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Assessing Water Quality in Sultanate of Oman Using a Newly Developed Dynamic Speciation Technique

A Theses Submitted for the Degree of Doctor of Philosophy

By

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In The Name of God,
The Most Compassionate and The Most Merciful

Declaration

I, Mohammed Majid AlKasbi confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Dedication

I dedicate this work to the soul of my father who passed away when I was 14 years old, may Allah forgive him and grant him his highest paradise (Ameen), and to my beloved mother and wife whose unconditional encouragement and support made it possible for me to achieve my dreams. And also to my mother-in-law who passed away during my studies.

To my family, I love you all.

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Assessing Water Quality in Sultanate of Oman Using a Newly Developed Dynamic Speciation Technique

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Abstract

Rapid increases in coastal developments in the Sultanate of Oman recently, including large ports with industries, crude oil refineries, mining and industrial activities, have often produced point sources of metal and organic contaminations in the local marine systems. Although advances have been made in measuring and understanding the trace metal speciation in aquatic system using a dynamic technique DGT (Diffusive Gradients in Thin-films) or using other equilibrium techniques, measuring metal speciation in situ in seawater that polluted by crude oil is still extremely challenging. Without the technology and the information, it is difficult to assess the effects of oil ligands on metal speciation associated with the oil refineries and industries.

In the present study, the DGT technique has been developed further for measuring metal speciation in seawaters in the presence of oil. The influence of oil ligands on the speciation of trace metals (Cd, Co, Cu, Ni, Pb and Zn) has been investigated in synthetic solutions of 0.5 and 0.7 mol/L NaCl containing different level of Oman crude oil. DGT of different types in diffusive layers (pore size and thicknesses), binding layers (Chelex resin and Fe oxide) and different types of membranes (dialysis membranes (1000 MWCO and 3500 MWCO) and 0.05 mm thickness Nafion112 membrane) were used. The diffusion coefficients were determined for each metal, using a diffusion cell, through filter membrane and diffusive gel with and without dialysis and Nafion112 membranes.

The measured diffusion coefficients of all metals in diffusive gel plus dialysis membrane were significantly lower than gel alone. When Nafion112 membrane was used with the diffusive gel, the diffusion coefficients of all metals were much lower, up to 80 times lower for Cu, Cd and Ni. The potential of using DGT for determining labile metals species in seawater in the presence of crude oil was evaluated in mixed solution of NaCl and oil with varying mixing periods (0.25 day, 0.5 day, 1 day, 2 days, 4 days and 6 days) and oil concentrations (1, 3, 5, 7, 25 OWR% (oil water ratio), w/v). It was demonstrated that organic ligands from crude oil influenced the lability of trace metals. The combination of five types of DGT devices (OP-DGT, RG-DGT, (dialysis 1000Da)-DG, (dialysis 3500Da)-DGT, (Nafion112)-DGT) were used for speciation of metals at 1 and 4 oil water ratio (OWR%), and 48 h mixing time. Lower concentrations of labile metals were determined with the higher level of oil in the synthetic solution when using Nafion112-DGT, due to the exclusion of large colloids and negatively charged metal complexes by Nafion112 membrane. No significance differences were observed between OP-DGT and RG-DGT for Co, Ni, Zn and Pb at 1% OWR and Co, Ni and Pb in at 4% OWR. This suggests the labile complexes of metals and organic ligands from oil may be smaller than the pore size of the restricted

diffusive gel. Comparing (Dialysis 1000MWCO)-DGT and 1000MWCO- Micro Float microdialysis measurements indicated that Co, Cd, Cu and Zn were complexed with ligands small enough to pass through the 1000 MWCO- Micro Float microdialysis but not labile enough to be retained in the (Dialysis 1000 MWCO)-DGT samplers.

DGT technique was applied to soils contaminated with both metals and crude oil to evaluate the effect of oil level and aging on the availability of metals in soils. The dissolved metals in soil solution (C_{soln}), labile concentrations by DGT (C_{DGT}) and extractable concentration by $CaCl_2$ were measured. Values of labile pool size, K_d, and R (ratio of C_{DGT} and C_{soln}) were calculated and the kinetic parameters (response time T_c and desorption rate k_{-1}) were obtained using DIFS (DGT Induced Fluxes in Soils and sediments) model. Increases of crude oil treatments in soils promoted the formation of non-labile species of Cu and Pb and limited the availability of both metals. The time scales of the kinetic exchanges obtained from DGT measurements and DIFS modelling was reflected by the range of determined T_c values: from seconds to 3 hours. The gradual decrease of K_d values for Cu with time in three studied soils with and without oil application may be attributed to the strong tendency of Cu to be associated with the solid phase with increasing incubation time. The K_d values of Ni were generally decreased with adding of crude oil amendments in three soils may be due to the release of Ni species from solid phase and crude oil to soil solution. Three soils were resupply of Cd and Pb in general very slow to measure. The generally slower release rates of Cd and Pb compared to other studied metals may reflect the lower concentration of Cd and Pb which allowed a higher proportion of them to associate strongly with organic ligands sites with slower release rates. The trend changes for k_{-1} values of studied metals in three selected soils were influenced by crude oil amendemnets and aging time.

All developed DGT of different types, including DGT with ferrihydrite for oxyanions (As, Se, Mo, V, Sb and W), were deployed in situ in seawater and groundwater around refineries and industrial areas in Oman. Soils and sediments in those areas were also collected for DGT deployments. The labile concentrations of Cr, Co, Ni, Cu, Cd, and Pb were generally low and not significantly different at all the sampling locations due to the formation of strong metals complexes with organic ligands that are less labile. The measured concentrations of labile V in all selected locations were much lower than the total V concentration in the filtered grab samples (C_{Sol} (0.45 μm filtered)) due to high levels of large colloidal ligands from crude oil. The low proportion of Ni labile species (11%-29%) was measured by (Nafion112)-DGT in all selected open wells because Ni is mainly complexed by negatively charged ligands and they were excluded by Nafion112 membrane. The labile Fe, Ni and Mn concentrations in Wells-1 and -2 were much higher than those in Well-3 and (RIE)'s wells reflecting the occurrence of more intense oil and industrial contamination in the area. For coastal sediments near the refinery discharge point at Al Fahal port, the DGT measured labile concentrations of Fe, Ni, Cu, and V were higher near the discharge point.

The DGT concentrations of Al, Fe and Mn in soils collected from SIR ranged from (12-22 μg/L), (14-63 μg/L) and (9-17μg/L) respectively, in line with the background level of those metals. For 15 selected soils, their K_d ranged from (1.8-33) ml/g for (Al, Cr, Mn, Fe, Ni and Cu). The K_d values of Pb were higher at soil locations (L2, L7, L8 and L11) of 266, 65, 43 and 55 gm/L respectively due to the higher metal retention by the solid phase through sorption reactions and low concentration in the soil solution.

The obtained results suggest that risk assessment of sandy soils could be carried out using measurements of metals in soil solutions. However, devices such as DGT dynamic technique, which respond to the kinetics of supply, are essential to evaluate available metal in high pH and crude oil contaminated soils. Because DGT is a dynamic technique and it can be readily deployed in situ, in seawaters, groundwaters, soils, and sediments, it provids kinetic information directly in crude oil contaminated environmental systems and allows better better understanding and risk assessments.

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Abbreviations

(SIR)	Sohar Industrial Region (Oman)
(RIE)	Rusayl Industrial Estate (Oman)
PDO	Petroleum Development Oman
WSF	Water soluble fraction of crude oil
ASV	Anodic stripping voltammetry
CLE-AdSV	Competitive ligand exchange – Adsorptive stripping voltammetry
D_M	Diffusion coefficient of metal, cm^2/s
IS	Ionic strength
ICP-MS	Inductively coupled plasma - mass spectrometry
DBL	Diffusive boundary layer
ICP-OES	Inductively coupled plasma -optical emission spectrometer
BDL	Below the detection limit
Δ	Thickness of the diffusive boundary layer
M	Free metal ion
L	Free ligand
PLM	Permeation liquid membrane
RSD	Relative standard deviation
SD	Standard deviation
f_e	Elution factor
C_{DGT}	DGT measured concentration
C_{sol}	Concentration of metal in the soil solution
DIFS	Diffusion Induced Fluxes in Soils
K_d	Distribution coefficient for labile metal

(R value)	The DGT-measured concentration (C_{DGT}) to water-soluble fraction
K_{-1}	Dissociation rate
T_C	Response time
Δg	Diffusion layer thickness
OM	Organic matter
DMT	Donnan membrane technique
DGT	Diffusive gradients in thin films
MWHC	Maximum water holding capacity
A	Area of the DGT window
APA	Agarose cross-linked polyacrylamide [gel]
MQ water	Millipore Milli-Q® I8-megOhm/cm deionized [water]
TOC	Total organic carbon
LOI	Loss on ignition
M	Molar (moles per liter)
Psu	Practical salinity unit
OWR%	Crude oil to water ratio
PAHs	Polyaromatic hydrocarbons
T	DGT deployment time
DOC	Dissolved organic carbon
$\boldsymbol{J}$	Flux
MWCO	Molecular weight cut off

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Chapter 1 – Introduction

The environmental quality represents an important issue in coastal and economic harbours areas. The Oman marine systems in particular represent a perfect example for the study of the relation between chemical contamination and economic activities along the coast. Recent studies have shown that the rapid rises in coastal developments in Sultanate of Oman include large economic ports with refineries and industries (Sohar, Salalah, Muscat and Alduqum), contributed to organic substances and trace metals inputs in the aquatic environments (Abdul-Wahab and Jupp, 2009; Al-Shuely et al., 2009; Al-Husaini, 2010; Al-Rashdi and Sulaiman, 2013). Apart from a few limited studies on soils (Ogbo and Okhuoya, 2011; Omaka et al., 2011; Fu et al., 2014), very little researches have been done on the effect of crude oil contamination on the trace metals concentrations. No information has been reported on the influence of crude oil from refineries and industrial activities on the migration, speciation and distribution of trace metals in Oman's aquatic environments. The speciation of trace metals is very important for assessing the quality of aquatic systems. To further our understanding of the effects of crude oil contamination on trace metal concentrations and availability in marine systems, a state of art in situ dynamic speciation technique, DGT (diffusive gradients in thin-films) has been adapted and tested for seawaters with oil. The accumulation of metals in DGT devices depends on the lability and mobility of metal complexes. The DGT devices can be fitted with varying thicknesses of diffusive layers (Δg), to give useful information on the lability and dissociation extents of metal complexes. They can also be fitted with diffusive layers of different pore sizes to discriminate between small labile inorganic species and larger organic complexes (Lehto et al., 2006; Panther et al., 2008). Recent studies demonstrated that DGT can be used in conjunction with dialysis membranes of varying molecular weight cut-off (MWCO) in the front of the diffusive gel layer to provide a separation of the smaller inorganic metal species from the larger colloidal species (Gimpel et al., 2003; Li et al., 2003; Fan et al., 2013; Pouran et al., 2014). More recent studies have used Nafion membrane in DGT and other passive samplers in direct contact with receiving phase to prevent the transport of negatively charged metal ligands complexes across the diffusion membrane and only allow positively charged species to be measured (Blom et al., 2003; Hurst and Bruland, 2005; Panther et al., 2008). However, this has not been thoroughly and systematically investigated for wider application.

The study presented here for the thesis is the first to investigate the influence of crude oil ligands on trace metal speciation using DGT. The aim of this study is to develop a simple in situ speciation method to assess the concentration, distribution and speciation of trace metals in Oman coastal aquatic environment and soil system. The objectives are:

i. To develop and test DGT method, with different types of devices, for trace metals speciation in seawaters, groundwaters and soils contaminated with crude oil matrix.
ii. To investigate the effects of crude oil on the trace metals availability in the aquatic environment and the impact of oil matrix on metal speciation and complexation.
iii. To investigate the effect of oil level and aging on the availability of metals in soils using DGT measurements and DIFS model.
iv. To assess the impact of oil industries on Oman coastal environment quality (seawater, groundwaters, sediments and soils) using developed DGT devices,

both Chelex DGT and Fe-oxide DGT, with different types of membranes, by measuring the labile concentrations of trace metals (Cu, Ni, Co, Zn, Pb, Cd, Al, Fe, Mn, Cr, Sb, Se, As, W, Mo and V) and by using DIFS model.

The following literature review in **Chapter 2** comprises a description and discussion of the past and the current research in the same and related areas. The review begins by defining the background and range of trace metal species present in marine waters and describes important processes affecting speciation and aquatic systems quality. Then importance of speciation measurements and trace metals toxicity were discussed and then briefly described the interaction between trace metals species and organic ligands. The effect of crude oil contamination on trace metals measurements in seawater, sediments and soils was also discussed. The source of crude oil contamination in Oman marine systems and the effect of oil components on the metals speciation, as well as the available analytical techniques for measuring bioavailability of metals fractions in seawater, groundwaters soils and sediments were also briefly reviewed. Various methods used for speciation measurements were also introduced briefly, followed by detailed review of DGT technique and of studies that have contributed to the development of the technique.

Chapter 3 is divided into three sections. The first one, the experimental section, describes the general procedures for the preparation of DGT devices, deployment solutions and the experimental details. In the section two, concerned with the measurement of diffusion coefficients of metals in diffusive gel using diffusion cell. In section three, comparing DGT measured labile metal concentrations with WSF (water soluble fraction) at a range of oil levels.

Chapter 4 is divided into three sections. The first section describes the experimental conditions and the metal speciation measurements in solutions with varying (OWR%) using DGT devices with different membranes. Five types of DGT devices were introduced with open pore (OP) and a restricted pore (RP) diffusive gels, 1000 MWCO and 3500 MWCO dialysis and Nafion112 membranes. The section two focuses on the measurement of diffusion coefficients of metals (Cd, Co, Cu, Ni, Pb and Zn) through diffusive gel and filter membranes with dialysis and Nafion 112 membranes placed in the front of them, using a specifically designed diffusion cell. Section three presents and discusses the results obtained by all DGT devices in solutions without and with oil. Labile metal concentrations by (1000MWCO)-DGT were also compared with equilibrium concentrations by Micro Float microdialysis of 1000 MWCO.

Chapter 5 has two main results sections addresses the effect of crude oil (at different OWR%) and aging (at different incubation time) on speciation and availability of metals (Co, Cu, Cd, Ni, Pb and Zn) in soils. In the second section uses the DIFS model to further understand the obtained results. The kinetic parameters, such as dissociation rate constant (k_{-1}) and response time (T_C) were modeled using DIFS. The ratios (R) and distribution coefficients (K_d) were obtained from the DGT, soil solution and $CaCl_2$ extraction measurements. All parameters R, K_d, Tc and k_{-1} were discussed and interpreted in the context of metal availability in soils.

In **Chapter 6** the developed DGT methods and knowledge were applied in Oman's marine water, groundwaters, sediments and soils around large economic ports with industries and refineries (Muscat and Sohar) and industrial region in Muscat to assess the impact of oil industries on the environmental quality of that region. Kinetic parameters of desorption from the soil particles to the soil solutions without and with oil were obtained from the DIFS model. The availability of metals, including both cation metals and oxyanion metals in soils and sediments were assessed based on R, K_d and kinetic parameters T_C and k_{-1}.

Chapter 7 provides the main conclusions of each chapter of the work and discusses the possibilities of the future research arising from these studies.

Chapter 2 – Literature Review

2.1. Trace Metals in the Marine Environment

The concentrations of trace metals in seawater exist at extremely low concentrations in the range pg/L to mg/L dissolved in a variety of physical and chemical forms and occur as oxyanions (MoO_4^{2-} and WO_4^{2-}) or as large monovalent cations like (Cs^+) or divalent cations like (Cd^{2+}, Cu^{2+}, Zn^{2+}) (Bruland and Lohan, 2006).

Table 2.1. Background levels of selected trace metals in different environments of seawater.

Metal	Background Concentrations in Seawater (µg/L)	Reference
Cu	0.14-0.90 (open ocean) 0.35-0.40 (coastal)	(Bazzi, 2014)
Cd	0.01-0.12 (open ocean) 0.01-0.17 (coastal)	(Bazzi, 2014)
Co	0.27	(Bowen, 1966)
Pb	0.02-0.07 (open ocean)	(Bazzi, 2014)
Ni	<1	(Rieuwerts, 2015)
Fe	2-7.3	(Yariv and Cross, 1979)
Mn	0.032-8	(Yariv and Cross, 1979) (Mackey et al., 2015)
Zn	<1 (open ocean) 0.30-70.0 (coastal)	(Bazzi, 2014)
Al	0.02-0.517	(Hydes, 1977) (Mackey et al., 2015)
Cr	0.057-0.234 (open ocean)	(Bryan and Langston, 1992)
As	1-2 (open ocean)	(Abernathy and Morgan, 2001)
Se	0.1-0.5	(Sturgeon et al., 1985) (Rieuwerts, 2015)
Sb	0.2	(Sturgeon et al., 1985)
Mo	10	(Pais and Jones Jr, 1997) (Verner, 1974)
V	1-3	(Ghani, 2015)
W	0.1-0.4	(Ishibashi et al., 1954) (Bowen, 1966)

Some trace metals (e.g molybdenum (Mo)) have a significant biological requirement; however, they tend to occur in seawater at a relatively high concentration relative to their requirement by the biota (Bruland and Lohan, 2006). Background concentrations of selected trace metals **Table 2.1** as assessment tools are intended to represent the concentrations of certain contaminants that would be expected in the seawater if certain industrial and crude oil activities had not occurred.

The distribution of trace metals in seawater are governed by a combination of processes that transport trace metals, naturally dissolved or from human activities, atmosphere (fluvial and downwind) and hydrothermal vents (heat flux in the sea floor release large volumes of heat) to the ocean (Sander and Koschinsky, 2011). Although trace metals are present in dissolved, colloidal and particulate forms, they occur at very low concentrations that are generally variables. Most of the trace metals species in surface seawater, especially those that are bioactive such as Cd, Co, Cu, Pb, Ni and Zn, are particularly chelated by natural organic ligands (Hatje et al., 2001; Wallner-Kersanach et al., 2009). The interaction of dissolved trace metals with particles suspended in seawater is a major control on the observed concentration and distribution of trace metals in seawater (Sherrell and Boyle, 1992).

2.2. Trace metal pollution and toxicity in the marine environment

Trace metal contamination in the coastal and marine environment is a widespread worry globally. Trace metals pollution in seawater received a great deal of attention especially in the last several decades due to their impacts on marine ecology and other aspects of the marine systems (Hwang et al., 2015). The increase of trace metals contamination in coastal waters pose a serious threat to the health of marine living resources, the people who consume seafood products and natural ecosystems because of their inherent enormous sources, persistence, toxicity and carcinogenic through bioaccumulation in living organisms and food chains (Arifin et al., 2012; Naser, 2013; Wang et al., 2013). Trace metals toxicity in seawater largely influenced by the biological availability of the metals, which is determined according to their physical and chemical forms. For example, the toxicity of metals can be reduced when they are adsorbed to organic complexes, therefore decreasing their ionic fractions in the seawater media (Mamboya, 2007). The small forms of organism in marines are considered the most sensitive to metals pollution (Mulak, 1997). Although trace metals such as Pb and Hg can damage an organism if a significant quantity is swallowed in a short time, most trace metals affects aquatic life in seawater by decreasing organisms' longevity and their recruitment (Madsen, 2013). Living organisms can be poisoned even with low levels of trace metals in marine systems. This is due to the biochemical function in metabolic processes and the degree to which the metals are absorbed and excreted by organisms. For example, blood and hematocrit levels of Pb and enzymatic tests, may suggest that animals are being poisoned with this metal. Lead is a dangerous chemical pollutant in ecosystem, as it able to accumulate in organisms and enter food chains. Exposure to high level of Pb can cause serious biological effects, depending on the concentration and exposure time, including damage to the kidney, brain and nervous system (Govind and Madhuri, 2014). Cd has a long half-life (>10 years in terrestrial mammals) and able to form Cd-Se complex (as in the case of Hg), suggesting the formation of a (Se) metabolite (as in the case of mercury), suggesting the formation of a selenium metabolite (Jakimska et al., 2011). Copper is one of the important metals known to be necessary to human's body. It is present in various proteins, such as oxidase, ceruloplasmin and galactose. However, uptake of more than 100 mg/kg is toxic to humans. Copper can block sulfhydryl group in enzymes and proteins, which causes toxicity in the human body. Chronic exposure to high levels of copper salts or ionic forms can affects nervous systems and kidney. Moreover, different diseases such as cardiovascular ones have been related to contaminated drinking water by Cu (Ayres and Hellier, 1997). Nickel (Ni) generally, in seawater is present at a very low levels ranged from 0.1- 0.5 µg/l. various studies demonstrated that the hepatic toxicity related to nickel exposure and dose affect enzyme activity (Cempel and Nikel, 2006).

Most of coastal areas in seawaters around the world suffering from the increase of trace metals pollution pressures due to the discharges through a variety of sources, including industries, wastewaters and domestic effluents and crude oil refineries (Pan and Wang, 2012). Human activities concentrated in industrial areas significantly influence the migration and distributions of trace metals in coastal marines (Peer and Safahieh, 2011; Lim et al., 2013; Jilani, 2014; Hernández-Crespo and Martín, 2015). Jilani (2014) reported that about 73.5% of effluents containing organic and trace metals contaminants reach Pakistan coastal waters through Karachi economic harbour due to receiving a continuous discharged of domestic and industrial waste. Moreover, the effluents from factories and oil production platforms: chemical spills; discharges from engines, releases from tankers and accidental spills are also considered a common source of trace metals contamination in coastlines. Kibria et al. (2016) found that the Karnafuli Estuary, and adjacent coastal areas of Chittagong in Bangladesh were highly affected by metal contamination problem (cadmium, chromium, copper, mercury, nickel, lead, uranium) through agricultural, domestic and wastes discharges into the waterways in coastal environments of Bangladesh (Luoma et al., 2008; Kibria et al., 2016). Study by Avila-Pérez et al. (1999) investigated about trace metal levels in water and bottom sediments of a Mexican reservoir. The work demonstrated that Hg, Pb, Cr and Fe were the high-risk metals pollution. The study also identified the spatial and temporal distributions of total metal concentrations. The high levels metals pollution being determined due to the anthropogenic activities such as: building industries, organic and inorganic chemicals, motor vehicles factories or for leaching of organic mercury pesticides possibly used in the agricultural practices around the area (Avila-Pérez et al., 1999).

