 0.05, 0.2, 0.35, 0.5, 0.65, 0.8, 0.95 in gray with a greater thickness for quantiles 0.35 and 0.65 and particularly thick for quantile 0.5. For representations where the quantile regression is based on all the available results (with the identified outliers), the purple line represents the regression line of the simple linear model with all the available results.

— on the top right: the graph represents the evolution of the quantile regression line slope value for each selected quantile (black dots) as well as its confidence interval (in blue). In addition, the solid red line corresponds to the regression line slope value of the classical linear model chosen in WP6 enlarged by its confidence interval in red dotted lines.

— on the bottom right: the table shows the slopes and intercepts for each regression line (the quantile and the classical linear used in WP6, illustrated with a light pink background).



	Slope	Intercept
0.05	0.3	0.2
0.2	0.7	-1.3
0.35	0.9	-2.4
0.5	1.1	-2.9
0.65	1	-0.5
0.8	1	3
0.95	1.4	7.6
LM	1	-1.5

Figure 1: Standard graphical output.

Analysis were performed with R software using the basic package ("stat") for the classical linear model (lm function) and, using the "quantreg" package for quantile regression (rq function with the default method based on the Barrodale and Roberts algorithm).

Comparison of the classical linear regression with selected data (outliers removed) vs the quantile regression based on all available data

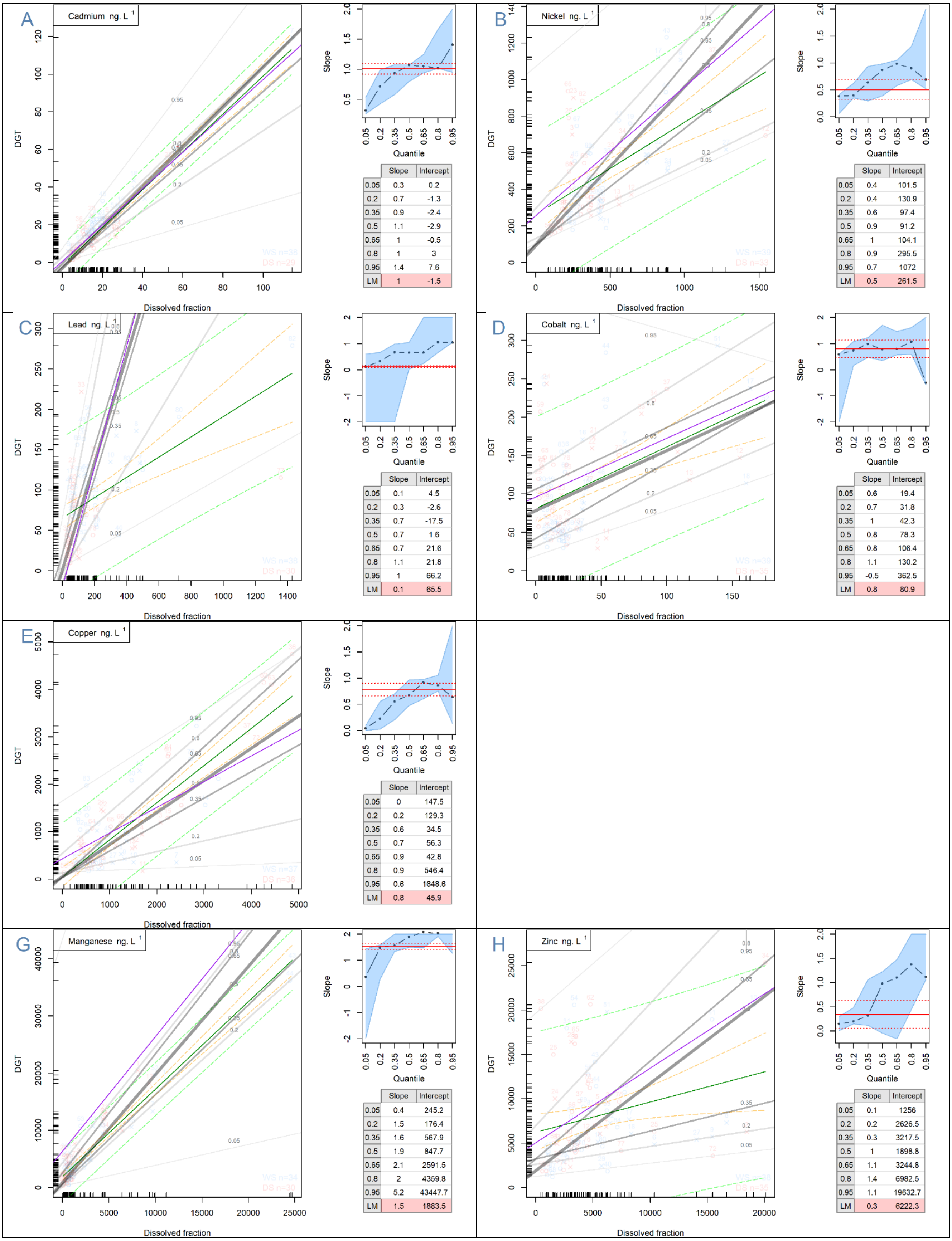
This comparison is based on Figure 2 (A to H).