Crude oil pollution of the marine waters affects the creatures of the seawaters, which in turn affects most of the environment. The accumulation of trace metals in seawaters has been reported for a number of countries including Gulf countries, Brazil, Korea and Nigeria (Bu-Olayan et al., 1998; Jung et al., 2013; de Souza et al., 2014; Ekpenyong and Udofia, 2015; Freije, 2015). Although there have been investigations on crude oil pollution in marine waters of Sultanate of Oman (Al-Husaini et al., 2014), data on trace metal concentrations and speciation for local seawaters affected by oil pollution are lacking. De Souza et al. (2014) demonstrated that the availability of trace metals at a northeastern Brazilian coastal area under the influence of oil production activities. The study showed that the total levels of Cd, Cu, Pb, Ni, and Zn in seawater samples collected at two different sites of two campaigns were released from oil industry (de Souza et al., 2014). The coastlines of the Arabian Gulf countries are recognised as hotspots for high levels of trace metals due to receiving of intensive industrial and refineries discharges along coastal marines. The marine waters in Gulf countries have been the scenes crude oil spill accidents. For instance, in the 1991 Gulf War, an estimated 10.8 million barrels of oil were spilled in the Arabian Gulf waters. Elevated levels in heavy metals were reported after this major oil spill. Petroleum refinery wastewaters are composed of different chemicals, which include oil and greases, phenols, sulphides, ammonia, suspended solids, and heavy metals like chromium, iron, nickel, copper, molybdenum, selenium, vanadium and zinc. People of the Arabian Gulf are related economically and socially to the sea.

Trace metals accumulated in fish and other aquatic animals from food and water that passes through their gills depending on the quantity of food ingested and trace metals levels present in the food. Accumulation takes more time and probably result in high concentrations in aged and big fish such as mercury in shark and tuna (Bremner, 2002). Approximately more than 97% of the worldwide catch of seawater fish comes from within less than 300 km of shore, and most of the decline in the global fishing industry is attributed to damage of coastal seawaters habitat. The seafood are necessary diet items for local communities and can be commercially exported items (Al-Awadhi, 1999). Marine waters of the Oman Sea, Arabic Gulf and Arabian Sea have been rich in varieties of fish and seafood, which are a main source of food especially for local societies. Al-Yousuf et al. (2000) measured the concentrations of some trace metals in various fish species obtained from different locations along the western coasts of the, Saudi Arabia and Kuwait and United Arab Emirates. This work found that the measured levels metals do not constitute a risk factor for public health and seem to be exceeded the permissible limits for human consumption (Naser, 2013). Study in Kuwait performed by Al-Majed and Preston (2000) measured the levels of Total-Mercury (T-Hg) and Methyl-Mercury (Me-Hg) fish species collected from Kuwait coastal marines. The work found that the concentrations of T-Hg and Me-Hg in 20.6% of the 330 fish species were above the WHO permissible limits, which is attributed to discharges from refineries and petrochemical industries (Naser, 2013).

Table 2.2. Concentrations of selected contaminants with increased concentrations in relation to coastal and marine areas pollution.

Country	Media	Reported Levels	Reference
China (Hong Kong)	Coastal Sediment	Cd, Cu, Cr, Hg, Ni, Pb, Zn and As, 1.3, 171, 51, 0.43, 23, 69, 223, and 7.5 mg/kg respectively.	(Wang et al., 2013).
Pakistan	Coastal seawater (Harbour)	Mg, Fe, Mn, Cu, Ni, Zn, Cr, Pb, Cd, and Co, (1.01-7.47 ug/l), (0.27- 1.05, 0.04-0.27, 0.05-0.43, 0.07-1.86, 0.09-1.77, 0.05-1.04, 0.43-0.62, 0.03-0.2 0.24-0.52 mg/L) respectively.	(Qari and Siddiqui, 2008).
Australia	Australian coastline marine	Cd (125 μg g−1), Pb (2,425 μg g−1) and Zn (7,974 μg g−1)	(Chakraborty and Owens, 2014).
Japan	Coastal sea sediment	Cu, Pb, Zn, Cr, As, 32, 25, 135, 46 and 11.7 (mg/kg) respectively.	(Ahmed et al., 2010).
Korea	Coastal sea sediment	Cu, Pb, Zn, Cd, Cr, As and Hg, 37, 35, 122, 0.25, 58, 9.1 and 0.05 (mg/kg), respectively.	(Hwang et al., 2015).
Singapore	Coastal environment	As, Cd, Cr, Cu, Ni, Pb and Zn, In the range, 0.34–2.04, 0.013–0.109, 0.07–0.35, 0.23–1.16, 0.28–0.78, 0.009–0.062 and 0.97–3.66 μg/ L, respectively.	(Cuong et al., 2008).
Iran	Coastal seawater	Cr, Zn, Cd and Pb, Range, 80-123, 61-97, 63-87 and 82-120 μg/L	(Saghali et al., 2014).
Iran	Iranian coastal sediment of the Oman Sea	Cu, Pb and Ni, 38.28, 50.37 and 26.90 μg/g, respectively.	(Peer and Safahieh, 2011).
United Arab Emirates (UAE)	Coastal sediment	Co, 45.2 μg/g	(Freije, 2015).
Oman	Coastal sediment, Al Fahal Port	Pb, Cd, V and Cu, 10.5, 1.8, 42.0 and 13.6, respectively.	(Al-Husaini et al., 2014).
Saudi Arabia, Jeddah Coast	Jeddah Islamic Port	As, Pb, Cu, Zn 0.31, 1.2, 0.40 and 0.41 (mg/L).	(Ali et al., 2011).
Bahrain	Coastal sediment	Pb, 111 mg/kg Cu, in the range, (4.53–119 μg /L).	(Freije, 2015).

Additionally, the source of freshest water in many Gulf countries obtained through desalination of seawater, which is account for more about 60% of the global total production. Large amounts of water from desalination plants were rejected due to the daily discharged trace metals to coastal waters. High concentrations of trace metals have been reported at the proximities of numerous desalination plants along the coastline of the marines Arabian Gulf (Lattemann and Höpner, 2008; Abdul-Wahab and Jupp, 2009). A numerous of trace metals contamination studies in coastal and marine areas were carried out globally were investigated in wide varieties of coastal media as shown in **Table 2.2**.

The Gulf in general and the Sea of Oman in particular represent a good example for the study of the relationship between the levels of trace metals and coastal situations (de Mora et al., 2004). Al Fahal port in Muscat and Sohar industrial harbor are the main locations for main economic activities involve crude oil transport, so there is the possibility of organic and trace metal contamination in the marine waters around these areas due to oil spills and leakage (Al-Husaini et al., 2014).

The cumulative information available on the levels of trace metals in coastal seawaters impacted by industrial and crude oil contamination is generally patchy and does not provide a complete picture of their migration, speciation and distribution in the Arabian Gulf countries and Oman Sea. Thus, monitoring study of trace metals in marine coastal seawater is crucial; to understand the source, distribution and fate of chemical contaminants in seawater in order to formulate effective plans and strategy for managing the marine system and protecting coastal environments. Furthermore, it is necessary to provide useful and reliable data for assessing trace metals contamination in the coastal seawater and predicting the influence of crude oil and industrial contaminants on trace metals loads in marine waters. Thus, to ascertain that marine waters quality with respect to trace metal concentrations are within acceptable levels for protecting both environmental health and public health (Hwang et al., 2015).

Effect of ionic substitution on toxicity.

Research on metal speciation and bioavailability in seawater shows that they vary considerably due to different ionic strengths and concentrations of organic ligands (Langston and Bebianno, 1998). Adsorption is insignificant for all metals because of high ionic strength, which reduces the density of metal ions on particle surfaces due to a competitive exchange process (Connell, 2005).

The ligands in seawater are occurring as complexes with metal ions in the presence of other major salinity components such as Ca^{2+}, Mg^{2+}. It must be noted that marine systems are considered as a ligand buffer of L in large excess concentrations of Ca and Mg. Thus, stability constants of a trace metal complex in freshwater can be higher than in seawater (Hirose, 2006). The competition in seawater between Cu and the major cations in seawater (i.e. Ca^{2+}, Mg^{2+}) for the same binding sites on the surface of the algae increases. This increased competition may explain the observed reduction in copper toxicity. Jones and Thomas (1988) investigated the effect of industrial activities and seawater originated humic ligands, NTA, EDTA substances on Cu, Pb and Zn speciation in contaminated areas. The work revealed the significance effect of metal-DOM on fractionation of these metals in seawater or fresh water (Kramer and Duinker, 2013). With an increase in ligand concentrations, the concentration of free metal ions is shifted towards lower values. These findings suggest that a weaker ligand has a greater influence than a stronger ligand on decreasing Cu toxicity in marine microorganisms. This agrees with the knowledge that a weaker ligand dominates in the speciation of Cu in coastal waters where Cu exists in higher concentrations (Donat et al., 1994).

2.3. Organic matter in seawater

The term “organic matter” can be used to describe all hydrocarbons found in aquatic environments or waste material other than living organisms and specific organic compounds originated from anthropogenic sources (Nollet, 2005). Dissolved organic matter (DOM) cannot be correctly considered as a chemical solution; it is a very small colloidal suspension. With filtration over 0.45-µm filters pore size it is possible to discriminate between particulate or organic matter (POM) and (DOM).

DOM is present in all aquatic environments and creates one of the largest pools of reduced carbon on Earth’s surface (Nebbioso and Piccolo, 2013). Dissolved organic matter (DOM) is a huge organic reservoir in the seawater composed of a variety of organic compounds, which are the main source of organic ligands, that acts as a chelating agent for trace metals and other nutrients, thus playing a key role in their circulation and availability (Ogawa and Tanoue, 2003; Matar et al., 2013). The nature of DOM in seawater presents in complex forms include humic substances, and a lesser extent fulvic acids, glycolic acid, and the molecular class of fractions such as peptides, amino acids. However, the humic substances in seawater are rare and complex mixtures of different molecules with numerous functional sites of a wide molecular weight range (Duursma and Dawson, 2011). Humic substances have been demonstrated to occur in coastal marine waters at levels of ranged between 40 µg/L and 400 µg/L, which is equivalent to 1-10 nmol/L, and at 1 nmol/L concentration in seawater (Yang and van den Berg, 2009). Other work performed by Dryden et al. (2007) on complexation of Cu with organic ligands in estuaries, however it is significantly less than that obtained for Cu complexation in marine waters, indicating that the humic substances are in a weaker type and are thus not the main ligands for Cu in seawaters (Kogut and Voelker, 2001; Whitby and van den Berg, 2015). In coastal areas DOM may consist of anthropogenic chelating ligands such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetate (NTA), phosphates, citric acid and various surfactants released from anthropogenic origin (Ndung'u et al., 2003). Substantial DOM inputs through industrial and oil refinery activities such as discharges into harbours are estimated to contribute high levels of organic ligands to the marine waters. In aquatic systems, DOM associated with polycyclic aromatic hydrocarbons PAHs and suspended organic or inorganic particles are in surface waters, which influence the transport, and distribution of contaminants in ecosystems (Shi et al., 2007). PAHs in contaminated marine waters span a wide range of molecular weight and associated physical/chemical properties. The solubility of aromatic hydrocarbons is governed by MWCO, salinity and temperature. The solubility of PAHs is inversely correlated with salinity and MWCO, and directly with temperature (Neff, 2002). Previous studies have shown PAH that industrial and oil contamination elevate the concentrations of DOM and influence their composition and trace metals measurements in the aquatic environment (Zhou et al., 2013).

2.4. Trace metals speciation in seawater

The distribution, mobility, lability of trace metals and their physicochemical associations in marine systems are essential to control the geochemical behaviour and bioavailability of various chemical forms and species (ABBASSE et al., 2003; Hirose, 2006). To avoid any misunderstanding, the International Union of Pure and Applied Chemistry (IUPAC) has defined chemical speciation as follows (Karst, 2004; Hirose, 2006):

- ***Chemical species.*** A specific form of an element defined as to isotopic composition, electronic or oxidation state, and complex or molecular structure.

- ***Speciation analysis.*** Analytical process for identifying and/or measuring the quantities of one or more individual chemical species in a sample.
- ***Speciation of an element; speciation.*** Implies knowledge of the distribution of an element amongst defined chemical species in a system. If elemental speciation is not feasible, the term fractionation is in use,
- ***Fractionation.*** Fractionation, which is distinguished from speciation, is a process involving the separation of an analyte or a group of analytes from a certain sample according to physical (e.g., size, solubility) or chemical (e.g., binding, reactivity) properties.

The term “speciation” is used to specify the physicochemical form of a particular element of interest. Three ways can be used to define speciation **Figure 2.1** (Lead et al., 1997).

Firstly, it is based on physical attributes such as size, density, electrical charge and shape. These attributes are usually measured by using fractionation methods such as dialysis, filtration, electrophoresis, and centrifugation. Fractionation can be dynamic like filtration or reflect equilibrium conditions like dialysis. The second way is based on complex lability with indirect estimated size from mass transport phenomena using experimental kinetic methods such as voltammetry. The third way is based on free ion activity or concentration at equilibrium that is measured by using an equilibrium speciation method (e.g. ion selective electrodes or batch techniques equilibrating a solution with ion exchange resin).

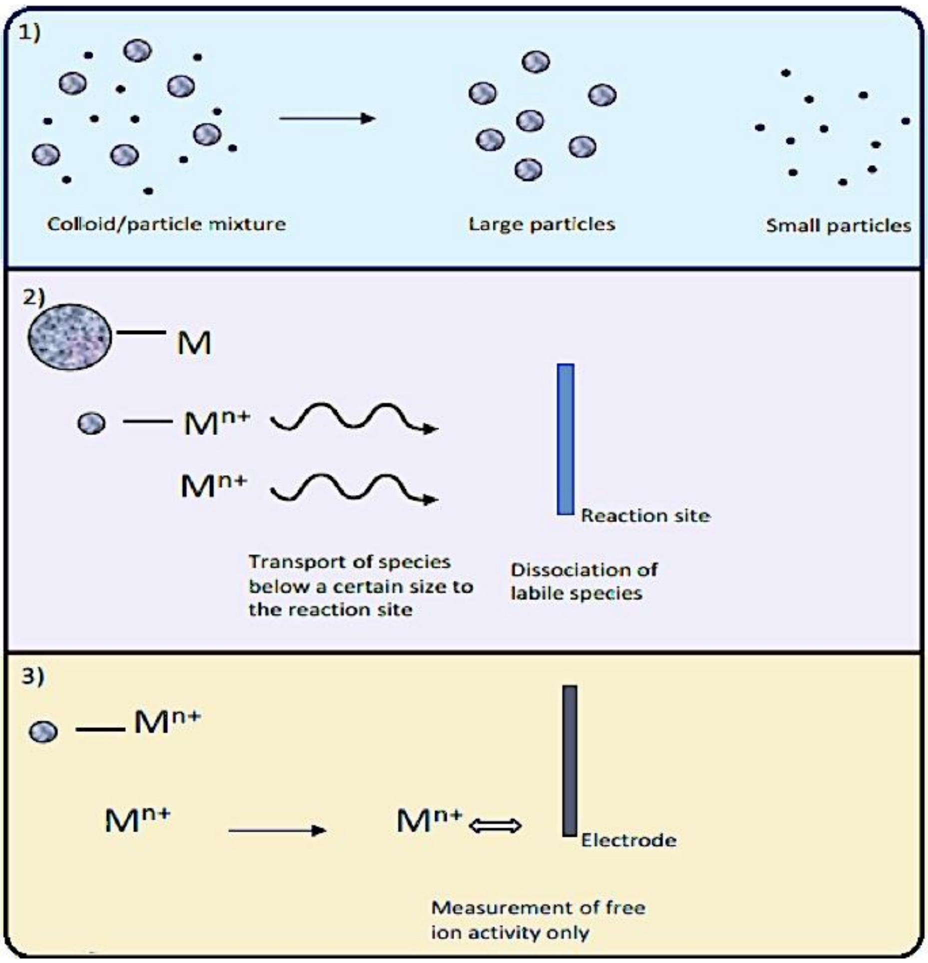


Figure 2.1. Representation of three types of speciation: 1) fractionation; 2) kinetic; 3) equilibrium speciation (Lead et al., 1997).

Most trace metals existing in seawater are distributed between different oxidation states in complexed forms (Holland and Turekian, 2010). At equilibrium, the trace metals species in seawater are influenced by various factors including pH, ionic strength and redox potential of the system that evaluate the progress of electron transfer reactions. The dissolved forms of trace metals mostly occur as free hydrated ions, ion pair, or are associated with inorganic and organic ligands of different molecular sizes forming complexes varying in stability according to their chemical properties (Morel and Hering, 1993; ABBASSE et al., 2003; Hirose, 2006). The trace metals may form, with the main inorganic ligand, neutral complexes which, in principle, are almost always very labile (ABBASSE et al., 2003; Bayen et al., 2009). For instance, trace metals can form labile complexes with inorganic ligands such as, SO_4^{2-}, CO_3^{2-} and OH^-. Moreover, many complexes able to form labile metals complexes except larger molecular weight of organic compounds like humic substances (Bernhard et al., 1986). The mobility and bioavailability of these metals fractions can be affected by various factors including pH, nature of the sorbents, presence and concentration of organic and inorganic ligands, including natural systems processes, humic and fulvic acid, microbial metabolites and nutrient, especially in marine waters impacted by economic activities (Balistrieri et al., 1992). Thus, combining kinetic and dynamic information together with the analytical data can provide reliable information on the bioavailability of metals in contaminated seawater (Forsberg et al., 2006). It is rarely feasible to measure the concentration of an individual complex. Most of the methods used to measure trace concentrations give the total element contents irrespective of the speciation. According to the total concentration, pH, Eh, chemical composition of the system and the complexation constant of the assumed complexes, the portion of metals corresponding to their chemical forms can be modeled. It is importance to know the concentrations of metal species in the marine environment to predict the toxicity and bioavailability.

The complexation of trace metals by organic and inorganic ligands in seawater is an important issue, as it determines to a large extent their bioavailability and mobility (Hirose, 2006). Although the concentrations of organic matter in the seawater exist at about 0.01% of the total level of salts, they may also be derived from phytoplankton. Crude oil entering seawater through anthropogenic activities can be an additional source of organic matter. The kinetics of associations of trace metals with different size fractions of dissolved and particulate organic and inorganic materials is extremely variable across different highly dynamic environment systems (Wells et al., 2000). The concentration of metal ions M in seawater can be given as a total of concentrations of varied chemical species of metal ions:

$$M = M^{n+} + \Sigma[MB] + \Sigma[MC] + \Sigma[M_{particles}]$$

M^{n+} : Free ion concentration.

$\Sigma[MB]$: Total concentration of inorganic complexes.

$\Sigma[MC]$: Total concentration of organic complexes.

$\Sigma[M_{particles}]$: Total of metal chemical form complexes with particles.

In a complexing medium the supply of metal species to interface always depends on the kinetics of the complex association and dissociation reactions. The inorganic ligands in seawater such as OH^-, Cl^-, SO_4^{2-}, CO_3^{2-}, S^{2-}, (HCO_3^-, and HS^- are included implicitly) usually form labile and very mobile complexes due to their high rate constants of formation and dissociation of the kinetic flux of metals toward the interface, so that diffusion of the metal species becomes rate determining (Morel and Hering, 1993; Pinheiro et al., 1999). The complex formation reaction of metal ions (M) with ligand (L) can be presented as follow:

$$M + L \ \underset{d}{\overset{a}{\Leftarrow\Rightarrow}} \ ML$$

The conditional stability constant, $K^C{}_{ML}$, can be defined as:

$$K_{ML}^{C} = \frac{[ML]}{[M^{n+}][L]} = \frac{K_a}{K_d}$$

There is a similar situation for weakly complexed metal-DOM. Stability constant is an important factor that can be used for characterising the metal complexation with organic ligands. It is thermodynamically unique for metal complexation with DOM (Chester, 1990; M.L.S. SIMÕES GONÇALVES, 1997).

In contrast, metals form more stable complexes with strong DOM compounds in the contaminated marine waters with oil constituents discharged from refineries and aromatic industries. Consequently, inorganic and organic trace metals complexes can be categorised electrochemically as either labile or non-labile (inert), according to the their association-dissociation rate constant (Chester, 1990). The supply of metal species from the complexing system towards an interface is strongly influenced by the kinetics of the complex association/dissociation reactions, regardless of whether one is dealing with living organisms in a marine system, or with an electrode in voltammetry, or with a membrane in a separation process (Pinheiro et al., 1999).

2.5. Sources of Oil in the Marine Environment

Crude oil provides approximately more than a third of energy consumption in the world, which has led to increases in the condensates of oil extract, refinery inputs and utilization, imports and exports worldwide (Brown et al., 2014). Concerns about the marine environment with increasing oil spill accidents and petroleum inputs into marine waters started to grow as well (Kennish, 1997). Oil enters the seawaters from multiple natural and anthropogenic sources, notably leakages from refineries, industrial wastewaters, tanker spills, losses from ships during transportation, production facilities, marine terminals and natural seeps (Kennish, 1996; Board and Board, 2003).

Petroleum hydrocarbon inputs into worldwide marine waters can be categorized into four major activities including natural seeps, extraction, transportation and consumption. *Natural seeps* contribute to the amount of oil to the marine environment, accounting around 46% of the annual load of petroleum constituents to the global marine waters exist when crude oil seeps from geologic formations below seafloor into seawater (Board and Board, 2003). These seeps are often found in regions where most of the crude oil extraction activities are located. As a result, vast amounts of petroleum constituents, surface slicks and tar balls caused by seeps are usually attributed to the releases from oil platforms, and significantly alter the nature of ecosystems around them (Board and Board, 2003). It is remarkable that massive rates of petroleum contamination in the marine systems worldwide are based on the availability of these seeps (Kvenvolden and Cooper, 2003).

Table 2.3. Sources of oil inputs in the marine systems from human activities.

Percentage of Oil Inputs in Marine Environment	**Derive From**
65.2%	- Discharges of municipal and industrial wastes. - Ocean dumping. - Atmospheric fallout.
26.2%	-Transportation (tanker accidents, deballasting and dry docking)
8.5%	Released from fixed installations such as coastal refinery, marine terminals and offshore productions facilities.

By inspecting the data shown in the **Table 2.3**, it is obvious that most of the oil entering marine waters originates from anthropogenic activities and exceeds natural sources (Kennish, 1996).

Extraction of petroleum associated with the release of both crude oil and refined products as a result of anthropogenic activities attributed to the efforts of petroleum production. The nature and size of these releases is highly variable, but is restricted to regions where active oil exploration and industrial development are concentrated. Nowadays, only about 3 % of the accidental oil spills in marine waters derives from platforms (Board and Board, 2003).

Transportation of petroleum associated with the refining and distribution of crude oil or refined products; results in releases of variable sizes of oil due to spills (e.g. tankers and pipelines leakages accidents) (Board and Board, 2003). *Petroleum consumption* either from cars, marine vessels, airplanes or industries contributes to the enormous majority of marine environments oil constituents' contamination introduced through anthropogenic sources. Unlike others sources, inputs from this category exist almost solely as slow, chronic releases (Board and Board, 2003).