For cadmium, whose results have been rather encouraging from the outset, it can be seen that the lines of the classical regression model with all the available results (purple line) or only with the selected results (outliers removed) (green line) are in agreement with the quantile regression line on the median (quantile 0.5, gray line) (Figure 2A, left hand graph). It can also be seen that the slopes associated with the majority of the quantiles tested (0.35, 0.5, 0.65, 0.8), respectively 0.9, 1.1, 1 and 1, fall well within the confidence interval of the slope of the regression line considered in WP6 (Figure 2A, right-hand graph and table).

A similar pattern can be observed for cobalt (Figure 2D), copper (Figure 2E) even managanese (Figure 2G). The slopes of the regression lines considered in WP6 (green line) are very close to those of the quantile regressions for the median (large gray lines): 0.8 vs 0.8, 0.8 vs 0.7 and 1.5 vs 1.9 for cobalt, copper and manganese, respectively (Figures 2D, 2E and 2G right-hand tables).

Nevertheless, for the other metals (nickel and especially lead and zinc) significant differences exist between regression lines based on the classical regression on the selected dataset (outliers removed) and those of the median quantum regressions, (Figures 2B, 2C and 2H left-hand graph : wide shaded line very offset from the solid green line).
On the other hand, we can see that the classical regression line based on all data matches quite well with that of the quantile regression of the median. This implies that despite the presence of statistical outliers, the slope of the median of quantile regression is not really different from those of classical linear regression: the median of quantile regression is therefore not really insensitive to outliers based on this dataset.

The position of the different quantile lines of these quantile regressions also gives another interesting information: indeed, we mainly observe for lead and zinc, the lines of the different quantiles can have very different slopes. This indicates that the datasets are not homogeneous and therefore present extreme values on some quantiles (on some range of values): for example, the 0.05 quantile for lead (Figure 2C, main graph) and the 0.05, 0.2 and 0.35 quantiles as opposed to the others (Figure 2H, main graph) or the 0.95 quantile for cobalt (Figure 2D, main graph). This justifies the removing of values that could bias our relationships; values that we have called statistical outliers.



A – Cadmium

	Slope	Intercept
0.05	0.3	0.2
0.2	0.7	-1.3
0.35	0.9	-2.4
0.5	1.1	-2.9
0.65	1	-0.5
0.8	1	3
0.95	1.4	7.6
LM	1	-1.5

B – Nickel

	Slope	Intercept
0.05	0.4	101.5
0.2	0.4	130.9
0.35	0.6	97.4
0.5	0.9	91.2
0.65	1	104.1
0.8	0.9	295.5
0.95	0.7	1072
LM	0.5	261.5

C – Lead

	Slope	Intercept
0.05	0.1	4.5
0.2	0.3	-2.6
0.35	0.7	-17.5
0.5	0.7	1.6
0.65	0.7	21.6
0.8	1.1	21.8
0.95	1	66.2
LM	0.1	65.5

D – Cobalt

	Slope	Intercept
0.05	0.6	19.4
0.2	0.7	31.8
0.35	1	42.3
0.5	0.8	78.3
0.65	0.8	106.4
0.8	1.1	130.2
0.95	-0.5	362.5
LM	0.8	80.9

E – Copper

	Slope	Intercept
0.05	0	147.5
0.2	0.2	129.3
0.35	0.6	34.5
0.5	0.7	56.3
0.65	0.9	42.8
0.8	0.9	546.4
0.95	0.6	1648.6
LM	0.8	45.9

G – Manganese

	Slope	Intercept
0.05	0.4	245.2
0.2	1.5	176.4
0.35	1.6	567.9
0.5	1.9	847.7
0.65	2.1	2591.5
0.8	2	4359.8
0.95	5.2	43447.7
LM	1.5	1883.5

H – Zinc

	Slope	Intercept
0.05	0.1	1256
0.2	0.2	2626.5
0.35	0.3	3217.5
0.5	1	1898.8
0.65	1.1	3244.8
0.8	1.4	6982.5
0.95	1.1	19632.7
LM	0.3	6222.3

Figure 2: Results by metals for quantile regression on all values vs classical linear regression on selected values

Comparison of the classical linear regression with selected data (outliers removed) vs the quantile regression based on all available data

This comparison is based on Figures 3A to 3H.

Contrary to the previous paragraph and figures 2, here there is a certain homogeneity of results for each metal when we compare the slopes of the two types of regression. The regression lines of the classical linear model (used in WP6) and the median of the quantile regression model are close: 1.01 vs 1. 07 for Cd (Figure 3A, right-hand table), 0.51 vs 0.55 for Ni (Figure 3B, right-hand table), 0.13 vs 0.17 for Pb (Figure 3C, right-hand table), 0.81 vs 0.84 for Co (Figure 3D, right-hand table), 0.78 vs 0.75 for Cu (Figure 3E, right-hand table), 1.53 vs 1.55 for Mn (Figure 3G, right-hand table) and 0.34 vs 0.35 for Zn (Figure 3H, right-hand table).

These results indicate that our values selection (by removing statistical outliers) is beneficial to linear relationships.
This can also be seen from the relative homogeneity of the slopes of the different quantiles for each metal (except any examples like quantile 0.05 for copper (Figure 3E, main graph). In all cases, more consistent than with the full data set (without outlier removal).

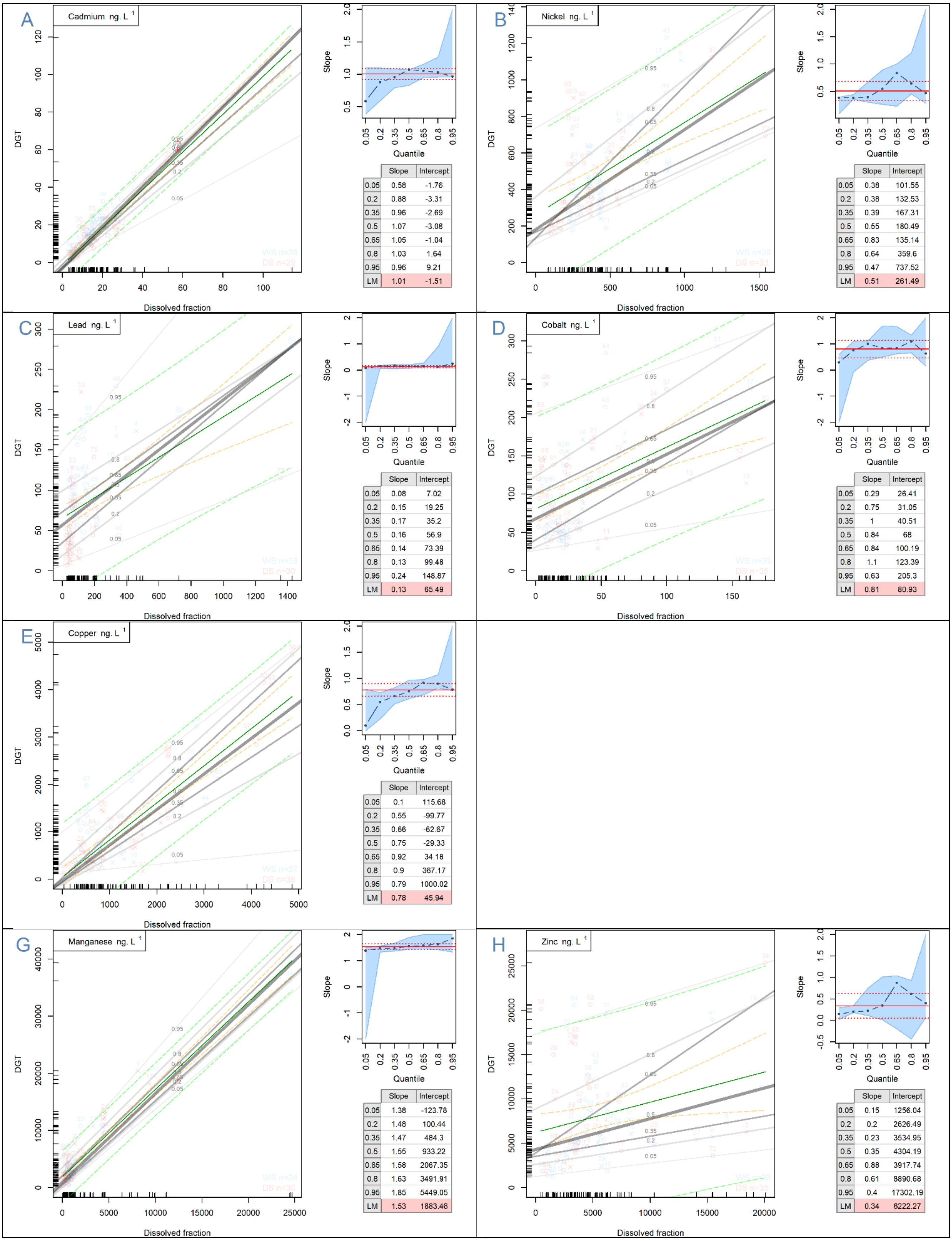
Comments

Although quantile regression (median) is by definition less sensitive to outliers than classic linear regression, a large effect of outliers on the results of quantile regression can be observed here (enough to justify the choice to eliminate them).