2.6. Oil Contamination in the Oman Sea

The Sultanate of Oman is one of the countries in the Gulf's oil Arab states located on the southeast of the Arabian Peninsula. Oman produces 980,000 barrels per day of crude oil. Of the produced oil in the world, more than 50% is transported through Oman Sea (Eissa-MA and Moharamy, 1990). This has led to an increase of crude oil activities in the economic harbours of the Omani coast (e.g Al Fahal, Sohar and Al duqum), which have therefore resulted in gross oil contamination of the marine environment and a reduction in Omani environmental marine quality (Awad et al., 1990; Al-Husaini et al., 2014). Oil industries (refining) in Al Fahal port and Sohar industrial region in particular represent the perfect example for the study to investigate the effect of oil spills on marine systems.

Al Fahal harbor being a heavily oil industrialised region in the Sultanate of Oman is thought to be a major contributor of marine environmental pollution due to receiving large oil loads. It contains three Single Buoy Mooring (SBM) systems, which are distributed in separate locations in the harbour. The stored crude oil at the tank farm is loaded onto tankers via two SPMs and the refined petroleum products are imported and exported using the third SPM. Furthermore, Al Fahal bay lies close to the most trafficked tanker routes in the world (Al-Husaini et al., 2014).

According to Eissa-MA and Moharamy (1990) the region of Al Fahal harbor and its surroundings are particularly vulnerable to crude oil contamination build-up. This owing to the measured high concentrations of polyaromatic hydrocarbons (PAHs) in all collected samples, especially for samples collected from Al Fahal harbor regions, which shows that discharges from the refinery activities and ship bilges are principally contribute to the seawater contamination beside the known ballast waters from the tankers anchoring at the SBM systems (Eissa-MA and Moharamy, 1990; Badawy et al., 1992; Al-Husaini et al., 2014).

The Sohar Industrial Area (SIA) approximately 123 km^2, represents another practical case study for assessing the levels and typologies of inorganic and organics contamination in Omani marine waters. It receives municipal effluents from industrial and refinery activities, where it refines crude oil produced in Al Fahal harbor in Muscat. A previous work (Alshuely et al., 2009) conducted on 63 coastal sediments samples from different sites around Sohar Industrial Area (SIA) provided a clear picture of the trace metals and crude oil contamination of the region emphasising the risk associated to the elevated Ni, Cr, Mn and V due to illegal discharges of industrial wastes and refined oil constituents from ballast tanks by tankers passing offshore in route to the Gulf (Al-Shuely et al., 2009). The higher levels of Ni, Cr and V in sediment samples were believed to be owing to the sourcing of oily waste during the export and import of crude oil in the harbour. Vanadium and Ni are the most abundant metals primarily existing in organometallic forms in crude oil. They can be used as an important factor for fingerprinting the source of oil contamination in marine systems (internal marker for hydrocarbons contamination) (Al-Husaini et al., 2014).

According to Folwer et al. (1993), most sediments around the coasts of the Omani Sea contain more than 20 mg/L of vanadium (Fowler et al., 1993; Al-Husaini et al., 2014). The study confirmed the provenance of the hydrocarbons and trace metals in the marine waters around the harbour as derived from the crude oil and industries related activities in the region.

Although various studies deal with heavy metals contamination in Omani marine systems and their adjoining coastal waters; both with respect to aqueous phase and sediment and soil phases, very little work has been carried out from the metals ions angle. Besides, there has been a lack of adequate comprehensive work using a reliable dynamic technique for assessing the effect of crude oil constituents on trace metals bioavailability (speciation) in Omani marine waters around the refineries and heavy industrial areas. The present study will discuss the change in mobility and liability of the selected metal species considering the potential influence of industry and refineries on the chemical cycles of metals in Omani marine systems.

2.7. The Fate of Crude Oil Spills on The Marine Systems

An understanding of the behavior and the environmental fate of the spilled oil are necessary in order to understand and predict the extent of any environmental impacts, which are useful to limit the damage caused by spills and facilitate cleanup strategies (Dutta and Harayama, 2000; Klemas, 2010). When crude oil enters the marine system, it undergoes a number of physical, chemical and biological processes (weathering), which start acting on it, and determinates fate **Figure 2.2** (Snow et al., 2014).

Typical crude oil has a density slightly less than that of water of 0.85 g/ml, and this factor combined with abiotic (e.g., water temperature, wind, tides, wave action, current) and biotic (e.g., microbial activity) factors leads to the rapid spread of the spilled oil over the sea surface as a single slick depends on the extent of the viscosity of the crude oil (Dutta and Harayama, 2000; Kennish, 2000). The slick starts to break up under the force of the wind and wave action, to form a narrow band parallel to the wind direction.

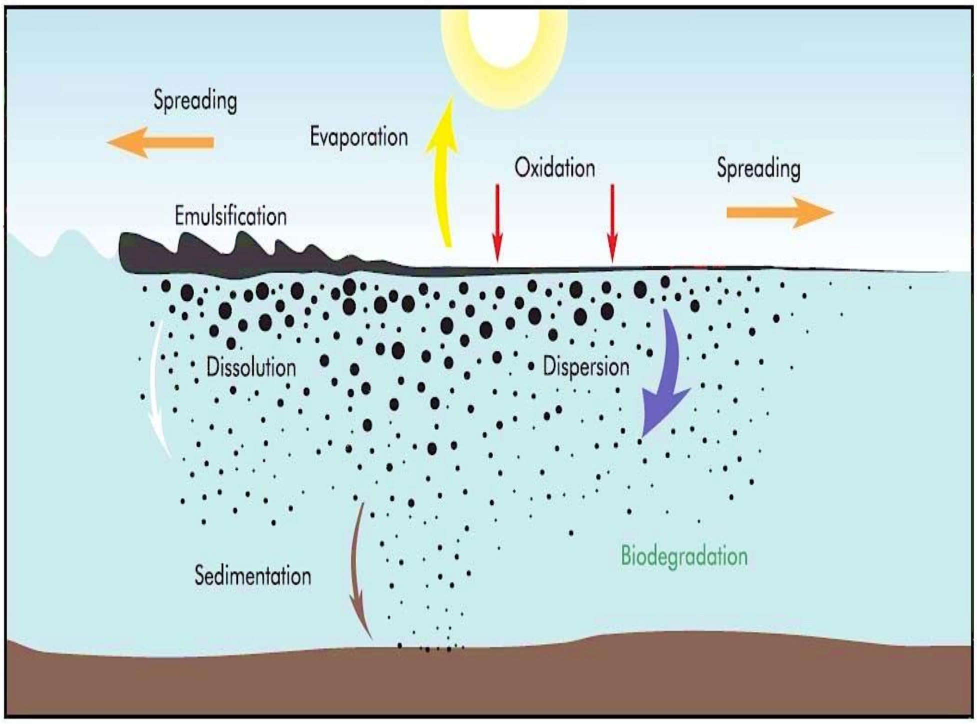


Figure 2.2. Processes (weathering) determining crude oil fate (Snow et al., 2014).

During the first days after the oil enters marine water, those constituents of crude oil (lower molecular weight components) volatise within one day, leading to the removal of about 35% of the initial constituents and the water surface becomes enriched with high molecular weight fractions (Dutta and Harayama, 2000; Sharma et al., 2002).

Dissolution process competes with evaporation on the overall rate of oil slick disappearance. The solubility of oil components is highly depending on the extent of oil dissolution in seawater. Moreover, the solubility of crude oil components decreases with the increase oil quantity and substitution reactions. For instance, aromatic compounds are more soluble in seawater than aliphatic compounds. This influenced by various parameters include oil source, oil composition, viscosity, photooxidation, winds and waves (Kumar and Häder, 2012).

Evaporation and emulsification appear to be the most important and dominant weathering processes following spreading, which can greatly increase pollutant volume and the density of the residual oil slick. This will hinder and slow down the mechanical removal of oil from the sea surface and delay other clean up processes such as microbiological degradation and sediment dispersion (Sharma et al., 2002; Fingas, 2012; Kumar and Häder, 2012).

The species composition of the floating oil is further governed by photooxidation, biodegradation, and dissolution into the marine water (Dutta and Harayama, 2000). Photooxidation is considered to be a potentially significant process affecting the chemical composition of oil spilled in the marine, but it is still not well characterised (Morrison and Murphy, 2010). The photochemical operation produces a variety of oxidized components elevated due to the high solar radiation of oil films (Morrison and Murphy, 2010; Fingas, 2012). The increased solubility is attributed to the formation of polar aromatic and aliphatic component species fractions in the seawater including alcohol, ketones, aldehydes, carboxylic acids, hydroxides, sulfoxides and phenols forming water-soluble fraction (WSF) (Board and Board, 2003).

Biodegradation is one of the primary factors affecting crude oil degradation. It is a natural process by which microorganisms such as fungi, bacteria and yeasts can partially or completely breakdown crude oil into soluble fractions, CO_2, nutrients and energy (Kennish, 1996; Board and Board, 2003). The rate of biodegradation is highly governed by salinity, oxygen, nitrogen and phosphorous in the water and the temperature (Fingas, 2012). At the end of the process, the high molecular weight molecules are involved in a metabolic operation called oxidative phosphorylation, or respiration (Prince, 2002).

2.8. The effect of crude oil contamination on trace metal concentrations

Crude oil is a complex matrix composed predominantly of chemical compounds that can be categorized as either saturated or aromatic hydrocarbons that vary in appearance and composition from one oil field to another. Crude oils vary according to the abundance of the components in the parent oil (Ahmad et al., 2010). It consist of low portion about 3% (v/v) of elements such as nitrogen, sulphur and oxygen, and less than 1% (v/v) of trace metals depending on the geochemistry of well it extracted from (Winegardner and Testa, 2000).

Various studies recognise that all oils contain trace metals at varying concentrations according to the geochemical conditions in which oil source beds originated (Witherspoon and Nagashima, 1957). The effect of crude oil on the trace metals concentrations in the marine systems depends on the type and composition of oil, solubility of crude oil components in the seawater to form water soluble fractions and the period of time under which the medium may remain in contact with oil (Eriyamremu, 2013). Conversely, the increased availability may result in weak bonds to the organic complexes (Relić et al., 2005; Iwegbue, 2011). The distribution and speciation of trace metals in marine systems have been shown can be affected by metals concentrations, abundance of organic ligands and colloids that transferred from oil to water. It is very challenging to assess the effect of every chemical exist in crude oil mixture. This is attributed to the complex molecular composition of crude oil and its chemistry, which alters from field to field. Despite of the extensive efforts devoted to studying metal contamination of aquatic systems, little attention has been paid to their potential contamination derived from oil spills. The main focus has been on the organic constituents as the only chemical contaminants (Patin, 1999; Maktoof et al., 2014; Pimsee et al., 2014). This is reflected in the very limited published works studying the metal pollution in the seawater following oil spill contamination. Apart from the published studies after the Prestige crude oil accident in the coastal marine waters of Galicia (Laffon et al., 2006), there are rare studies reported similar situations, i.e. the Gulf countries coasts after the Gulf War spills (Bu-Olayan et al., 1998; Freije, 2015). The fresh and marine waters in Egypt were also polluted due to tanker oil loading and waste effluents discharge (Shimy, 1997). The marine waters in Arabian Gulf countries were exposed to an enormous oil spills accidents in 1991 in which about 6–8 million barrels of Kuwait crude oil were released into marine waters as well as different spills from other oil operations and tankers oil related spills (Freije, 2015). De Souza et al. (2014) found that the measured fractions of trace metals Cd, Cu, Pb, Ni, and Zn at northeastern Brazilian coastal seawaters were under the influence of oil production activities. The metals (Cd, Co, Cr, Mo, Ni, Pb, V, and Zn) were measured in the marine waters were collected from various sites on the Saudi and Kuwait coasts after Gulf war. The studies concluded that the elevated levels of trace metals have been attributed to the Gulf War oil spills (Bu-Olayan et al., 1998; Freije, 2015).

Therefore, metal contamination in combination with crude oil pollution in seawaters could pose a more serious challenge for monitoring and protection of marine system. It is crucial to have techniques that can measure metal concentration and speciation correctly and reliably.

2.9. Different techniques for measuring metal speciation

2.9.1. Equilibrium methods

A great challenge in the area of trace metal monitoring is the development of an ideal speciation technique adequately sensitive and selective enough to be applied directly in aquatic systems without any or minimal perturbation of the sample (Patterson, 1987; Pujol et al., 2014). Due to the development of the Free Ion Activity Model (FIAM) in the 1970s (Batley et al., 2004), the uptake of metals by the biota in aquatic system is related to the free ion activity of the metal in water, some equilibrium speciation techniques have been developed for measuring free ion concentrations. Some of these methods are briefly described in the following section.

2.9.1.1. Potentiometric methods

Potentiometric measurements with ion-selective electrodes (ISEs) are sensitive analytical methods for discriminating free metal species. They can be used for investigate metals distribution and transfer in the environmental compartments in fresh water at low concentrations millimolar (Broekaert et al., 2013).

However, there are various weaknesses in the use of these methods. First, the detection limit of using ISE response to free ions is quite high at about 1µmol/L. In addition, they are inapplicable in marine waters for metals cations analysis, owing to the high ionic strength and presence of matrix interferences effects (Sadiq, 1992).

Despite ISE having been improved by a factor of up to one million and the discrimination factor of interferences from ions by up to one billion, it is allowed to limit the number of trace metals at their levels in seawater such as Cu, Pb, Cd and Zn which do not include Ni^{2+} and it cannot identify some metals such as ligands (Bakker and Pretsch, 2002; Ure and Davidson, 2008).

The potential of a single half-cell cannot be measured directly. Thus, the potential of a lone indicator electrode is measured against a reference electrode in the test solution of which it is constant (Broekaert et al., 2013). The response of potentiometric electrodes to samples is regulated by various factors including composition and thermodynamic and the kinetic properties of the membrane on the electrode, solution, membrane/analyte and membrane/solution interfaces (Burtis et al., 2012).

2.9.1.2. Permeation Liquid Membrane (PLM)

Permeation Liquid membrane (PLM) is a pre-concentration method based on the carrier-mediated transport of the metals ions across a hydrophobic membrane, which separates the two aqueous compartments. It can be used for an *in situ* discrimination between various trace metal species (Gunkel-Grillon and Buffle, 2008). The PLM is composed of a thin polymeric support soaked with a water insoluble organic solution containing a carrier.

The latter discriminates chemical fractions of interest in the hydrophobic membrane and enhances their diffusion in the membrane. The targeted metals species transport through the membrane and finally will released into receiving solution (strip). Metals will form more stable complexes in the strip than with carrier in the membrane or they will dissolve in the solvent. In either case, the analyte will continue to transport to the receptor through the membrane and at the end it is released by more stable metal-ligand in comparing to that of sampling solution. This happens due to the tailor-made carrier that impregnates the membrane, which is selective for a given trace metal, thus allowing the use of this technique for a broad spectrum of elements. Then the metal of interest will be allowed to pre-concentrate in the receptor (strip) solution, which might be subsequently analysed using ICP-MS. This diffusion process is regarded as an extraction and back extraction sequence combined by transport across the membrane and in solutions. In both extractions processes at both sides of the PLM membrane, liquid–liquid interface is involved (Scarpetti, 2007). Thus, PLM can be operated for free metals ions concentration measurements, labile hydrophilic through a liquid membrane with respect their fluxes providing adequate information for metals speciation researches (Slaveykova et al., 2004). The overall transport flux that is driven by the chemical potential gradient between solutions on each side of the membrane is influenced by: (i) mass transfer to the membrane including diffusion of the metal through the solution diffusive boundary layer; (ii) complexation/dissociation in the diffusive boundary layer; (iii) complexation/dissociation by membrane based on carriers and (iv) transfer through the membrane (Slaveykova et al., 2004).

Although the PLM method is simple and quick, the measurements of free metal ion concentration or the total concentration of labile complexes depend on conditions e.g. pH. Another drawback of this method is that it is applicable for a limited number of metals such as Ni, Pb, Cu, Cd and Zn (Zhang et al., 2006; Gramlich et al., 2012).

2.9.1.3. Donnan Membrane Technique (DMT)

The DMT is based on the theory of Donnan membrane equilibrium. It can be applied to measure a wide range of free ion concentrations both in laboratory and in situ in the field. For the analysis using cation-Donnan technique, it will be based on the use of a 'donor solution' that contains the 'free' metal ions and their complexes, and an 'acceptor solution' separated by a semi-permeable, negatively charged, cation exchange membrane. The ionic strength is fixed in the receptor solution, inside a chamber and on the other side of the exchange membrane. Due to the negative charge and electric potential in the membrane, the cationic species will be promoted to enter and transport across the cation exchange membrane to the acceptor side until the 'Donnan equilibrium' can be reached.

The negatively charged anionic species are largely excluded from entering the membrane due to the negative charge in the membrane and strongly retarded anions from the transport to the receptor solution. Furthermore, the structure of the membrane could also exclude transport of colloidal particles through the membrane.

The metals concentrations in both sides of the solutions can be measured using an analytical instrument such as AAS or ICP-MS (Temminghoff et al., 2000; Weng et al., 2011). For measuring anionic species where we need to use anion-DMT, a positively charged anion exchange membrane will be applied instead. The anionic species will be allowed to transport through the membrane from the donor solution to the acceptor until so-called Donnan equilibrium can be reached (Weng et al., 2011).

Donnan membrane techniques (DMT) are often restricted by lengthy equilibrium requirements (may take days) and high limits of detection. Therefore, various strategies need to be taken for designing DMT experiments, depending on the limit of detection; whether the addition of ligands is required for accumulation (Collins and Kinsela, 2010; Weng et al., 2011). If the free ion concentration in the sample is below the detection limit of the analytical technique, a ligand needs to be added to the acceptor side. Subsequently, the time required to reach equilibrium is decreased and the limit of detection will be reduced to accumulate labile ligands of interest (Weng et al., 2011).

2.9.1.4. Equilibrium dialysis

The equilibrium dialysis method has been used in environmental studies to fractionate metals species according to their differential rates of diffusion through porous membranes. The discrimination of metals species depends on the pore size used in dialysis membranes.

However, some relatively high molecular weight species smaller than pore size may transport through the membrane (Saxena, 2013). The membrane materials can be from cellulose nitrate, collodion or gelatin. The receiving phase in the equilibrium dialysis can be either a chelating binding layer or small volume of blank solution with the same ionic strength as the outside solution.

The transport of negatively charged species can be impeded by the charge on the membrane. The diffusion of metal species could be influenced also by other factors including membrane swelling, adsorption effects and interaction between solute and membrane (Batley, 1989; Caroli, 1996).

The major drawbacks of the dialysis method are: the longtime of equilibration from hours to several days and the negative charge in the membrane causes interferences with the diffusion rates of charged molecules.

Moreover, the leakage of small organic molecules can cause error measurements. If receiving resin is used for ionic metal species, the diffusion of ionic metals species is highly dependent on the metals concentration in the water (Beneš, 1980; Caroli, 1996). The chelating resin, Chelex 100, was applied for environmental study and proved a measurable uptake of Cd, Pb and Zn at low concentrations in water (Vrana et al., 2005).

2.9.2. Dynamic techniques

Dissolved inorganic and organic species in seawater are a complex mixture with various sources and composition, and play an important role in influencing the environmental behavior of trace metal species and their biogeochemical cycles in marine systems (Zhou et al., 2013). With more and more research findings on the limitations of the FIAM, some dynamic speciation techniques for measuring labile metal concentrations have been developed.

2.9.2.1. Voltammetry

Voltammetry techniques have been used in the study of complex systems based on the recording of a current, which flows between electrode and auxiliary electrode regardless of the number of ligands associated with the metal ions. The voltammetric signal depends on the concentration of free metals in the seawater and the reversibility of the redox reaction (Achterberg and Braungardt, 1999).

Lability in anodic stripping voltammetry depends on the kinetics of complex dissociation in the diffusion layer during the time scale of each step during the consumption or release of metal at the electrode surface. The lability of complexes ML depends on the thermodynamic equilibrium at the electrode surface during the redox processes (Coso, 2004). The dissociation time for complex (residence time) in the diffusion layer influenced by layer thickness, and if the rotating disk electrode is well defined hydrodynamically, the diffusion layer thickness and the residence time can be estimated and controlled by altering the rotation rate (Capodaglio et al., 1995).

A direct measurement of labile trace metals is highly in demand for the rapid screening of contaminated marine systems. Voltammetry has been an essential and widespread analytical method, which is applied for distinguishing trace metals species (Stockdale et al., 2015). Voltammetry is based on the current measured as a function of the applied potential for an electrochemical cell. The technique combines two steps including stripping voltammetry and pre-concentration, which enhances sensitivity and selectivity (Denuault, 2009).

During the preconcentration or accumulation step, the trace metal of interest is deposited onto or in a working electrode for a fixed period of time. During the quantification stage the accumulated metal is oxidised or reduced back into solution (Achterberg and Braungardt, 1999). Anodic Striping Voltammetry (ASV) is widely applied for measuring trace metals in seawater at concentrations as low as 10^{-10} M and studying their speciation based on metals lability. In this case the preconcentration stage under forced convection can be carried out using electrodeposition. The deposition potential usually ranged between 0.3- 0.4 V more negatively than the reduced potential of the metals to be measured. During the deposition stage metal ions are reduced to a metallic state, then collected in the Hg and amalgamated with the Hg. Small fractions of metals are normally collected during this preconcentration step (Noyhouzer and Mandler, 2013).

The analysis of sensitivity and selectivity is determined by the preconcentration time of metals ions in the sample. In the anodic scan step, the peak current is can be controlled by various factors from the deposition and stripping steps including metal ion properties, the diffusion of trace metal species to the electrode, metal complexes lability and the reversibility of an electrode process.

During ASV analysis, all the steps may comprise the stirring of the solution using a magnetic stirrer, where the measurement is convection dependent. Measurements using microelectrodes can be performed in quiescent solutions, which is attractive for in-situ deployments in natural waters (Achterberg and Braungardt, 1999). The major difference between macro- and microelectrodes is that planar diffusion occurs on the former compared to radial diffusion in the latter. Microelectrodes are more preferred in field monitoring than macroelectrodes due to theirs unique features, which are (Achterberg and Braungardt, 1999; Buffle and Tercier-Waeber, 2005):

- Their small size enhances direct measurements in low ionic strength freshwater.
- Due to rapid mass transport because of radial diffusion, the reliability of environmental analysis is improved.
- The microelectrode is covered with an agarose gel for developing gel-integrated microelectrodes (GIME) to prevent fouling of its surface. The probe can be used for measurements down to 500 m in seawater and is able to determine trace metals with sub-nanomolar detection limits in the presence of oxygen. This greatly extends the uses of voltammetry for broad field and not only for environmental samples (Buffle and Tercier-Waeber, 2005).

The complexing gel integrated microelectrode (CGIME); and the PLM-GIME micro-total analytical system (PLM-GIME-μTAS) are examples of modified (GIME). CGIME is used for measuring the free metals ions in freshwater systems (Buffle and Tercier-Waeber, 2005).

It is based on placing small amount (μm) of resin gel like; Chelex by depositing the resin layer on the microelectrode array of the GIM, and then followed by deposition of the agarose gel and then electro-deposition of Hg semi-drops. In PLM-GIME-μTAS the GIME used a hydrophobic permeation liquid membrane (PLM) to extract metals species by binding to a carrier and transported by diffusion.

Then a channel consist of strip solution, where the metal complexed and accumulated over a period of time (Buffle and Tercier-Waeber, 2005).

The major drawback of voltammetric measurements of trace metals in freshwaters is adsorption of organic compounds, which arises from the contamination of hydrophobic aromatic and aliphatic functional groups of DOM. This causes an increase of peak current and shifts the peak potential toward more negative values.

Therefore, a Nafion-coated thin mercury film-rotating disk electrode was used to prevent the adsorption and fouling by organic complexes in the contaminated areas. Hurst and Bruland (2005) found that the low thickness used in the Nafion-coated electrode study has no effect on the enhancement, but rather a gradual decrease in sensitivity with increasing film thickness. The observed trend in the values has been suggested as a result of depression of the mercury plating efficiency during the deposition step.

In contrast, studies by HOYER and FLORENCE (1987), and Hurst and Bruland (2005) reported an improvement of sensitivity in DPASV mode by using cation exchange membrane a Nafion-coated of the same film thickness to an increase in redox cycles at the electrode surface during the stripping step. Moreover, to deal with the organic-rich seawater matrix and to measure ASV-labile copper in seawater matrix contains high level of DOM.

Therefore, although these voltammetry methods are useful and powerful, they are expensive and difficult to make in ordinary laboratories. Furthermore, the properties of the electrodes are their inherent stability with very low background currents (Dragoe et al., 2006).

2.9.2.2. Competitive ligand exchange - adsorptive stripping voltammetry (CLE-ACSV)

Competitive ligand exchange-adsorptive stripping voltammetry (CLE-ACSV) is the primary method used for measuring the complexed metals ions and distinguishing metals species in the seawater (Buck et al., 2012). The method involves an exchange reaction with an added ligand followed by electrochemical detection of the adsorbed metal complex using adsorptive accumulation and subsequent reduction of the metal.

The added ligand is usually one which forms rather stable metal-binding complex with metal ion of interest. The ambient ligands, such as tropolone, 8-hydroxyquinoline, salicyl aldoxime, catechol and dimethylglyoxime, usually are added in a large quantity to the sample solution. The added ligand is left to equilibrate with the metal present in the sample for at least 24 hours before analysis (van Leeuwen and Town, 2005; Buck et al., 2012). After the addition of the ligand, the sample solution contains at least three types of metal species; metal-DOM, metal-added ligand and free metal. The kinetic detection window is defined by the requirement of the equilibration phase before the accumulation of the metal complex with the added ligand at the electrode surface. For all metal complexes with stabilities beyond the thermodynamic detection window, the rate constant for dissociation is smaller than that for association of metals to added ligands (van Leeuwen and Town, 2005).

Although the CLE-ACSV is a sensitive analytical technique used in many previous speciation studies, it is not suitable for *in situ* measurement speciation. The AdSV using the hanging mercury drop electrode (HMDE) can detect very low concentrations of metals in samples having a wide range of pH, and rather fast dissociating complexes with high sensitivity and high precision.

2.9.2.3. Ion Exchange Resins

Ion exchange resins (cation and/or anion exchangers) can be used for separating metal fractions according to their chemical structure, stability and kinetic lability. Strong chelating ion exchange resins (complexing resins) like Chelex-100, comprising iminodiacetates, or Chelamine, containing pentamines, have been employed by a number of studies for preconcetrating of trace metals fractions from marine waters and fresh waters samples (Nickson et al., 1995).

Haraldsson et al. (1993) encouraged the use of a speciation system based on metals fractionation on three adsorbents, Chelex-100, SepPak Cl8 and Fractogel DEAE, which differentiate between labile complexes, non-polar organic matter and ion-exchangeable metals fractions (Nickson et al., 1995).

The solid-phase extraction method also was applied with minicolumns packed with Ca-form Chelex-100 to separate labile metal species and define the weakly complexed fraction of different metal ions. The extent of metals species lability can be varied with the time of contact between samples and resins. The time allowed for these techniques-samples equilibration can be altering from hours, in batch extraction method, to seconds, in column stationary phase chromatography. The level of the dissociated metal fractions sorbed onto the resin depends on the amount of the competing metals ions and ligands, contact time between samples and resin and resin capacity (Stockdale, 2005; Bowles et al., 2006; Pesavento et al., 2009).

Although these methods can determine strong ligands, they have some drawbacks. The added resin could change the composition of the mixture and its influence. The organic material can be escaped from the resins (Walther, 1989; Pesavento et al., 2009).

The resins can also be used for equilibrium techniques. The batch extraction technique involves increasing contact time with the small-added quantity of ion exchange resin to the sample by stirring or shaking the mixture and then leaving this to reach the equilibrium. The measured concentrations of free metals in the sample solution can be used to determine the degree of complexation stability according to measured time (Hart and Davies, 1977).

2.10. DGT (Diffusive Gradients in Thin films)

The dynamic technique of diffusive gradients in thin films (DGT) was invented and developed in 1994 by Hao Zhang and William Davison for in situ speciation measurements of trace metals in waters, sediments and soils (Davison and Zhang, 1994; Zhang and Davison, 1995). The technique consists of a plastic piston with a cylindrical cap of 20 mm diameter window comprising three layers. The first one is a resin binding layer laid on the base plate and separated from bulks solution by a well defined diffusive gel layer and filter membrane. The metals species of known diffusion coefficients allowed the transport through the diffusive gel of a certain thickness (Δg) to the binding layer. Numerous binding layers have been developed and are available for extending the range of determinants of trace metals to include other cations, oxyanions and targeted species in aquatic environments **Table 2.4**.

In most studies of measuring cations, the resin layer is made up of Chelex-100 of high affinity whose properties are strongly pH dependent. The resin Chelex excludes large metals colloids due to the pore size of 150 μm and prevents any dissociation of trapped metals to for reproducing metal complexes (Lead et al., 1997; Garmo et al., 2003; Stockdale, 2005; Davison and Zhang, 2012). The DGT device is a time-integrated technique. The gradient of labile factions of metals species in a diffusive layer will be constant until the resin gel becomes saturated. The metals species concentration at the resin gel/diffusive gel interface remains effectively zero, leading to the continuous flux of free ions into a passive device. The DGT device is robust, pre-concentrates analyetes at very low concentration and can be deployed directly in waters without any pretreatment.

Therefore, a low risk of contamination of the sample and chemical changes of the analyte's properties are eliminated. Furthermore, quantitative concentration measurements can be performed in sample solutions with no need for separate calibration. The technique can be used for speciation measurement of trace metals at low concentrations and is applicable for an *in situ* measurement of labile metal species in aquatic systems at a low cost (Munksgaard and Parry, 2003; Peters et al., 2003; Forsberg et al., 2006; Chen et al., 2012).

Table 2.4. DGT development and applications by different research groups.

Binding Layer	Application	pH	Reference
Chelex-100	Most of metals in aquatic system.	4.7 - 6	(Garmo et al., 2003)
AG50W-X cation exchange resin	Measuring of Cs and Sr in natural water.	4 - 9	(Chang et al., 1998)
Silver Iodide (AgI)	Measuring of sulphide, (S) in water.	-	(Teasdale et al., 1999)
Ferrihydrite, $5Fe_2O_3.9H_2O$	Measuring dissolved phospourous, (P) in natural water and oxygenated metals As, V, Se, Sb, Mo,W and U.	2 - 10	(Zhang et al., 1998; Stockdale et al., 2008; Huynh et al., 2015)
Ammonium molybdophosphate (AMP)	Measuring of Rediocaesium in natural waters	6.1 - 8	(Murdock et al., 2001)
cellulose phosphate-based Whatman P81 membrane	Measuring of Cu, Cd, Zn, Mn, Ni, K, Na, Ca, and Mg in natural water.	4 - 9	(Li et al., 2002)
poly(4-styrenesulfonate) (PSS) liquid binding layer	Measuring of Cd^{2+} and Cu^{2+} in Lake water	3 < pH	(Li et al., 2003)
suspended particulate reagent-iminodiacetate (SPR-IDA)	Measuring of Co, Ni, Cu, Cd and Pb in sediment and synthetic solution.	2 - 9	(Warnken et al., 2004)
MBL consisted of ferrihydrite and Chelex-100 cation-exchange resin	Synthetic solution and soil (Cd, Cu, Mn, Mo, P, and Zn).	5 - 9	(Mason et al., 2005)
DGT devices with varying diffusive gel thicknesses	To determine the thickness of the physical diffusive boundary layer (DBL) and apparent diffusive boundary layer (ADBL) in laboratory and natural environment.	5 and 7.5	(Warnken et al., 2006; Levy et al., 2011)
Spheron-Oxin®ion exchanger	Measuring of Cd, Cu, Ni and Pb under laboratory conditions, natural water	6 - 8	(Gregušová et al., 2008)
MnO_2 resin	Radium Ra in water and sediment	-	(Leermakers et al., 2009)
Metsorb and ferrihydrite adsorbents	Measuring As^{3+} in seawater	3.5 - 8.5	(Bennett et al., 2011)
Yeast Saccharomyces cerevisiae	Cd and Pb In seawater and river water	4.5 - 7.5	(Menegário et al., 2010) (Pescim et al., 2012)
Two sequential binding layers Chelex-100, a “front” and a “back” layer.	To investigate kinetic studies of Ni with nitrilotriacetic (NTA) and Suwannee River fulvic and humic acids (FA and HA) in solution at pH 7	6.93-7.08	(Shafaei Arvajeh et al., 2012)
polymer-bound Schiff base (Py–PEI) derived from poly(ethyleneimine) and 2-pyridinecarboxaldehyde as the binding agent (Py–PEI DGT)	Measuring labile Cu^{2+}, Cd^{2+} and Pb^{2+} in waters.	pH 4–8.5	(Fan et al., 2013)

2.10.1. Factors affecting the DGT performance

The DGT sampler has the potential to be a suitable tool for the environmental assessment of water quality monitoring in different fields of research owing to its advantages mentioned above. However, various factors affect its accuracy of measurements, as described and discussed in the following section.

- **Diffusive boundary layer (BDL).**

When DGT is deployed in water, there is a region between the filter membrane and solution known as the diffusive boundary layer (DBL) of defined thickness (δ), where the transport of trace metals species occurs by molecular diffusion. The mass transport changes from advection and diffusion processes in the bulk solution, to diffusion in the hydrogel layer (Warnken et al., 2006).

The DBL is governed by both flow rate and deployment geometry and effectively extends the diffusion gradient (Δg) of the deployed DGT. The immersed DGT in the water is generally negligible in well-stirred solutions and natural waters. Warnken et al. (2006) estimated the DBL thicknesses based on the use of multiple DGT devices of varying thicknesses and different geometric window areas, and found that were no significant differences of measured DBLs at both moderately and increased stirring speed solutions with a mean value of 0.023 cm. Whereas, at unstirred solution the DBL approaches 0.15 cm, which indicating that the DBL cannot be ignored. It is important to take into account material diffusion material MDL when referring to the gradients through the diffusion layer and filter, of total thickness (Δg) DGT measurement in low flow conditions: diffusive boundary layer and lability considerations (Warnken et al., 2006; Davison and Zhang, 2012; Uher et al., 2013).

- **Temperature.**

Temperature is an essential parameter for estimating diffusion coefficient. The diffusion coefficients of most metals were measured at temperatures between 5-35 °C. It is an important factor for calculating analytes concentrations in each DGT deployment (Zhang and Davison, 1995).

- **pH and ionic strength.**

The effect of pH and ionic strength on the performance of the DGT sampler has been investigated in a wide range of pH using different resin gels and diffusive layers. There are some limitations to the DGT sampler connected with properties of Chelex-100 at low and high pH.

At pH 5-9 standard DGT using open pores hydrogel and Chelex-100 binding layer functions best with a ratio of $C_{DGT}/C_{solution} \approx 1$. While at pH <2, the Chelex-100 will shrink and there will be a considerable ionisation, then the adsorptive capacity will be reduced. If the sampler is exposed to the medium of pH>9 the resin gel and diffusive layer will start to swell, which will affect the measurements.

Moreover, the dissociation and association of metal complexation in aquatic system is influenced by pH. The organic acids dissociation will increase at high pH and increase metals complexation (Zhang and Davison, 1995; Gimpel et al., 2001; Huynh et al., 2015).

The response of DGT sampler to ionic strength reflects the effect of ionic strength of solution on the diffusion coefficients analytes. Numerous studies showed that a standard DGT dynamic technique is independent of ionic strength, except at very low strengths ≈ 0.1 mmol/L where the diffusion coefficient is low.

The diffusion coefficients in the sampler at high ionic strength ≈ 0.7 mol/L $NaNO_3$ solution or in seawater have been estimated to be approximately 8% lower than in pure water (Davison et al., 2000; Scally et al., 2006). During the production of DGT it is required to wash hydrogels gels to get rid of any impurities and decrease any products of polymerization that were not reacted. The DGT performance can be affected by gel washing and conditioning. Deploying unwashed diffusive gel at pH ≈ 9 at an ionic strength of 10 mmol/L showed a little effect on DGT measurements, but the measured theoretical response for $C_{DGT}/C_{solution}$ =1. If the hydrogel is not very well washed it will have a negative charge due to the occurrence of reagent products.

The measurement accuracies could be affected by charged diffusive gel due to the created Donnan potential. At pH> 7 rinse water is not enough to remove all impurities. This will give $C_{DGT}/C_{solution}$ >1, due to the increased metal diffusion to the resin at low ionic strength enhanced by the negative charge in the hydrogel. Washing gel copiously at pH <7 indicated that the well washed gel and a ratio of $C_{DGT}/C_{solution}$ <1 may be found at very low ionic strength of 0.1 mmol/L, caused by a positively charged gel hindering the metal flux across the gel to the binding layer.

The DGT measurements can be performed accurately at low ionic strength solutions (I < 1mmol/L) if the diffusion coefficients are provided at the same ionic strength (Warnken et al., 2005; Davison and Zhang, 2012).

- **Biofouling.**

In natural waters, the accuracy of DGT measurements is affected by the formation of biofilms at the surface of the samplers as a consequence of the exposure. Biofilms is an aggregation of bacteria, algae and fungi and also contain extracellular polymers substances resulting from metabolism (Uher et al., 2012). The biofouling growth on the filter membrane affects the thickness of the diffusion layer and hampers molecular diffusion. If the deployment takes more than 7 days, it is recommended to use several types of DGT devices to correct the deviation of DBL thickness. In most cases, the effect of biofilms is not taken into account and can be avoided if the DGT sampler is deployed less than 7 days (Kersanach et al., 2009; Uher et al., 2012; Turner et al., 2014).

Figure 2.3 illustrates a modified cross -section of DGT components and the elution accumulated trace metals from Chelex-100 resin. The gradient of metal species concentration of DGT deployment in solution can be seen.

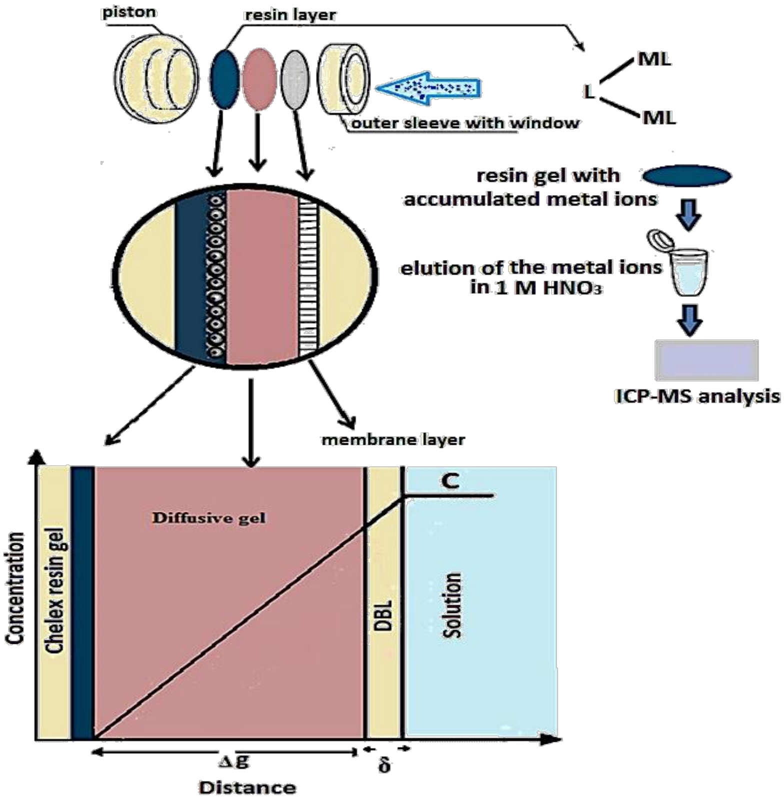


Figure 2.3. Modified cross -section of DGT components and the elution accumulated trace metals from Chelex-100 resin (Zhang and Davison, 1995; Wallner-Kersanach et al., 2009)

The deployed DGT sampler was rinsed with Milli.Q water and the resin was immersed in 1 ml of 1 M HNO_3 for overnight before being diluted and analysed in

ICP-MS. The obtained results were expressed in terms of mass (ng) and concentration (µg/L) of the metal in the resin gel. Where (C) is the solution concentration, Δg is diffusive layer thickness, (A) is the surface area, (D) is the diffusion coefficients; and t is the exposure time. The mass of metal in the resin gel (M) was obtained using **equation (2.1)**:

$$M = C_e (V_{acid} + V_{gel}) / fe \qquad (2.1)$$

C_{DGT} can be estimated by rearranging **equation (2.2)** (Kersanach et al., 2009):

$$C_{DGT} = \frac{M(\Delta g + \delta)}{DAt} \qquad (2.2)$$

Even if all metals ligands in natural waters are considered fully labile, the measured concentrations in DGT using **equation (2.2)** will tend to be smaller than the total content in solution, due to the existence of fractions with diffusion coefficients that are smaller than that of the free metal ions (Zhang and Davison, 2015).

2.10.2. Use of DGT for trace metals speciation measurements

The DGT sampler is capable of distinguishing to an extent the trace metals fractions according to their size and the rate at which they can liberate species (Zhang and Davison, 2015). By using DGT devices with different hydrogels of varying thicknesses and different pore sizes in equivalent, allows for more information on metal speciation (Scally et al., 2003; Forsberg et al., 2006; Degryse et al., 2009).

The following discussion presents the results of some experimental work in the laboratory and in the field achieved by various researchers to assess the performance of DGT under controlled conditions.

To investigate whether the diffusive boundary layer (DBL) is small and can be ignored in well-stirred laboratory solutions, Warnken et al. (2006) used DGT devices containing varying diffusive layer thicknesses (Δg = 0.14 (filter membrane only), 0.54, 0.94, and 1.34 mm) were carried out for 50 h in synthetic solutions of 0.01 mol/L $NaNO_3$ ionic strength containing ~10 μg/L Co, Ni, Cu, Cd, and Pb. The thicker diffusive layer showed a higher accumulated mass of Cd than the theoretical uptake, the thinner 0.40-mm diffusive layer showed the theoretical accumulation in the same synthetic solution, and lower mass accumulated in the device with 0.14-mm gel (filter membrane only) comparing to the theoretical uptake. The work found that the DBL of Cd was 0.17 ± 0.018 mm during this deployment. The obtained DBL thicknesses of metals Co, Ni, Cu, and Pb were ranged from 0.15 to 0.17 mm with a mean value of (0.16 ± 0.0086 mm) with C_{DGT}/C_{SOLN} ratio of 1.23 ± 0.015. The study suggested that DBL cannot be ignored and DBL thicknesses were increased significantly from 0.44 ± 0.014 mm in the synthetic solution stirred at 60 rpm to 1.5 ± 0.13 mm in the unstirred synthetic solution. The study suggested that to obtain a value of 1 for C_{DGT}/C_{SOLN}, it is required to use a larger effective area (A) of 3.08 cm^2 for the soil DGT devices and 3.80 cm^2 for solution DGT devices (Warnken et al., 2006). Levy et al. (2011) used DGT containing different thicknesses (Δg) to investigate the lability of metal-exudate complexes. The study also measured the values for the physical (DBL) and apparent (ADBL) thicknesses of metals Cd, Cu, Al and Fe in synthetic solution. The work found that iron (Fe) metal kinetically limited by the dissociation of Fe-complexes with calculated ADBL values ranged between 1.8 to 2.8 mm. When metals are labile, the measured concentration of metal in the binding layer should be decreased when the hydro gel thickness increases. The study also found that, the concentrations of Fe on the binding layer did not always increase with reducing of hydro gel thicknesses. Moreover, the dissociation of aluminium (Al) from complexes was also kinetically limited in all solutions; however, the Al exudates were more labile compared to Fe species. The work also found that the calculated ADBL values were 0.62 ± 0.09, 0.50 ± 0.07, 0.35 ± 0.07 mm for Al in the synthetic solutions containing C. vulgaris, A. flos-aquae and C. pyrenoidifera exudates respectively. The obtained ADBL values of (Cu) and (Al) were high and attributed to the kinetic limitation in the C. vulgaris filtrate, corresponding to the high stable organic ligands (Levy et al., 2011).

Shafaei Arvajeh et al. (2012) deployed DGT devices containing two sequential binding layers, a “front” and a “back” layer to investigate the penetration into the Chelex binding layer of complexes of Ni with nitrilotriacetic (NTA) and Suwannee River fulvic and humic acids (FA and HA) in solution at pH 7. The study found that in Ni−NTA tests, the accumulated masses of Ni in the front and back binding layers were similar due to the slowly dissociating complexes. For Ni−FA/HA solutions, a higher Ni masses were up taken by the front resin and consistent with rapid dissociation from a high amount of the binding sites. The obtained ratio of Ni in the front/back resins was markedly lower ($p < 0.05$) for solutions containing Ni−HA compared to those found in the solution of Ni−FA, attributed to the less lability of Ni−HA complexes than Ni−FA complexes in similar synthetic solutions containing (FA = 10 mg/L and HA = 8 mg/L). Also the work has shown the potential of using the two double resin gels in DGT device as an alternative approach to using varying thicknesses of hydro gels to obtain kinetic data. Moreover, the work concluded that in situ application of DGT with double binding layers could provide more clear picture regarding the kinetic information of metal organic complexes in natural environmental systems and will improve the perception of metal speciation (Shafaei Arvajeh et al., 2012).

Recently DGT technique equipped with a dialysis molecular cut membrane placed in front of the diffusive gel layer to prevent large molecular metal-DOM to measure only simple inorganic species (Pouran et al., 2014).