The interest of using quantile regression for this purpose is therefore limited in the case of our data set.
The other interest of quantile regression, which would aim to categorise our contamination levels (the highest 10%,...), does not necessarily make sense for the objective of our work, especially as our data set is not exhaustive over the whole range of values encountered, especially on middle high and high contamination.

Nevertheless, the quantile regression reveals information on the quality of our data set. Indeed, when we put the quantile regression on the whole data set in perspective with those on the selected data, we notice that there are numerous and important slope changes between the different quantile marking a homoscedasticity problem (but we do not find this problem or only in a small scale on the result based on selected values). This illustrates the fact that our initial data set presents important outliers which it is desirable to remove for a good modelling of the DGT labile concentration/Dissolved concentration relationship.

It is also important to notice that for the majority of metals the slopes of the medians of the quantile regressions fall well within the confidence interval of the slopes of the classical linear regressions that we chose to estimate DGT EQS (Figure 3A to 3H, right-hand graphs); which globally consolidates the choice of classical linear regression in WP6.



A – Cadmium

	Slope	Intercept
0.05	0.58	-1.76
0.2	0.88	-3.31
0.35	0.96	-2.69
0.5	1.07	-3.08
0.65	1.05	-1.04
0.8	1.03	1.64
0.95	0.96	9.21
LM	1.01	-1.51

B – Nickel

	Slope	Intercept
0.05	0.38	101.55
0.2	0.38	132.53
0.35	0.39	167.31
0.5	0.55	180.49
0.65	0.83	135.14
0.8	0.64	359.6
0.95	0.47	737.52
LM	0.51	261.49

C – Lead

	Slope	Intercept
0.05	0.08	7.02
0.2	0.15	19.25
0.35	0.17	35.2
0.5	0.16	56.9
0.65	0.14	73.39
0.8	0.13	99.48
0.95	0.24	148.87
LM	0.13	65.49

D – Cobalt

	Slope	Intercept
0.05	0.29	26.41
0.2	0.75	31.05
0.35	1	40.51
0.5	0.84	68
0.65	0.84	100.19
0.8	1.1	123.39
0.95	0.63	205.3
LM	0.81	80.93

E – Copper

	Slope	Intercept
0.05	0.1	115.68
0.2	0.55	-99.77
0.35	0.66	-62.67
0.5	0.75	-29.33
0.65	0.92	34.18
0.8	0.9	367.17
0.95	0.79	1000.02
LM	0.78	45.94

G – Manganese

	Slope	Intercept
0.05	1.38	-123.78
0.2	1.48	100.44
0.35	1.47	484.3
0.5	1.55	933.22
0.65	1.58	2067.35
0.8	1.63	3491.91
0.95	1.85	5449.05
LM	1.53	1883.46

H – Zinc

	Slope	Intercept
0.05	0.15	1256.04
0.2	0.2	2626.49
0.35	0.23	3534.95
0.5	0.35	4304.19
0.65	0.88	3917.74
0.8	0.61	8890.68
0.95	0.4	17302.19
LM	0.34	6222.27

Figure 3: Results by metals for quantile regression on selected values vs classical linear regression on selected values

Annex 2: Determination of Concentration Factor (CF), and EQS $_{DGT}$

The CF is calculated on the basis on the MONITOOL data. Then the EQS is calculated using this CF (The CF can integrate the low IC95 to be more protective). EQS are then calculate.

$$EQS_{DGT} = EQS_{water} \times CF_{DGT}\ [\mu g.L^{-1}] \qquad \text{with} \qquad CF_{DGT} = \frac{C_{DGT}}{C_{dissolved\ fraction}}$$

	Concentration Factor method				Linear regression model method	
	CF mean (geometric mean)	CF mean (geometric mean) - IC95	EQS $_{DGT}$ (using CF mean)	EQS $_{DGT}$ (using CF mean - IC95)	EQS $_{DGT}$ N°1 (model linear regression)	EQS $_{DGT}$ N°2 (model linear regression - IP95)
Cd	0.91	0.81	181.36	162.21	199	181
Ni	1.27	1.09	10917.87*	9393.44*	4607	3079
Pb	0.79	0.65	1023.39	844.21	229	116

*These EQS $_{DGT}$ are calculated. Of course it could not be proposed an EQS $_{DGT}$ higher that the EQS $_{marine\ water}$.

The proposed EQS $_{DGT}$ appear in blue cells. They are determined by the linear regression model. If the EQS $_{marine\ water}$ value is in the valid range of the model, the EQS $_{DGT}$ is determined using the regression value, if the EQS marine water value is above the valid range of the model, the EQS n°2 is recommanded: correspondant to the value of the model minus the IP95 in order to be more protective.