Furthermore, the DGT technique can be used to pre-concentrate metals via diffusive transport through the soil solution (Zhang et al., 1998) and induces resupply from metal species associate to the solid phase (Harper et al., 1998) with very good sensitivity, especially at longer deployment time (Davison and Zhang, 1994). It does not significantly cause any changes in physical or chemical properties of soil. It has been showed to behave analogously to plant uptake for a variety of trace metals, including of Cd and Zn (Zhang et al., 2006) and Cu (Zhang et al., 2001). Previous analytical techniques used to predict bioavailability of trace elements have shown some correlations with metal uptake in soils and plants (Guo et al., 1996; Hergert, 1998; Zhang et al., 1998; Buszewski et al., 2000; Zhang et al., 2006; Garrido Reyes et al., 2013). Although DGT technique has been considerably assessed for the purpose of environmental monitoring of soils (Harper et al., 1998; Zhang et al., 2001) no research has been carried out to date on assessing the suitability of the DGT technique for metals speciation in soil contaminated with crude oil.

The performance of DGT has been assessed on a wide variety of solutions ranging from model solutions to direct in situ measurements in lakes, river systems, seawater and sediments. In most seawaters, the trace metals exist in different chemical species such as free ionic, labile bound metal-ligands and non labile more stable metal-ligand, and varying molecular sizes such as soluble colloidal ranged between (nominally >1000 kDa) to less than 0.2 µm) to (particulate >0.2 µm) (Baeyens et al., 2011; Österlund et al., 2012).

Zhang and Davison (1995) conducted a series of tests to assess the performance of DGT in solutions at varying ionic strengths. They adjusted the ionic strength of a 3 µg/L solution with NaNO3 ranged from 10 nmol/L to 1 mol/L. the obtained results were expressed as the ratio of measured concentration in DGT to the total concentration in the solution measured by Zeeman GF-AAS. The measured concentration in DGT was no more than ≈10 % different from the total concentration in the solution, irrespective of ionic strength.

Similar study achieved by Gimpel et al. (2001) using calcium salts to increase the ionic strength similar to the seawater (10 nmol/L). The DGT devices were deployed in solutions contain 5 and 10 Cd and 50 and 100 Cu at varying ionic strengths, 0.1, 1 and 10 mM of Ca. The study found no difference and concluded that DGT devices can be used to measure trace metals in hard waters (Gimpel et al., 2001).

Although the DGT technique has been showed to be very effective for freshwater systems, few works also have been performed in marine systems (Wallner-Kersanach et al., 2009). Zhang and Davison (1995) deployed DGT in the North Atlantic Ocean using different thicknesses of hydrogel. The measured concentration of Cu was 0.15 ± 0.01 µg/L was about twice of the Cu concentration for surface waters of the Atlantic Ocean reported by Li (2000).

Kersanach et al. (2009) used DGT to determine labile fractions of Cd, Co, Cu, Mn, Ni and Zn in the Patos Lagoon estuary in seawater of Brazil. The DGT concentrations of Cd, Cu, Ni and Zn were low because of colloidal ligands in the area affected by pollution from fertilizer, oil and petrochemical industries (Kersanach et al., 2009).

Panther et al. (2012) evaluated DGT performance for measuring the dissolved aluminum (Al) species in seawaters and freshwaters using Chelex-100 and titanium dioxide-based (Metsorb) adsorbents. Metsorb-DGT showed a more accurate measurement for dissolved Al in freshwaters above pH 7.7 and in seawater where the predominant Al species is predicted to be $Al(OH)^{4-}$. However, Chelex-DGT underestimated the dissolved Al concentration in freshwaters (>pH 7.5) and in seawater (Panther et al., 2012).

2.11. Assessment of trace metals availability in soils

Soil quality assessment is one of the key factors for evaluation the extent of contamination in the environment has increasingly emphasised the need to consider metals fractions reactivity in soils around anthropogenic activities (Lock and Janssen, 2001; Masto et al., 2015). Based on various studies, organic ligands, trace metals, inorganic fractions and microbial proportions have been used as soil quality indicators (de Haan and Visser-Reyneveld, 1996; Li et al., 2005; Ivezić et al., 2015). Trace metals in soils can be originated from a natural source or varying consequences of economic activities. Thus, aquatic soils constitute the most important pool or sink of different chemical forms of metals and other contaminants governed by lithology of the soils and rock in contact with them (Liang et al., 2014). Soils scientists have long emphasised that trace metals fractions and their toxicity are essentially absorbed and uptaken by biota from the soil solutions (Zhang and Young, 2005; Wuana and Okieimen, 2011). The behavior of trace metals in soils can be influenced by their sorptions and desorptions reactions with varying soil components and matrix. The bioavailability of trace metals in soil solutions can be influenced by various processes including metals dissociation and release from chemical contaminants (e.g., crude oil, agricultural practices (pesticides and fertilizer), paints and economic ports activities)

(Zhang and Young, 2005; Rocha et al., 2011). Furthermore, the chemical forms of metals in soils; water-soluble fractions, organic/or inorganic ligands, exchangeable and Fe/or Mn oxides bound, are kinetically determine the metals lability and mobility (Iwegbue, 2011). Soil contamination with crude oil has become a global environmental concern especially regions surrounding oil exploration, heavy industries and oil refineries, which are more threatened. Crude oil contains different concentrations of saturated, aromatic, and resins constituents at varying molecular weight (MW) range, depending oil type on degradation and microbial activities as described above (Xiao et al., 2010; Iwegbue, 2011). Within hydrocarbons in soils or sediments derived from spilled or discharged oil, organic complexes matrix, recalcitrant hydrocarbons as poly aromatic/substituted aromatic molecules (Wang and Stout, 2010; Omaka et al., 2011), including resins and hydrocarbons containing different functional groups (like carboxylic acids, ethers, other organic acids etc.), are the most dominant fractions, and represent more than 45% of the released oil components in the contaminated area (Tissot and Welte, 1984; Abha and Singh, 2012; Osam et al., 2013).

In most circumstances, free metals ions, inorganic and organic fractions released from crude oil spill are the key species that influence the trace metals speciation in the soil (sediments) (Guéguen et al., 2011; Majolagbe et al., 2012; Adesina and Adelasoye, 2014; Fu et al., 2014).

However, there is a lack of consistency may be partially interpreted by the lack of a standardised experiments to generate and ensure reliable, reproducible and comparable obtained data. Very little fieldwork has been reported in the literature regarding the effect of crude oil contamination on trace metals loads in soils applying conventional techniques and extraction methods. However, still a lack of important standardised laboratory protocols to better understand the influence of crude oil constituents on the trace metals speciation in soils impacted with crude oil using reliable technique. It was found (Omaka et al., 2011; Shukry et al., 2013; Fu et al., 2014) that crude oil complexes in soils can either enhance or decrease the availability of trace metals depending on the oil composition. The decreased concentrations were probably due to the complexation with strong organic and inorganic ligands of high molecular weight from oil.

Considerable research has been conducted in Nigeria and the Dammam zone in the east of Saudi Arabia on the effect of crude oil contaminated soil on the availability of nutrient elements and the properties of soil (Agbogidi, 2013; Shukry et al., 2013). They treated the soils with different levels of oil (w/w). The results in both areas showed that an increase of trace metals Cu, Mn, Cd and Pb, Fe and Pb in soils and plant tissues with increasing crude oil concentration oil. Iwegbue (2011) and Omaka et al. (2011) investigated the effect of organic and inorganic fractions on the trace metals mobility and bioavailability in soils contaminated with crude oil in the Niger Delta using conventional extraction methods and 0.2-µm nucleopure polycarbonate membrane filters before being analysed for metals by atomic absorption spectrophotometry (Perkin Elmer, A3100). Cu and Cd were found at low concentrations in the soils affected with oil due to the formation of organometallic complexes with organic matter from oil. Ni and Cr were governed by residual fractions and found at higher concentrations maybe due to their release from oil contamination. Fu et al. (2014) pointed out that oil industries in the field contribute to the trace metal loads in the soil located nearby oil refineries and extraction processes using acid conventional extraction and high pressure microwave digestion before analysis by ICP-MS, 7700i, algilent, USA. The results demonstrated that all targeted metals were increased and by fractionation analysis the mobility of them in soil contaminated with crude oil decreased in the order Cd > Mn >Zn > Ni > Pb > Cu > Cr > V. All studies revealed that some trace metals (Ni, Cu, Cd and Cr) in contaminated soils and sediments were found at a wide range of varieties, maybe due to the oil composition and level of pollutants entering the soil.

Most studies on the effect of crude oil constituents on trace metals in soils focused on measuring the total concentrations rather than speciation and investigating the influence of the matrix in biogeochemical processes in the environment. All studies revealed that some trace metals (Ni, Cu, Cd and Cr) in contaminated soils and sediments were found at a wide range of varieties, may be due to the oil composition and level of pollutants entering the soil.

Relatively limited or no sufficient information is available regarding the effect of crude oil constituents on trace metals availability in soils. For the three decades the sultanate of Oman relied on crude oil and petroleum products as a main source for economic support. Moreover, the industrial estates and economic port activities were increased. On the other hand, this rapid growth leads to serious environmental problems on the environment in terms of its increasing risks of contamination of coastal soils and communities. Sohar industrial region (SIR) in Sultanate of Oman has crude oil refinery and large number of industries operating in a confined area closer to agriculture farms, which cultivates area as fodder for their livestock (Jamrah et al., 2007; Abdul-Wahab and Jupp, 2009; Al-Rashdi and Sulaiman, 2013). (SIR) has indicated an interest in evaluating the potential influence of industrial and crude oil ligands on the trace metals availability in costal soils around industrial area. However, there is still limited studies of heavy metals in economic ports in Sultanate of Oman; in particular, published work is scarce for the main economic ports and industrial regions (Al-Husaini et al., 2014). Moreover, there was lack information about trace metals speciation in these regions. Therefore, it is very difficult to interpret the contaminants inputs due to unavailable of natural concentrations of dissolved trace metals. These ambiguous findings probably can be explained by lack of standardised laboratory protocols, by treating different soils of varying properties with different levels of crude oil (%w/w) followed by field assessment to see the contribution of oil ligands to trace metals fractionation (Omaka et al., 2011; Kleindienst et al., 2015). The in situ speciation technique, DGT, has alternatively been used to determine the amount of metals that kinetically resupplied from the solid phase to the soil solutions (Zhang et al., 2004; Zhang and Young, 2005). The reduction in the resupply rate of metals fractions from solid phase into soil solution is typically attributed to the presence of high levels of large organic ligands and colloids from contamination. This could increase the amounts of binding sites for retaining cations (Kovaříková et al., 2007). If the $R = C_{DGT}/C_{soln}$ is $0.1 < R < 0.9$, it indicates the soil solid phase able to resupply metals fractions into soil solution. When greater than (0.9), the metal is present in soil solution kinetically labile fractions and mobile due to high capacity of solid phase to resupply soil solution with metals species. If the R value is very low and less than 0.1, it indicates that capacity of solid phase to resupply soil solutions by metals species is very low or no metals can be resupplied and kinetically limited (Zhang et al., 1998; Senila et al., 2012).

2.12. Assessment of trace metals pollution in sediments

Sediment pollution poses one of the serious nationwide environmental problems in marine systems especially in economic ports. Sediments samples act as a pools or sinks of inorganic and organic contaminants coming from seawaters through various processes including complexation, adsorption, bioaccumulation or precipitation, this will affect the sediments quality (Li et al., 2012; Diop et al., 2015). Discharges from oil refinery production can make a great and numerous contributions to coastal contamination of metals in the sediments. Studies on the species of trace metals in coastal sediments around refinery discharge point can provide information on the degree of pollution and contribution of crude oil ligands on the trace metals discrimination (Omaka et al., 2011; Liang et al., 2014; Ngeve et al., 2015). These discharges, despite they treated in the refinery by oil companies still affecting the trace metals speciation measurements. Within organic compounds in sediments derived from discharged oil, organic and inorganic fractions, aromatic/substituted aromatic molecules (Wang and Stout, 2010; Omaka et al., 2011), including resins and organic complexes containing various functional groups such as carboxylic acids and organic acids etc), are the most dominant species released oil constituents in the polluted area (Tissot and Welte, 1984; Abha and Singh, 2012; Garrido Reyes et al., 2013; Osam et al., 2013).

It was found (Omaka et al., 2011; Shukry et al., 2013; Fu et al., 2014) that crude oil complexes in soils and sediments could either enhance or decrease the availability of trace metals depending on the oil composition. The decreased concentrations were probably due to the complexation with strong organic and inorganic ligands of high molecular weight from oil.

Sohar and Al Fahal ports are a significant harbor located in Oman's as mentioned above in **section 2.1**. Effluents from Al Fahal port contribute to the release of trace metals such as Pb, Cr, Fe, Cu, Zn, Cd and V into the marine sediment. Al-Husaini et al. (2014) evaluated heavy metals contamination of Pb, Cd, V and Cu in the marine sediments at Al Fahal port and found concentrations V and Cu were high around SBM3 station due to the high effluents of ballast water from the tankers anchoring near exporter zone. Also Al-Shuely et al. (2009) assessed the heavy metals contents of V, Ni, Cd, Pb, Cu, Zn, Mn, Cr and Se in coastal sediments around (SIR). The study observed that the concentrations of Cr, Mn, Ni and as contents were high in some selected locations as shown in **Table 2.5**.

Table 2.5. The measured heavy metals contents in (SIR) (mg/kg) and compared with other studies (Al-Shuely et al., 2009).

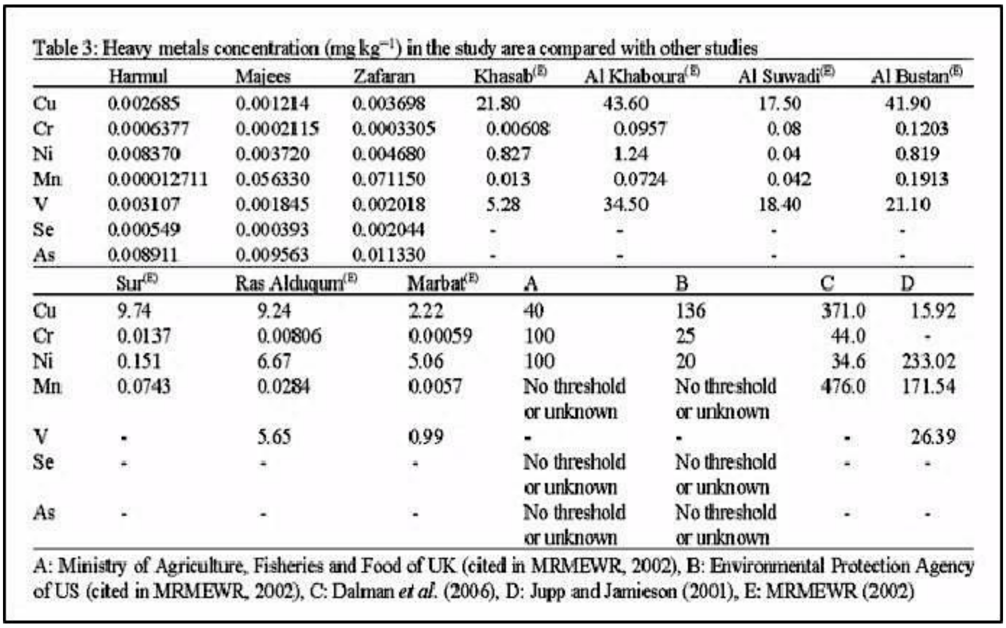


Table 3: Heavy metals concentration (mg kg^{-1}) in the study area compared with other studies

	Harmul	Majees	Zafaran	Khasab(E)	Al Khaboura(E)	Al Suwadi(E)	Al Bustan(E)
Cu	0.002685	0.001214	0.003698	21.80	43.60	17.50	41.90
Cr	0.0006377	0.0002115	0.0003305	0.00608	0.0957	0.08	0.1203
Ni	0.008370	0.003720	0.004680	0.827	1.24	0.04	0.819
Mn	0.000012711	0.056330	0.071150	0.013	0.0724	0.042	0.1913
V	0.003107	0.001845	0.002018	5.28	34.50	18.40	21.10
Se	0.000549	0.000393	0.002044	-	-	-	-
As	0.008911	0.009563	0.011330	-	-	-	-

	Sur(E)	Ras Alduqum(E)	Marbat(E)	A	B	C	D
Cu	9.74	9.24	2.22	40	136	371.0	15.92
Cr	0.0137	0.00806	0.00059	100	25	44.0	-
Ni	0.151	6.67	5.06	100	20	34.6	233.02
Mn	0.0743	0.0284	0.0057	No threshold or unknown	No threshold or unknown	476.0	171.54
V	-	5.65	0.99	-	-	-	26.39
Se	-	-	-	No threshold or unknown	No threshold or unknown	-	-
As	-	-	-	No threshold or unknown	No threshold or unknown	-	-

A: Ministry of Agriculture, Fisheries and Food of UK (cited in MRMEWR, 2002), B: Environmental Protection Agency of US (cited in MRMEWR, 2002), C: Dalman *et al.* (2006), D: Jupp and Jamieson (2001), E: MRMEWR (2002)

Fowler et al. (1993) reported that the total concentration of vanadium (V) in the most coastal sediments regions in Sultanate of Oman were exceeded 20 mg/kg, which reflects the presence of crude oil contaminants in these areas. Vanadium (V) could be used as a potential marker for exposures for crude oil hydrocarbon contamination (Al-Husaini et al., 2014). However, the environmental behavior of trace metals fractions in sediments are not only associated to their total contents, but also requires to a large extent to determine their chemical fractions. Moreover, Al Fahal and (SIR) coastal areas are regions that strongly influenced by crude oil constituents. Thus, the interactions of trace metals with natural and oil ligands play an important role in their transport, fate, and bioavailability in coastal sediments (Gao et al., 2012; Al-Husaini et al., 2014).

The organic matter in sediments often takes place by biological activities and followed by release of fractions (solid phase) such as Fe/Mn oxyhydroxide releasing metals after reduction process. Therefore, an reliable information required regarding metals distributions and exchange between the solid and solution phases for managing the trace metals contamination in sediments (Gao et al., 2012).

2.13. Determination of labile trace metals fractions in groundwaters

Trace metal contamination in groundwaters is one of the important environmental issues and it can be increased by anthropogenic activities (Li et al., 2014). Trace metals transported from soil to underground waters. Groundwater contains a wide variety of dissolved organic matter and inorganic elements in different concentrations that influenced by dissolution/precipitation reactions and adsorption including the rates (kinetics) of the geochemical process. The use of municipal solid waste (MSW) compost as fertilizer may pose a threat to groundwater quality due to the leaching of the high content of trace metals humic substances and EDAT are the major organic materials in in groundwaters, occurs as a mixture of phenol-carboxylate polyelectrolytes influence the lability and mobility of trace metals. Additionally, the metal complexation of metals could enhance the transport of trace metals fractions to groundwater. Most of the organic ligands are stable and uncharged or could be present as a negatively charged sites ions not easily removed from solution (Komy, 1993; Nowack et al., 1997). The groundwaters in Sultanate of Oman are increasingly under pressure due to overexploitation in view of population growth, activities related to development as well as environmental degradation. Groundwaters (open wells) around industrial regions, (SIR) and Rusyal Industrial Estate (RIE) in Sultanate of Oman were studied to assess the contribution of industrial activities around these sites on the degree of loads in irrigation open wells (CHOUDRI et al., 2015). Moreover, there is no comprehensive research concerning the speciation of trace metals in Oman's open wells to see the contribution of industrial and refineries activities to the trace metals loads in groundwaters.

2.14. Water quality challenges in Oman

Oil refineries, wastewater treatment plants, heavy industry, atmospheric deposition and industrial by-products often produce point sources of primary trace metals contamination in marine systems (Alagarsamy et al., 2005; Freije, 2015). Recent rapid rises in coastal developments in the Sultanate of Oman include large economic harbors and ports with industrial and crude oil activities which will result in increasing risks of the contamination of coastal habitats and communities by trace metals and oil constituents (Abdul-Wahab and Jupp, 2009; Hamzeh et al., 2013).

Sohar industrial region (SIR) and Al Fahal port have been identified as the important commercial regions in the Sultanate of Oman. Considerable amounts of trace metals and organic substances are transported to the Omani coastal environment by anthropogenic activities in the economic ports in the form of industrial effluents, oil refinery discharges and ballast waters from tankers and ships.

Trace metals are not easily degraded or destroyed in the environment due to their stability and persistence, they are neither degraded nor destroyed, and can bioaccumulate through the food chain, with serious health and environmental impacts (Patrick, 1978). The potential exists for the formation of toxic organometallic compounds that could affect the coastal ecosystem. Heavy metal contaminants can lead to a dramatic deterioration in terms of biodiversity by depleting ecologically sensitive species and eliminating water quality. Such a study in the coastal region is necessary to provide a good benchmark for the establishment of control strategies to improve marine environmental quality (Wan et al., 2008).

Therefore, water quality assessment is an important concern for determining the state of Omani aquatic systems, and regulating anthropogenic activities, which can result in preventing the distribution of trace metals and so maintaining good marine environmental quality (Sekabira et al., 2010; Hussein, 2012). Furthermore, seawater quality issues are of extreme importance due to socio-economic reasons, protecting aquatic species and the fact that many Omani regions depend on desalinated seawater as a source of potable water for domestic and industrial use (Freije, 2015). Prior to this time, the lack of full understanding of trace metals behavior in Omani seawater and groundwater due to the lack of more sensitive and applicable techniques that provide reliable information with adequate data quality is a serious hindrance to understanding Omani aquatic systems (Sekabira et al., 2010).

This study is directed towards the development of the dynamic diffusive gradients in thin films (DGT) technique for assessing water quality and providing a good benchmark for the establishment of control strategies to improve marine environmental quality in the Sultanate of Oman.

Chapter 3 – Effects of Crude Oil Contamination on Trace Metals Availability in Seawater Using Diffusive Gradient in Thin Films

3.1. Introduction

Trace metals are the main inorganic constituents in seawater that are perceived to be contaminants of concern. They result from industrial and oil refinery activities in economic harbours and are discharged into marine waters at many sites. There are still limited research studies of trace metals in global seawater and the impact of oil spills on the quality of marine systems, in particular, published data are scarce for this study area (Sadiq and McCain, 1993). According to study conducted by Al-Sayed et al. (1994), Cu, Zn, Pb, Mn, Ni, Cd, and Fe recorded highest concentrations in two sites around Bahrain (Gulf country) after Gulf war oil spill. Based on study by Santos-Echeandía et al. (2008) enrichment factors for Sr, Zr, Pb, Ba, and Fe were very high in all collects seawaters samples due to the heavy fuel spill from the Prestige tanker wreckage in the overlying seawater column in North Atlantic ocean. In Lebanon, a work conducted by Barbour et al. (2009), demonstrated that the Jiyeh oil spill in the Eastern Mediterranean Sea caused the levels of Pb, Ni and V in seawater higher than normal values. Basically, trace metal contamination assessment in marine systems under oil spill incidents are lack of reliable dynamic technique, assessing of environmental impacts associated with the oil industry as a whole, from drilling to refining for meaningful interpretation of the large set of environmental data (Ziolli and Jardim, 2002; Mustafa et al., 2015).

Recent increases in coastal development in the Sultanate of Oman including large economic ports with oil refinery industries in Muscat, Sohar, Al duqum and

Salalah have made the scientific community aware of the possibility of metal loads around contaminated areas (Abdul-Wahab and Jupp, 2009). The oil composition introduced to seawater in the form of WSF and WISF is also strongly governed by the type of oil and weathering processes as described and discussed in **Chapter 2**. Some oil constituents of lower molecular weight are soluble in seawater and while oil spreads over the surface of sea it tends to dissolve rapidly. The chemical constituents of WSF of crude oil in seawater principally influence the determination of labile trace metals species in crude oil contaminated marine systems. Therefore, it is worth proposing a reliable method for speciation measurements of trace metals in order to assess water quality around economic ports. The environmental impacts of trace metals pollutants strongly depend on the fractionation and mobility of metals in marine systems. It is necessary for understanding the mobility, lability and pathways of trace metals to have reliable information about their physicochemical properties in seawater. None or little research has been conducted to assess the impact of crude oil contamination on trace metals fractionation. Ambiguous and incomparable findings were obtained by previous studies. This could be explained by a lack of standardised laboratory experiments by using varying concentrations of WSF containing low concentrations of trace metals from different ratios of oil to water (OWR%) to evaluate the effect of oil ligands on the trace metals speciation in seawater.

In this study, a series of laboratory experiments will be conducted to develop a robust and reliable DGT method to further quantitatively understand the effect of crude oil ligands on trace metals fractionation in the synthetic solution of high ionic strength.

3.2. Materials and Methods

3.2.1. Reagents, materials and solutions

Crude oil was provided by the Ministry of Oil and Gas in the Sultanate of Oman, high purity Milli-Q water (≥ 18 MΩ/cm) was used to prepare all solutions. A 1000 mg/L stock solutions of multielements (Cd, Ni, Zn, Cu, Co and Pb) were prepared from their nitrate salts by dissolving the salts in Milli.Q water. All experimental components were acid-cleaned in 10% (v/v) HNO_3 overnight and rinsed thoroughly with Milli.Q water before use. The binding layer used is (Chelex-100, Bio-Rad). The diffusive layer 0.78 mm was prepared in the Lancaster DGT research clean labs. Diffusive gels and filter membranes were soaked in 0.5 M $NaNO_3$ solution before use to take a shorter time to attain equilibrium and eliminate diffusional artifacts present at low ionic strengths. The plastic moldings for the DGT devices were provided from DGT Research Limited (Lancaster, UK). In this study all diffusive gels were soaked in the $NaNO_3$ solution of the same ionic strength of solutions in the laboratory experiments or seawater for field deployment for ions equilibrium.

3.2.2. Diffusion coefficients measurements

The diffusion coefficients of trace metals ions through filter membrane and diffusive gel were measured according to the procedures described by Zhang and Davison (1999) and Scally et al. (2006). The diffusion cell consists of two compartments of about 120 ml with 2 cm diameter openings in each. Discs of filter membrane and hydrogel 2.5 cm each were placed between the openings and the compartments were clamped together properly. The filter membrane soaked in Milli-Q water overnight and washed in 0.1 M v/v HNO_3 overnight, then removed from acid and washed with Milli-Q water then stored in Milli-Q water. The hydro gel used in the experiment was APA gel sort, which is mainly used for the DGT method.

The diffusive gel membrane was stored in 0.5 M $NaNO_3$. Then both partitions were filled with 100 ml solutions of the same matrix synthetic solution of 0.5 M NaCl. One of the compartments, A (source solution) contained 5 mg/L of (Ni, Zn and Cu) and 1 mg/L of (Cd, Co and Pb) as a carrier. The other compartment, B (known as a receptor solution), aimed to accumulate the masses of the diffused metals ions. The temperature was measured at the beginning, middle and the end of the experiments using a thermal thermometer. Both sections were stirred properly and continuously using an overhead stirrer to prevent the effect of DBL. The experiment was carried out for 8 hours. Sub-samples of 0.2 mL were taken from each compartment at various intervals and analysed by ICP-MS. In total 12 subsamples were taken from each compartment. The diffusion coefficients D were calculated at registered temperatures during the experiment, using **equation (3.1)**:

$$D = \frac{m.\Delta g}{C.A} \qquad (3.1)$$

m: slope of the linear part of the plot of diffused masses versus the time.

g: the thickness of membranes and hydrogel.

C: the concentration in the compartment (A, receiving).

This equation estimates the diffusion coefficient for the temperature, T, at which the experiment was performed.

Equation (3.2) can be applied to estimate diffusion coefficients at any given temperature D_T, from its value at 25 °C, D_{25} (Zhang and Davison, 1995; Scally et al., 2003).

$$\mathrm{Log}D_T=[(1.37023(T-25) +8.36\times10^{-4}(T-25)^2)/(109+T)] +\log(D_{25}(273+T)/298) \qquad (3.2)$$

Temperature effects on the diffusion coefficients of the metals were corrected according to Stokes–Einstein **equation (3.3)**:

$$\frac{D_1 \eta_1}{T_1} = \frac{D_2 \eta_2}{T_2} \tag{3.3}$$

Where D_1 and D_2 are the diffusion coefficients of metals ions at known temperatures T_1 and T_2, respectively. η_1 and η_2 are denoted for the viscosities of water at temperatures T_1 and T_2, respectively (Fan et al., 2013).

3.2.3. DGT Performance

In order to investigate the effect of high ionic strength on the DGT performance, the DGT devices were deployed in triplicate in 8 L well-stirred 0.5 mol/L NaCl solution with Cd, Cu, Pb, Ni, Zn and Co (all at about 100 μg/L) over periods of time from 4 to 15 h. A dequate volume of the sample solution was used to ensure that the depletion of studied metals, by the DGT can be ignored. The DGT devices were also tested in 0.7 mol/L NaCl solution, spiked with 50 μg/L of Cd, Cu, Pb, Ni, Zn and Co, for the same deployment periods. The DGT validation was performed by assessing the linear relationship between the accumulated mass (M) of metals ions in resin gel and the deployment periods (t) using theoretical lines, derived from the DGT equation with known concentrations of deployment. Assessment can also be made by comparing C_{DGT} to C_{soln} and the ratio of close to 1 indicating good performance.

3.2.4. Effect of crude oil ligands on the trace metals fractions

To investigate the reliability of the DGT method for measuring trace metal fractions in synthetic solutions affected by complex matrices of crude oil, a series of experiments were conducted in the laboratory environment.

The testing of DGT was performed in separated 8 L capacity containers filled with well-stirred synthetic solutions containing ≈ 20 µg/L of the targeted trace metals ions impacted with varying OWR% and mixing times. The devices were exposed to the water-soluble fractions (WSF) solutions of OWR to investigate the effect of crude oil ligands on the measurement of labile metals.

3.2.4.1. Measurement of labile trace metals in crude oil

To measure labile metals in crude oil, standard DGT devices were carried out in 8 L of WSF of 3% OWR (w/v) at pH ≈ 5.8 for 14 h. The WSF was prepared according to Anderson et al. (1974), and Maher (1986) by adding 240 g of crude oil to 7760 ml of synthetic solution of 0.5 mol/L NaCl ionic strength. The mixture was gently stirred for 48 hours using a magnetic stir bar so that a vortex was not produced. Then the mixture was left overnight for standing before separating the lower phase using a plastic tap or clean pipette.

The temperatures were measured at the beginning and at the end of the deployment by thermometer for trace metals, so that the diffusion coefficient of the metal across the diffusive layer can be estimated. The mean temperature was 20 ºC. Solution samples (1 ml) were taken before and after adding oil (WSF). Also a liquots (1 ml) of the solution samples were taken at the onset and at the end of the DGT deployment for subsequent analysis.

At the end of deployment, the DGT units were removed out from the solution and rinsed with Milli-Q water thoroughly. Then, the DGT units were disassembled and the binding layers were immediately removed from the devices and placed in a clean 1.5 ml polypropylene micro centrifuge vial. Then 1 ml of 1 M HNO_3 was added and left overnight for eluting the metals from resin gels. The solutions were diluted accordingly for ICP-MS analysis (ICP-MS, Thermo X-7, Thermo Fisher, Cheshire, U.K.). The internal standard in all samples was rhodium (Rh).

The accumulated mass (M) of trace metals in the resin gel was calculated using the following **equation (3.4)**:

$$M = \frac{C_{e(ICP-MS)}(M_{HNO3} + V_{resin\ gel})}{f_e} \tag{3.4}$$

Where C_e is the concentration of trace metals in the 1 M HNO_3 elution solution (in µg/L), measured using ICP-MS, V_{HNO3} is the volume of added acid (1ml) to binding gel, V_{gel} is resin gel. The used elution factor (f_e) for calculating mass of trace metals accumulated in the binding layer (Chelex-100) = 0.85. The estimated concentrations of trace metals in DGT (C_{DGT}) were calculated by using **equation (3.7)** (Zhang and Davison, 1995; Warnken et al., 2006).

The following sections investigate the factors that could affect the trace metals lability in crude oil contaminated synthetic solution of high ionic strength using DGT.

3.2.4.2. Effect of mixing time of oil and water

To examine the effect of mixing time on DGT measured labile studied metals species in crude oil contaminated waters, DGT devices were deployed in triplicates in 8 L of synthetic solutions for 16 h. The solutions were prepared in separate containers by stirring gently synthetic solutions of 0.5 mol/L NaCl containing (35-40) µg/L, (30-60) µg/L, (25-45) µg/L, (50-60) µg/L, 60 µg/L, (40-60) µg/L of Cd, Cu, Co, Pb, Ni, Zn and at pH ≈ 5.6, treated with 3% (OWR) w/v at varying periods (0.25 day, 0.5 day, 1 day, 2 days, 4 days and 6 days), all batches were left overnight to stand before DGT deployments. The DGT measurements, labile fractions (C_{DGT}), are compared with the total dissolved concentrations of targeted metals in water-soluble fraction (WSF), in solution. The WSF of metals were measured using Chelex resin extraction as described in **section 3.2.6**.

3.2.4.3. Effect of oil to water ratios (OWR%)

In order to assess the effects of oil concentration on the DGT performance and on metal speciation, DGT devices were deployed in 8 L of solution containing oil at OWR% of 1, 3, 5, 7, 25 w/v, being mixed for 24 h in separate batches, left overnight to stand. The devices were deployed for 14 h. The measured concentrations in DGT measurements are compared with the total dissolved concretions in water-soluble fraction, WSF, in solutions.

3.2.5. Influence of the diffusive layer thicknesses on the lability of metal complexes.

The lability of Cd, Co, Cu, Ni, Zn and Pb were studied using twelve DGT devices with diffusive layers of varying thicknesses ranging from 0.014 cm (just the filter membrane), 0.052 cm, 0.094 cm, and 0.146 cm. The DGT devices were deployed for 12 hours in 8 L of well-mixed synthetic solutions of 0.5 M NaCl with no oil containing 50 µg/L of mixed metals (Cd, Cu, Co, Ni, Zn and Pb).

In the presence of oil, DGT devices with the diffusive layer thicknesses of 0.14, 0.53, 0.93, 1.2 and 1.50 mm were deployed for 24 hours.

The diffusive boundary layers (DBL, δ) on the surface of the DGT devices were estimated from the plot of 1/M versus Δg -using **equation (3.1)-** is a straight line with a slope (S) = 1/ ($C_{DGT}AD_{gel}$) and a y- intercept (I) = $\delta/C_{DGT}AD_wt$. The equation was obtained using the following steps (**equations (3.7) - (3.11)**):

$$M = \frac{D.t.A.C}{\Delta g + \delta} \tag{3.5}$$

$$\frac{1}{M} = \frac{\Delta g + \delta}{D.t.A.C} \tag{3.6}$$

$$= \underset{\substack{\downarrow \\ Slope}}{\frac{1}{D_{gel}.t.A.C}} \Delta g + \underset{\substack{\downarrow \\ Intercept}}{\frac{\delta}{D_w.t.A.C}} \tag{3.7}$$

$$\frac{I}{S} = \frac{\delta}{D_w.t.A.C} \cdot D_{gel} \cdot t \cdot A \cdot \mathrm{C} \tag{3.8}$$

$$\frac{I}{S} = \frac{\delta}{D_w} \cdot D_{gel} \tag{3.9}$$

$$\delta = \frac{I}{S}\left(\frac{D_w}{D_{gel}}\right) \tag{3.10}$$

The values of D_{gel}=0.85D_w, where D_w is the value measured in water at an infinite dilution. The mass (M) of the analyte accumulated in the resin gel eluted for ICP-MS analysis can be expressed by **equation (3.9)** (Zhang and Davison, 1995; Warnken et al., 2006; Chen et al., 2012; Panther et al., 2012).

3.2.6. Chelex resin extraction method

The total water-soluble metal concentrations (or total dissolved metal concentrations) in solution were measured by Chelex resin extraction before ICP-MS analysis as the ionic strength was too high and the metal concentrations were too low for appropriate dilution. Chelex-100 resin (Bio-Rad Laboratories, 100-200 mesh and Na form) was used. An aliquot of dry resin (0.3 g) and 17 ml of the synthetic solutions were placed in 50 ml centrifuge tubes. The mixtures were shaken for 2 h in closed tubes to allow complete extraction.

Then, the aqueous solutions were carefully removed using clean pipettes. In order to elute trace metals preconcentrated on the Chelex resin, 2 ml of 1 M HNO_3 was added and left over night. The schematic representation of the resin extraction procedure is shown in **Figure 3.1**. Samples of (1ml) each at the beginning and at the end of the experiments were taken from deployment solutions to determine total metal concentrations. The samples were diluted 20 times for ICP-MS analysis.

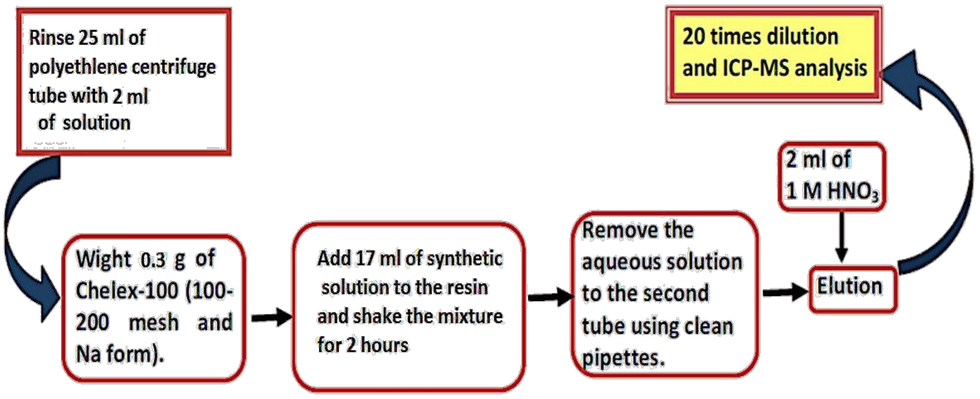


Figure 3.1. Chelex-100 resin extraction method using ion-exchange resin Chelex-100 for measuring WSF of metals.

3.3. Results and Discussion

3.3.1. Diffusion Coefficients

The diffusion coefficients of trace metals ion of Ni, Cd, Cu, Co, Zn, Pb were measured in the solutions 0.5 M NaCl using the diffusion cell. The plots of mass *vs* time were linear and they are presented in the **Figure 3.2.** The values of diffusion coefficients were calculated using **equation (3.1)**. The slops and intercepts of the linear lines and the parameter of $\Delta g = 0.92$ mm (diffusive gel + filter membrane), A = 1.78 cm^2 and C= 5 mg/L of (Ni, Zn and Cu) and 1 mg/L of (Cd, Co and Pb) are used. The measurements were carried out at pH 5.6 and temperature of 19.0 ± 0.5 °C. For comparison with literature data, the D values at 25°C were calculated from the measured data using the **equation (3.3)**. Here was about 7% difference in the measured values of ***D_{25}*** compared with the diffusion coefficients of metal ions in pure water at 25 °C.

Table 3.1. Diffusion coefficients of metal ions through filter membrane and diffusive gel in 0.5 M NaCl ionic strength at temperature.

Metals	Measured (D) (E^{-6} cm^2/sec) from Lancaster research table at 19 °C	Measure (D) (E^{-6} cm^2/sec) at high ionic strength 0.5 M NaCl in 19 °C	Measured (D_{25}) (E^{-6} cm^2/sec)	D_M (E^{-6} cm^2/sec) in pure water at 25 °C (E^{-6} cm^2/sec)
Co	5.02	4.7	4.8	5.16
Ni	4.88	4.6	4.69	5.1
Cu	5.27	4.82	4.91	5.22
Zn	5.14	4.76	4.87	5.11
Cd	5.15	4.8	4.92	5.25
Pb	6.79	6.4	6.6	6.9

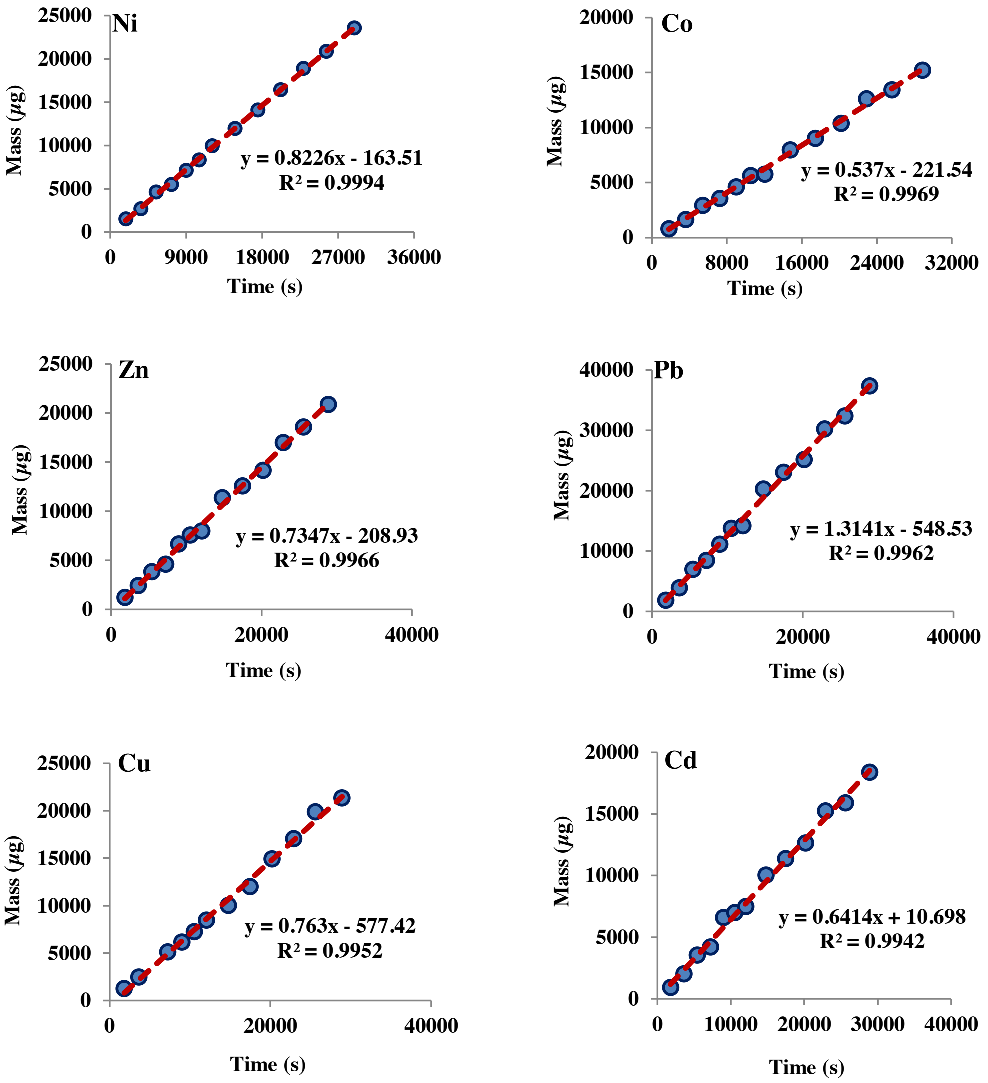


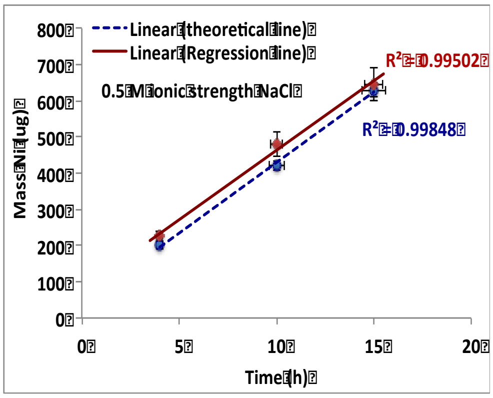
Figure 3.2. Trace metal masses diffused across the diffusive gel and filter membrane with time during targeted metals diffusion cell experiment. The ionic strength 0.5 NaCl and the average temperature during the experiment was 19 ± 0.5 °C at pH ≈ 5.6.

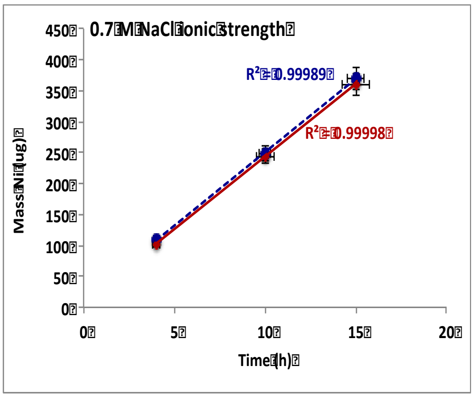
The results showed that the diffusion coefficients of metal ions in a solution of 0.5 M NaCl ionic strength are at most only about 7% lower than that in pure water. The difference could be attributed to the difference in the viscosity between the gel and the water. It confirms previous observations (Sangi et al., 2002) of free diffusion for ion Cd^{2+} in the $NaNO_3$ solution in the range 0.01 mol/L to 1 mol/L using D_{DGT}

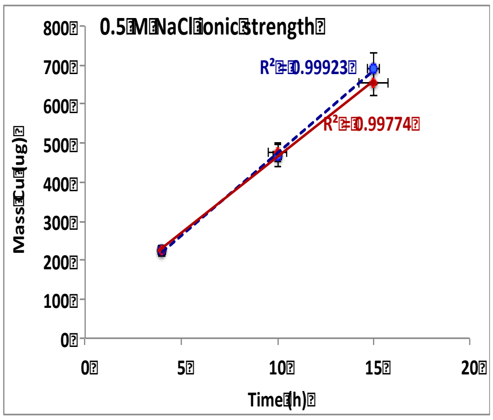
agarose cross-linked polyacrylamide gel. More likely explanations are that the slight decrease in the Cd diffusion coefficient was observed by Alfaro-De la Torre et al. (2000) and he attributed this to the viscosity caused by ionic strength. Some variations in diffusion coefficients could be expected and not more than 8% between pure water and seawater. Some charges at the gel surface may affect the diffusion coefficients in freshwaters at low ionic strength according to previous studies (Chang et al., 1998; Zhang and Davison, 1999; Scally et al., 2006; Warnken et al., 2006; Panther, 2008). These will not be a problem for this study, because the gels were conditioned in 0.5 mol/L $NaNO_3$, and all experiments were carried out in 0.5 mol/L $NaNO_3$

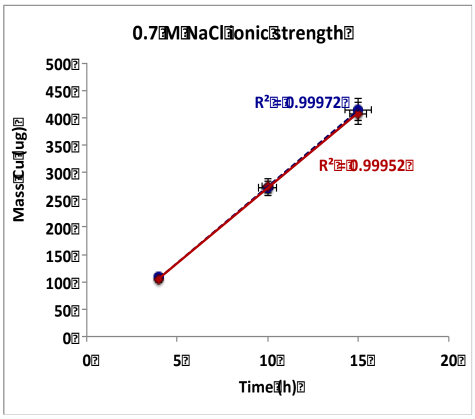
3.3.2. Effect of deployment time and ionic strength on the DGT measurements

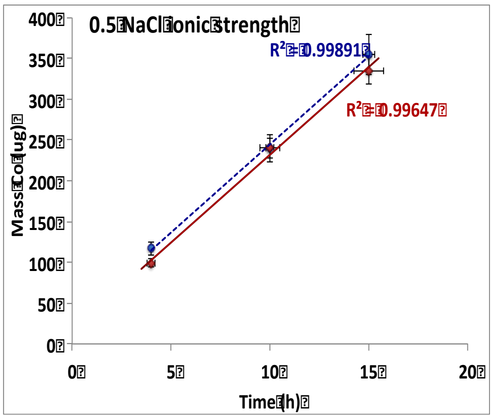
The effect of ionic strength on the capability of DGT devices to accumulate metal ions in the resins as a function of time was investigated in two synthetic solutions of 0.5 and 0.7 mol/L NaCl contain 100 µg/L and 50 µg/L, respectively. The experiment investigated whether DGT sampler meets the application of the DGT equation as shown in **Figure 3.3**. The regression lines are very close to the theoretical lines for all metals in both 0.5 M and 0.7 M NaCl solutions. Good agreements between the experimental data and DGT theoretical lines in **Figure 3.3** indicate that DGT principle works well at high ionic strength.

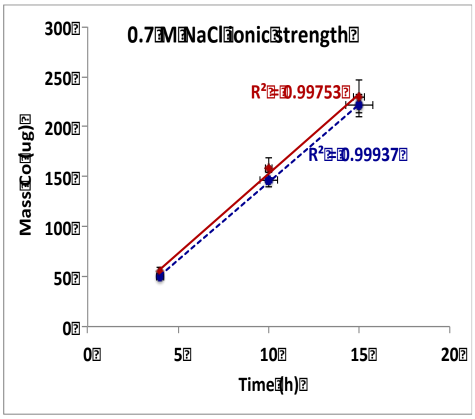

Linear (theoretical line)
Linear (Regression line)
R² = 0.99502
0.5M ionic strength NaCl
R² = 0.99848
Mass Ni (ug)
800
700
600
500
400
300
200
100
0
0
5
10
15
20
Time (h)

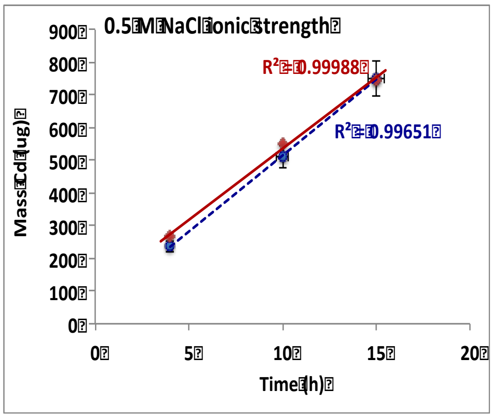

0.7M NaCl ionic strength
R² = 0.99989
R² = 0.99998
Mass Ni (ug)
450
400
350
300
250
200
150
100
50
0
0
5
10
15
20
Time (h)

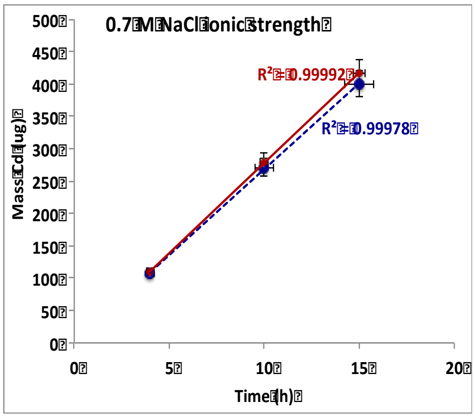

0.5M NaCl ionic strength
R² = 0.99923
R² = 0.99774
Mass Cu (ug)
800
700
600
500
400
300
200
100
0
0
5
10
15
20
Time (h)


0.7M NaCl ionic strength
R² = 0.99972
R² = 0.99952
Mass Cu (ug)
500
450
400
350
300
250
200
150
100
50
0
0
5
10
15
20
Time (h)


0.5 NaCl ionic strength
R² = 0.99891
R² = 0.99647
Mass Co (ug)
400
350
300
250
200
150
100
50
0
0
5
10
15
20
Time (h)


0.7M NaCl ionic strength
R² = 0.99753
R² = 0.99937
Mass Co (ug)
300
250
200
150
100
50
0
0
5
10
15
20
Time (h)


0.5M NaCl ionic strength
R² = 0.99988
R² = 0.99651
Mass Cd (ug)
900
800
700
600
500
400
300
200
100
0
0
5
10
15
20
Time (h)


0.7M NaCl ionic strength
R² = 0.99992
R² = 0.99978
Mass Cd (ug)
500
450
400
350
300
250
200
150
100
50
0
0
5
10
15
20
Time (h)

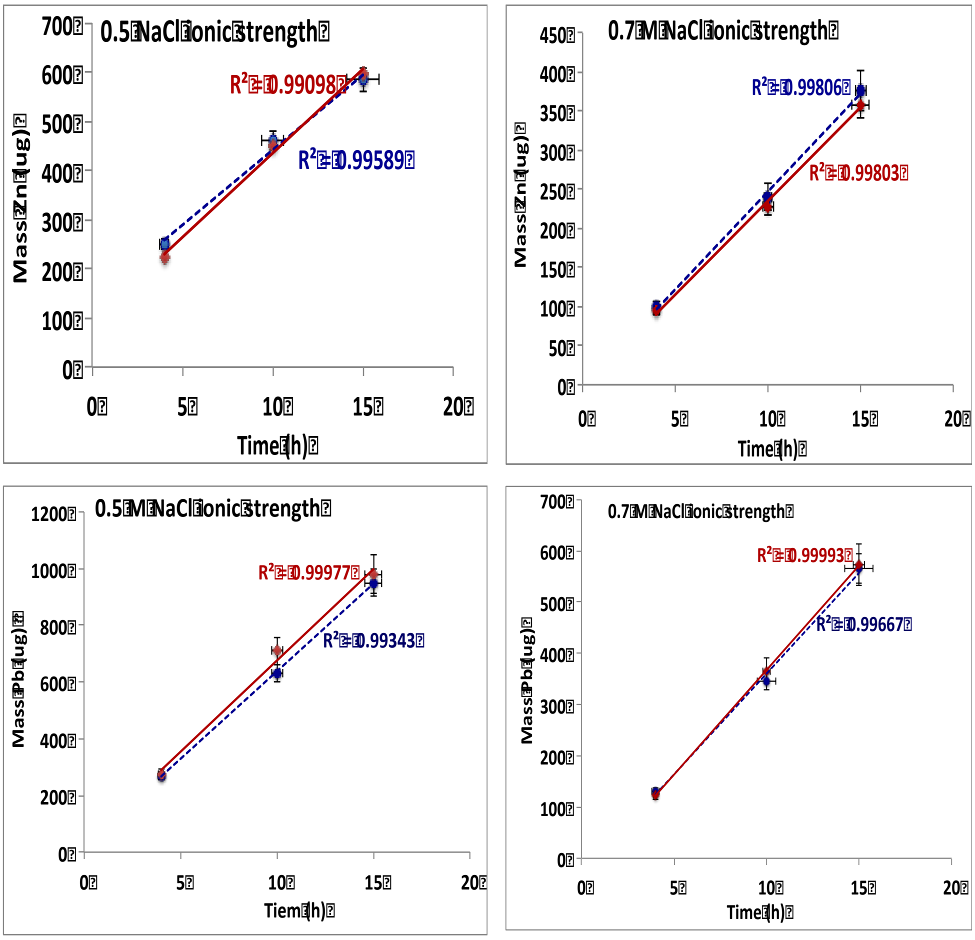


Figure 3.3. The mass of the metals accumulated by resin gel DGT devices as a function of time. DGT devices were suspended in a well-stirred solution 0.5 M NaCl and 0.7 M NaCl containing known concentrations for different time periods. The solid lines are the lines of best fit for the experimental data. The dashed lines are predicted relationships calculated from known deployment conditions and the DGT equation.

In all DGT deployments, enough volume of solutions was used to ensure that the depletion of Cd, Cu, Co, Ni, Zn and Pb was negligible. When DGT devices were deployed for varying times, the accumulated mass (M) of metals on the resin gel increased with time (t), at both ionic strengths with R^2 ranged between 0.983- 0.999 for all metals solutions as shown in the **Figure 3.3**.

DGT performs well with a good agreement between measured C_{DGT} and deployment concentrations solutions at both ionic strengths at pH ≈ 5.67 with ratios ranged between 97% ± 4.6 - 102% ± 4.3 of all targeted metals, confirming previous findings of free diffusion for simple ions obtained by Zhang and Davison (1995) and Sangi et al. (2002).

The relative standard deviations (RSDs) of the DGT measurements in both solutions were in the range between 4% and 10%, which indicate good precision of DGT technique.

3.3.3. Resin extraction for labile metals (WSF)

Six series of experiments were conducted to determine the trace metal ions in the same synthetic solutions where DGT deployments were carried out. From the results presented in **Table 3.2** it can be observed that the uptake of metals ions onto Chelex-100 in Na^+ form was independent of ionic strength. Within the precision of the analytical technique, the concentrations measured by resin extraction agreed well with the direct solution measurements after dilution with a ratio of C_{resin}/C_{soln} ranged between 91% ± 2.6 - 107% ± 5.4 of all metals.

Table 3.2. Measured trace metals by resin extraction (WSF) and DGT methods in synthetic solutions of 0.5 M and 0.7 M NaCl, contain 100 µg/L and 50 µg/L, respectively at pH ≈ 5.64.

Metal	0.5 M NaCl, I.S		0.7 M NaCl, I.S	
	WSF	C_{DGT}	WSF	C_{DGT}
Ni	87.5	87	45.96	45.13
Cu	80.97	81.1	41.96	42.16
Co	44.7	44.3	21.85	23.83
Cd	90.0	96.4	41.62	47
Zn	78.8	78.5	40.25	38.2
Pb	90	90.35	42.19	45.00
Average	**78.7**	**79.61**	**38.97**	**40.22**
Correl		**0.99**		**0.95**

3.3.4. Comparison between DGT and resin extraction methods

The measured metal concentrations by both DGT and resin extraction methods are presented in **Table 3.2** and showed a good correlation. The results indicated that there were no differences in the measured concentrations of ion-exchangeable Cd, Cu, Pb, Zn, Co and Ni at both ionic strengths of t-test that p value P (T<=t) two-tail = 0.73 is high (greater than 0.05).

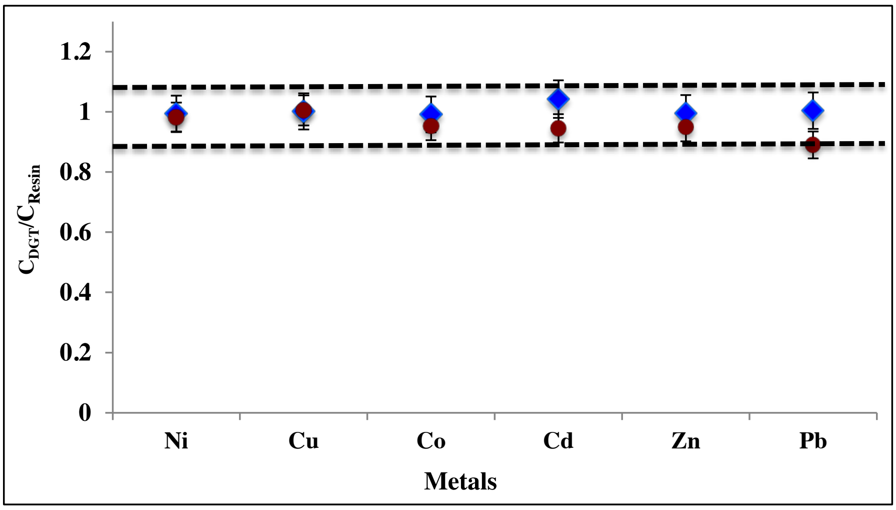


Figure 3.4. Percentages of C_{DGT}/C_{resin} of determined trace metals ions by resin extraction and DGT methods in synthetic solutions of 0.5 M (◆) and 0.7 M NaCl (●), contain 100 µg/L and 50 µg/L, respectively at pH ≈ 5.64.

This is consistent with observations from studies found by Sangi et al. (2002), Veguería et al. (2013), and Amara-Rekkab and Didi(2015), which assessed the influence of the ionic strength of solutions medium on the equilibrium uptake of Hg^{2+} and Cd^{2+} from the aqueous solution by DGT and Chelex-100 resin. The ratios of the measured concentrations obtained by both C_{DGT} and resin extraction methods to the concentrations measured by ICP-MS in both ionic strengths solutions were similar and in the range 0.9 – 1.1 as shown in **Figure 3.4**.

From **Table 3.2**, t-test it is illustrated that p value P (T<=t) two-tail = 0.73 is high (greater than 0.05).

From the above results it can be noted that the DGT and resin extraction methods agree well in both solutions for all metals, which indicate that DGT can provide reliable measurements for trace metals in seawaters.

3.3.5. Effect of mixing times in the presence of 3% OWR

The DGT-labile measurements of Cu, Co, Cd, Ni, Zn and Pb in different solutions containing 3% OWR at varying mixing times were obtained and presented in **Table 3.3** and **Figure 3.5**. The relative standard deviation values (RSD%) at all measurements were 2% - 5%, which indicate a good precision for DGT. The DGT-labile fractions Cd showed a dramatic decrease with time (from 38.5 ± 1.5 µg/L to 14.2 ± 1.6 µg/L and labile Cu showed generally increase with time (6.7 ± 2.6 µg/L to 28.4 ± 0.7 µg/L), see **Table 3.3**.

Table 3.3. Trace metal fractions measured in WSF of crude oil at varying mixing times.

Mixing Time (days)	Trace Metals (µg/L)																	
	Cd			Cu			Co			Pb			Ni			Zn		
	Before Oil	C.DGT With oil	STD	Before Oil	C.DGT With oil	STD	Before Oil	C.DGT With oil	STD	Before Oil	C.DGT With oil	STD	Before Oil	C.DGT With oil	STD	Before Oil	C.DGT With oil	STD
0.25	39	38.5	1.5	58	6.7	2.6	29	30	2	55	51	2.6	60	65	3	60	57.76	10
0.5	38	35	2	55	5	1	30	29	1	55	49.31	3.7	60	67.3	10	60	61	3.1
1	34	23	2.3	42	3.1	0.2	25	25	1.3	45	46	2	60	60	3	55	48	2
2	37	12.4	0.9	45	12	0.8	32	36	1.5	60	53	1.7	59	58	2	40	55	2.4
4	36	13	0.3	31	27	1.7	33	29	1.4	61	50	2.2	61	54	3	40	48	2.9
6	37	14.2	1.6	50	28.4	0.7	36	28	1.1	60	49	1.4	61	53	1	47	59	1.7

The higher concentrations of labile Cd than that of labile Cu, is attributed to the tendency of Cd to form inorganic complexes especially with chloride (Cl^-) in solution and the predominantly stronger organic complexes DGT-labile forms of Cu than Cd fractions, impeding fast dissociation. The complexation of Cd with the large excess of Cl^- ion (forming $CdCl_2$ and $CdCl^+$), depresses organic chelation (Simpson, 1981; Christensen and Christensen, 2000).

The inorganic and organic ligands released from oil to solutions increase with time and form strong complexes with Cd and reduce the mobility and lability of Cd. The complexation by strong large aromatic ligands DOM cannot dissociate fast enough to be measured by DGT (Zhang and Davison, 1995; Montero et al., 2012). Large complexes may be too big to diffuse through the diffusive gel layer. All these factors can cause reduction in DGT measured concentrations.

The increase in Cu concentration indicates release of Cu from oil and complexation of Cu from the organic ligands did not compete with the total input of Cu. previous studies showed that the increase of Cu and other trace metals associated to crude oil contamination. An increase on dissolved copper (2.8–4.7 nM) and nickel (2.2–8.0 nM) with respect to natural values (1–3 nM for Cu and 1.6–5 nM for Ni) was observed in the column above the Prestige wreckage (NE Atlantic ocean) associated with the mixing of seawater with the fuel spill from the Prestige tanker (Santos-Echeandía et al., 2008). Liu et al. (2012) evaluated the impact of weathering processes on the chemical composition of crude oil in seawater after released during the Deep-water Horizon (DWH) oil spill accident in the northern Gulf of Mexico. The obtained results showed that concentrations of V, Ni, Co, Cu, As and Pb increased due the crude oil spill to seawater (Liu et al., 2012).

There was no significant overall difference with time for DGT labile Ni, Co, Pb, and Zn. This can likely be attributed to the used crude oil samples provided by the Sultanate of Oman (Arabic Gulf) containing relatively low contents of these metals, which can be released to water.

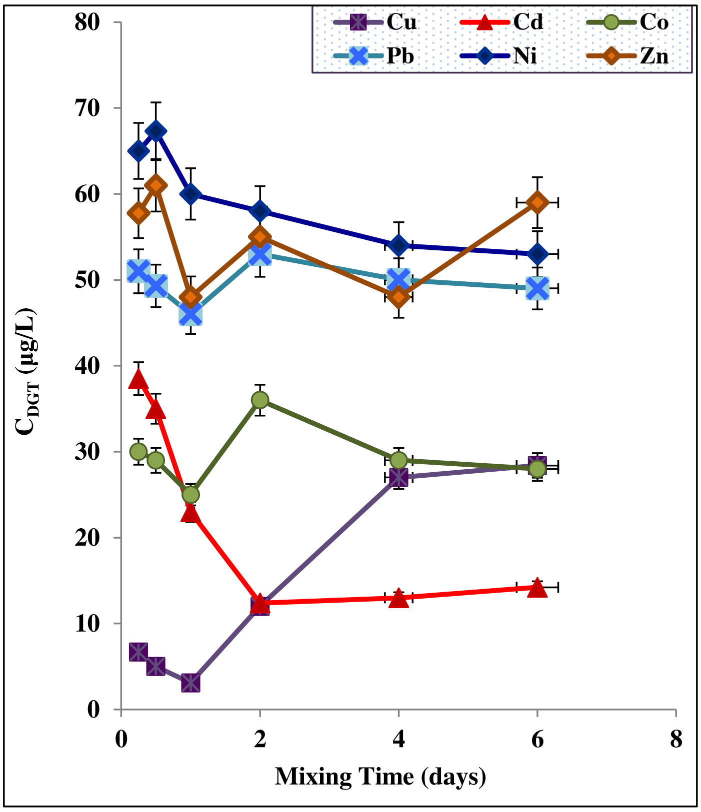


Figure 3.5. The influence of mixing time of oil to water on DGT-labile fractions of Cd, Cu, Co, Pb, Ni, Zn in WSF (dissolved species) of 3% OWR, containing 50 µg/L of targeted trace metals and at pH ≈ 5.6 and 16 h deployment, using varying mixing periods (0.25, 0.5, 1, 2, 4 and 6 days).

It is similar to the observations obtained by Bu-Olayan et al. (1998) which found high concentrations of trace metals Zn, V, Pb, Cr, Mn, Ni, Cu, and Cd in Persian Gulf along the coastal belts of Kuwait after the Gulf War oil spills.

As metal concentrations become stable after 4 days of mixing, the mixing time of 4 days was used before DGT deployments for this work.

3.3.6. Effect of oil to water ratios OWR% on DGT measurements

The DGT measured concentrations of labile metals in solution containing 3% oil (OWR, w/v) after 14 hours deployment are shown in **Table 3.4.** Low OWR (1%-5%) is more suitable to measure the trace metal concentration in the crude oil using oil/water emulsion method as it reduces compounds saturation extent, and increases their partitioning in water medium (Tsvetnenko and Evans, 2002).

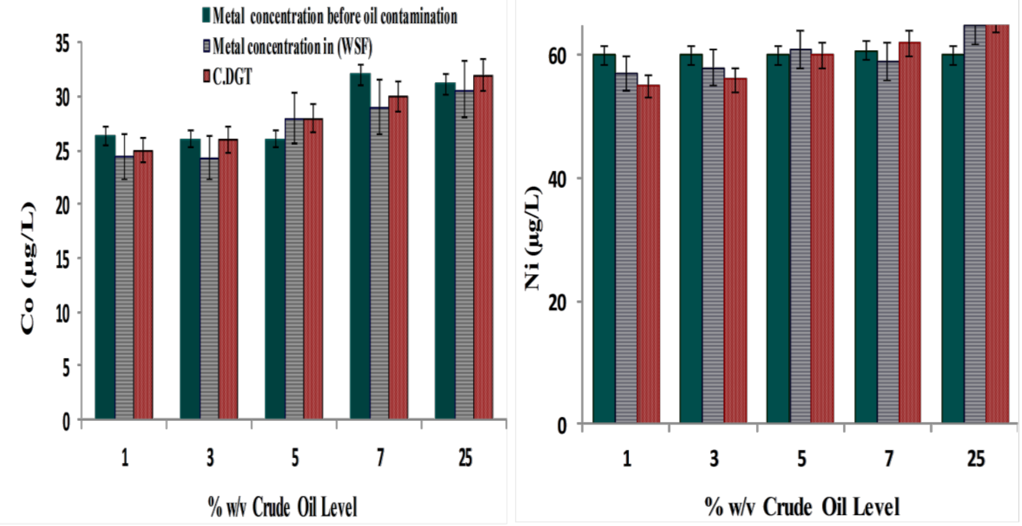
The results show that the water soluble fraction of metals and the DGT measured labile metals are very low compared to the total concentrations in Oman crude oil. The complete analysis of Oman crude oil using the 389 UOP method (using wet ashing and ICP-OES) are provided by Petroleum Development Oman (PDO) in **Appendix (A)-Table (1)**. This is similar with previous studies of trace metal determination in various types of crude oils (Witherspoon and Nagashima, 1957; Dekkers and Daane, 1999; Silset, 2008). The much lower labile concentrations indicate DGT discriminating metals in WSF fractions based on dissociation kinetics, only labile fractions including free metal ions, inorganic complexes and some small organic complexes.

Table 3.4. Measured trace metals in crude oil using DGT compared with the obtained results in Oman oil provided by PDO.

Metals	**C_{DGT} in solution of 3% oil, (µg/L)**	**Total concentrations of WSF (µg/L) in solution**	**Total concentrations in oil provided by Oman (PDO), (µg/L)**
Cd	0.01	1.6	2.8
Cu	1.35	4	10
Co	2	4.1	10
Ni	3	7	12
Zn	4.1	10	60
Pb	2	1.24	10
Al	20	31	120
Cr	0.3	5	10

In order to investigate the effect of crude oil ligands on the DGT measurement, deployment solutions were spiked with varying oil to water ratios (%OWR, w/v) as described in the experimental section. The DGT measured concentrations for each metal are plotted against the varying OWR% and are presented in **Figure 3.6**.

Nickel (Ni) and Cobalt (Co). The total dissolved Ni and Co concentrations (by ICP-MS) in solutions before adding oil (control), DGT measured labile concentrations and resin measured WSF were almost the same. This indicates: i) the low concentrations of Ni and Co in Oman's crude oil, ii) metal association with inorganic species and aromatic complexes are small enough to diffuse through the hydrogel of the DGT and iii) they can all dissociate and accumulate in the binding layer (Zhang and Davison, 2001; Guéguen et al., 2011). This is inconsistent with information in the literature showed that Ni is present almost in crude oils at high concentrations depending on the geochemistry of the original well of extracted oil (Duyck et al., 2008; Khuhawar et al., 2012). Similar information obtained by others (de Mora et al., 2004; Al-Husaini et al., 2014; Freije, 2015) who investigated the levels of trace metals in the Sultanate of Oman near refineries and in seawaters affected by industrial and crude oil activities.



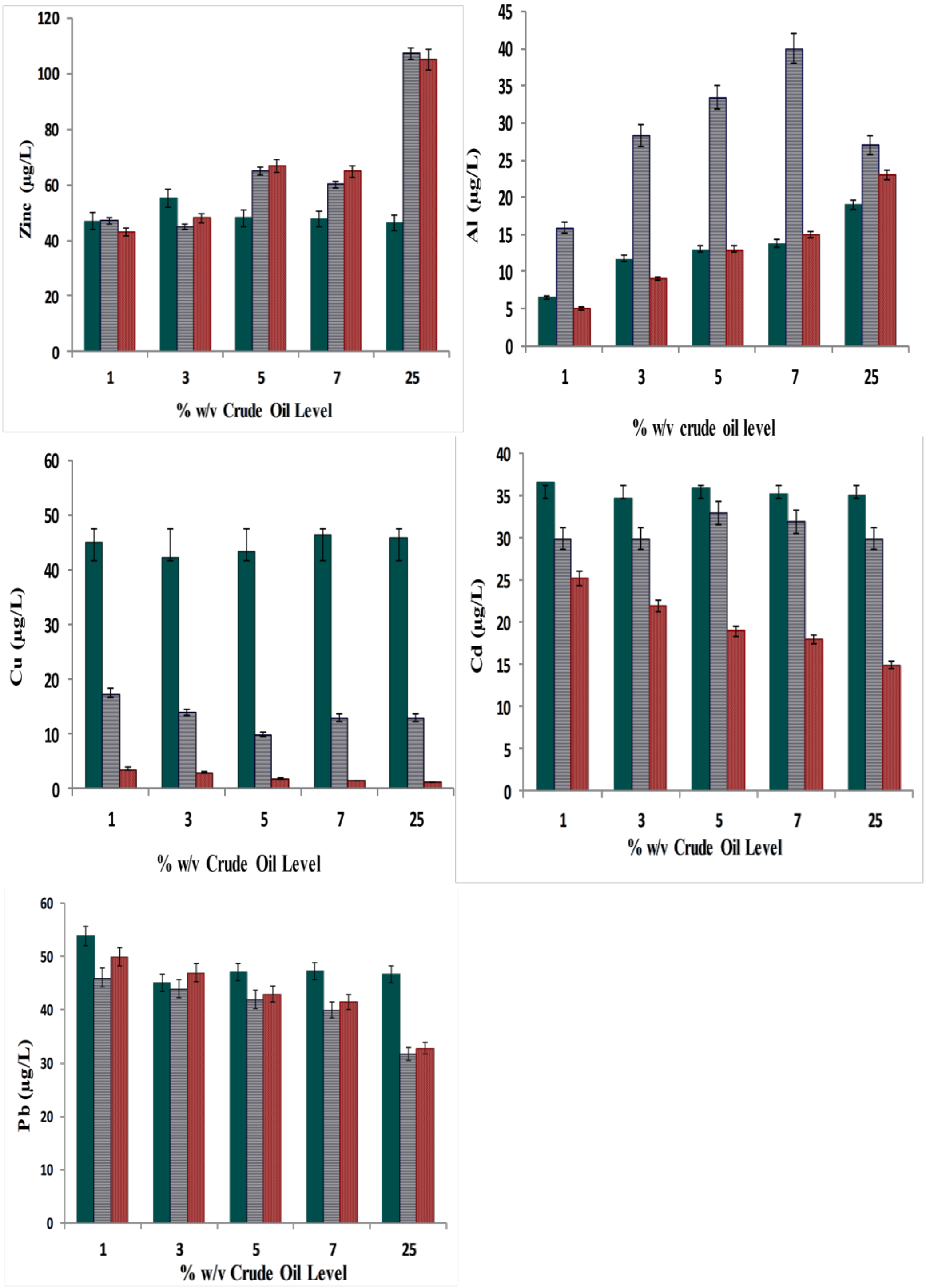


Figure 3.6. The measured concentrations by C_{DGT} in WSF and ICP-MS in WSF and before adding oil with various concentrations of WSF (dissolved species) (1,3,5,7 and 25 OWR%, w/v): ionic strength of 0.5 mol/L NaCl containing (35-40) µg/L, (30-60) µg/L, (25-45) µg/L, (50-60) µg/L, 60 µg/L, (40-60) µg/L of Cd, Cu, Co, Pb, Ni, Zn at pH ≈ 5.6.

Aluminium (Al). The added crude oil contributed to the alumnium (Al) load in solutions with increased WSF of Al compared to the control solution. The WSF of Al increased proportionally with increasing oil to water ratio up to 7% OWR and decreased at 25% OWR. The percentages increase was ranging from 32 ± 1.20% to 85 ± 6.14%. The total dissolved concentrations of Al (directly measured by ICP-MS) in control solution are comparable to labile C_{DGT}. DGT measured Al concentrations were consistently lower than those of WSF Al. This suggests that Al contributed from oil as WSF was complexed by organic ligands and they are too large to diffuse through the DGT diffusive gel.

Zinc (Zn). Slight increase in concentrations of Zn at 5% and 7% OWR showing contribution of Zn from oil. More than doubled the concentration at 25% OWR. DGT measured concentration of Zn and WSF of Zn are very similar indicating all the contribution of Zn from oil were complexed with oil-ligands and they are small enough to diffuse through DGT gel and labile enough to dissociate and to be measured.

Lead (Pb). DGT-labile Pb has an inverse relationship with WSF concentrations and slowly decreases with the increasing of OWR%. No significant change in Pb concentration with added oil up to 7%. At 25% OWR marked decrease for C_{DGT} and WSF Pb. This could imply low concentration of Pb in the oil and possibly form strong organic complexes with oil ligands unable to dissociate and be accumulated by DGT. Similar observations were found in the studies performed by Baeyens et al. (2011) and Omanović et al. (2015). It can be observed that, in the presence of crude oil, C_{DGT} and WSF Pb were consistently lower than the total dissolved concentrations of Pb in control solutions due to the formation of inert Pb complexes with oil's ligands.

Cadmium (Cd). No significant change of WSF Cd concentration with increasing of oil addition up to 25% OWR. This indicates no net contribution of Cd from oil. Slightly lower WSF compared to total dissolved Cd before the oil addition, suggesting strong and inert complexes of Cd and oil-ligands were formed. DGT measured Cd was decreasing with increasing of OWR and also significantly lower than WSF Cd. The results indicate: i) increased ligand contribution from the oil, ii) large complexes of Cd with oil-ligands that not able diffuse through gel and iii) inert complexes of Cd with oil-ligands that cannot dissociate and unavailable to DGT. This agreeing with the findings obtained by Wallner-Kersanach et al. (2009) and Omanović et al. (2015). They demonstrated that non-DGT-labile of Cd fractions were in general high due to the formation of strong complexes by organic ligands that are less immobile and non-labile in the contaminated sites around oil and petrochemical industries.

Copper (Cu). C_{DGT} for Cu were much lower than other metals and dropped from 3.7 ± 0.12 µg/L (at 1% OWR) to 1.3 ± 0.34 µg/L (at 25% OWR). The results of Cu were similar to those of Cd, but with much more pronounced differences of the three measurements (control, C_{DGT} and WSF) suggesting much stronger and larger complexes of Cu oil-ligands compared to Cd complexes with oil-ligands.

3.3.7. Effect of oil to water ratio on WSF of metals

Four series experiments were carried out using Chelex resin (Bio-Rad Laboratories, 100-200 mesh and Na form) to extract water soluble fraction (WSF) of trace metals in synthetic solution without and with different amount of crude oil (3%, 5%, 25% OWR, w/v). After 24h mixing time, the results are shown in **Figure 3.7** and **Table 3.5.**

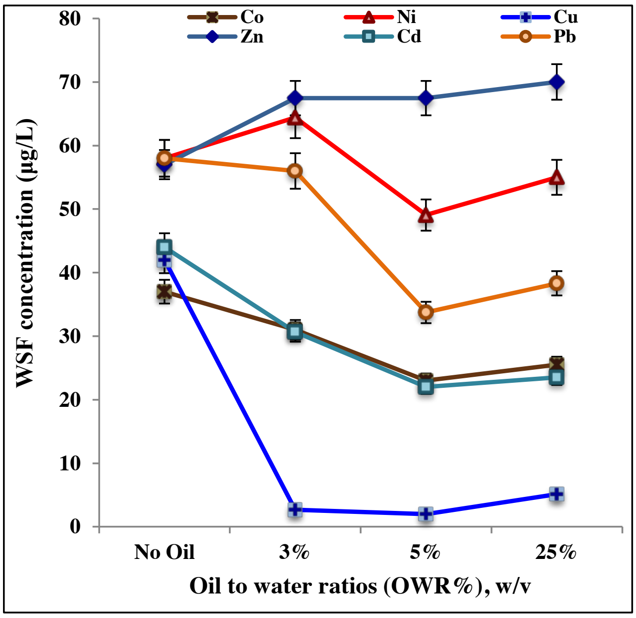


Figure 3.7. The determined labile fractions of metals Co, Ni, Cu, Zn, Cd and Pb using resin extraction method in the synthetic solutions without oil and with varying OWR (3%, 5% and 25%, w/v), containing 50 µg/L targeted metals, pH 5.6 at 0.5 mol/L NaCl ionic strength

There were general decrees in WSF metals with increasing of oil concentration over (0% - 5% OWR) for Co, Ni, Cd and Pb after which the metals concentrations slightly decreased with increasing of oil ratio to 25% OWR. This suggests that the contribution from oil is predominantly organic ligands and they form inert complexes with the metals.

The concentration of WSF (dissolved species) Cu decreased significantly from initial 42 µg/L without oil to 2.7 µg/L when oil was added to solution at 3% OWR. There was no further decrease at 5% and 25% OWR. The results could be explained by strong complexation of Cu with over a wide range of the molecular weights of ligands released from oil into water, which cannot be uptaken up Chelex-100 resins. There was a slight increase for Zn, probably due to the high concentration of Zn in

Oman's oil or/and weakly complexed Zn and oil-ligands which easily available to Chelex resin (Hart and Davies, 1977; Figura and McDuffie, 1980).

Table 3.5. The measured concentrations of labile trace metals (µg/L) in synthetic solutions with and without varying concentrations of WSF of different OWR%.

Metals	No Oil	3%	5%	25%
Co	**37**	**31.00**	**22.00**	**25.48**
Ni	**58**	**64.40**	**49.07**	**55.13**
Cu	**42**	**2.70**	**2.00**	**5.13**
Zn	**57**	**67.47**	**67.47**	**70.1**
Cd	**44**	**30.67**	**22.00**	**23.5**
Pb	**58**	**56.00**	**33.73**	**38.31**

3.3.8. The influence of diffusive gel thicknesses (Δg)

To investigate whether the DGT measurements in solutions with and with no oil are dependent on **(Δg)**, DGT devices of varying diffusive gel thicknesses were deployed in solutions without oil and with oil at 3% OWR for 24 h with a 700 rpm stirring rates as described in the experimental section. The plots of 1/M (ng^{-1}) *vs.* diffusive layer thicknesses (Δg, cm) obtained for solution without oil are presented in **Figure 3.8**. The DBL (δ) thicknesses were estimated using **equation (3.10)**. The results were not significantly different for all 6 metals studied, ranged between 0.011 cm to 0.030 cm with the mean value of (0.020 ± 0.0072 cm), which is about 21.28% of the diffusion layer thickness (Δg) of the standard DGT sampler. It is similar to the results obtained previously (Zhang and Davison, 1995; Warnken et al., 2006).

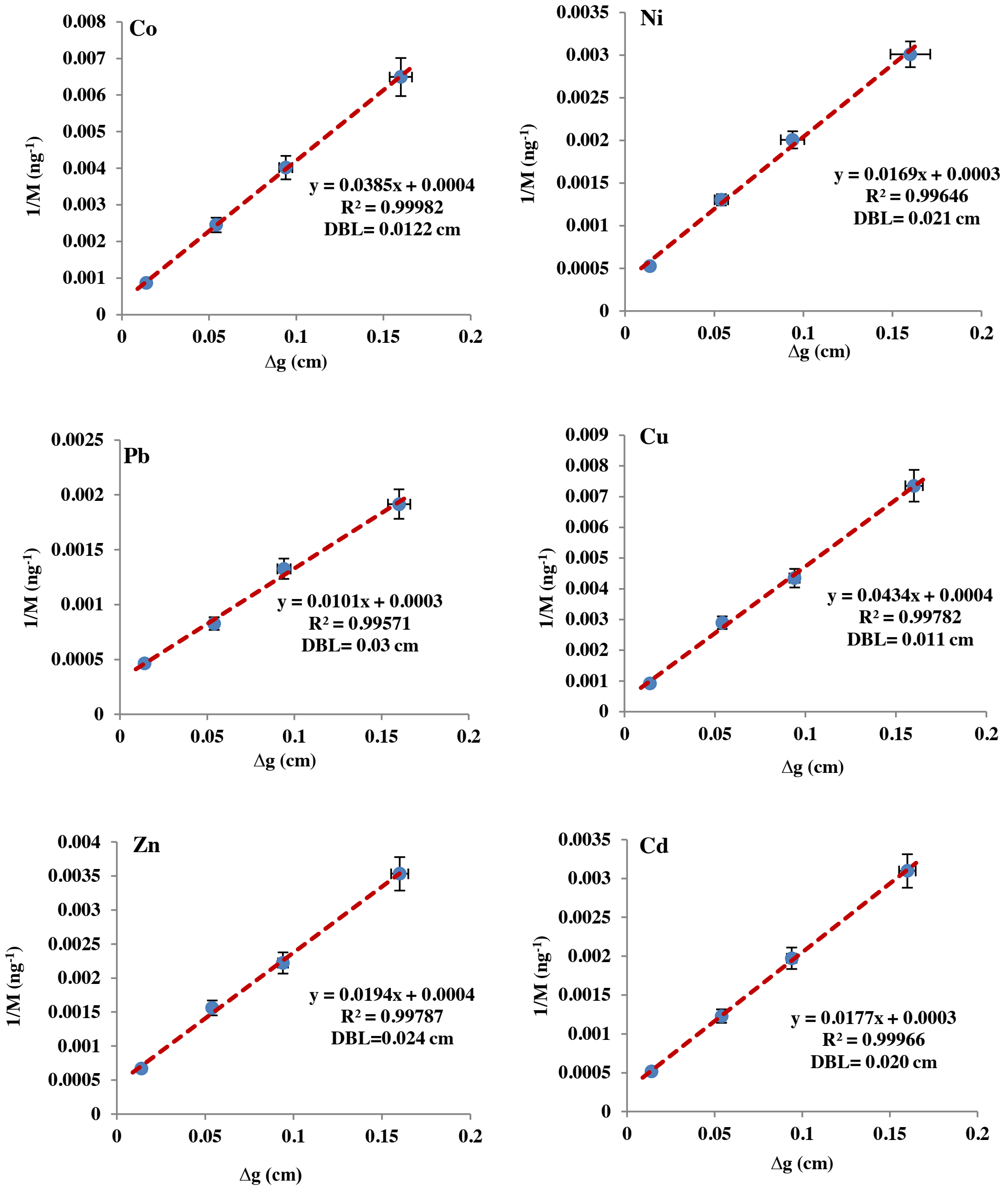
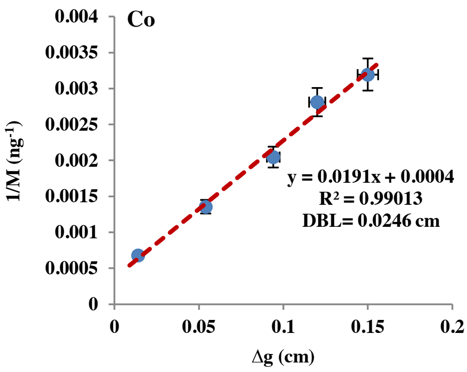


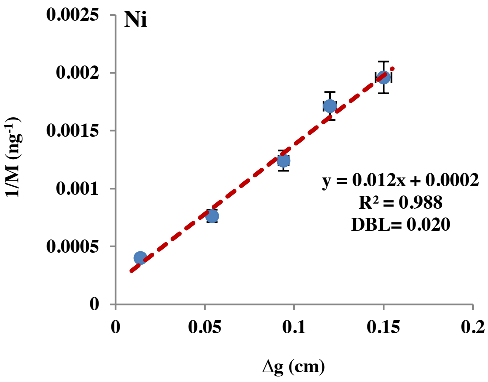
Figure 3.8. DGT results for Zn, Cd, Ni, Zn, Co and Pb deployed 12h in the synthetic solution of 0.5 mpl/L NaCl with no oil, at pH ≈ 5.4 and T= 19 °C, plotted as 1/mass (ng^{-1}) versus the diffusive layer thickness (Δg; cm), DBL values for trace metals are illustrated on the plots.

The plots of inverse mass transport through the diffusive gel to binding layer (1/M) vs. diffusion layer thickness (Δg) of all six metals in solution with 3% OWR are illustrated in **Figure 3.9**. Good linearity can be noted with R^2 of 0.983 to 0.998.

The DBL thicknesses obtained from Cu, Co, Ni, Pb and Zn plots were similar with mean value of 0.027 ± 0.0079 cm, which is approximately 29% of the diffusive layer (Δg) in the standard DGT sampler. It is approximately 26% higher than the estimated DBL in the solution without oil. The measured DBL of Cd was significantly larger with a thickness about 0.08 cm, which is about 85.11% of the diffusion layer (Δg) of the standard DGT sampler and 75% higher than the obtained DBL layer in the solution not affected by oil. This could be explained as a result of the slow dissociation of Cd, Pb and Cu complexes that can be enhanced when increases the thickness of diffusion layer (Turner et al., 2014).

From the above discussion it can be observed that DBLs are influenced by oil ligands (apparent layer) and it is greater than the (physical layer) (δ) explained according to the Eigen mechanism (Warnken et al., 2006; Uher et al., 2013). The apparent layer is caused by chemical dissociation of trace metals from larger ligands. The differences in the thicknesses of DBL for the targeted metals in solutions with and without oil were attributed to the kinetic limitation.





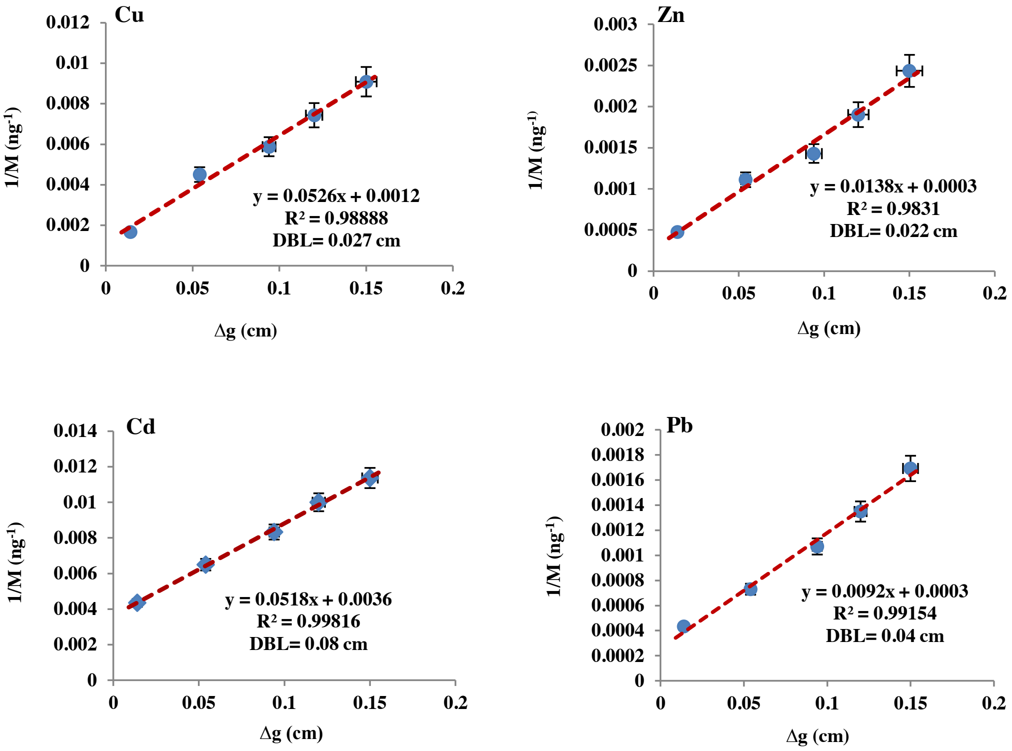


Figure 3.9. DGT results for Zn, Cd, Ni, Zn, Co and Pb deployed 24h in the 3 % OWR, WSF solution of 0.5 mol/L NaCl, at pH ≈ 5.4 and T= 19 °C, plotted as 1/mass (ng^{-1}) versus the diffusive layer thickness (Δg; cm), DBL values for studied trace metals are illustrated on the plots.

To further understand the effect of diffusive gel layer thickness on DGT measurements, C_{DGT} was calculated with and without DBL being added to the diffusion layer. When DBL was considered the effective surface area of 3.08 cm^2 was used in the calculation. Otherwise, the physical surface area of 2.54 for the DGT exposure window was used.

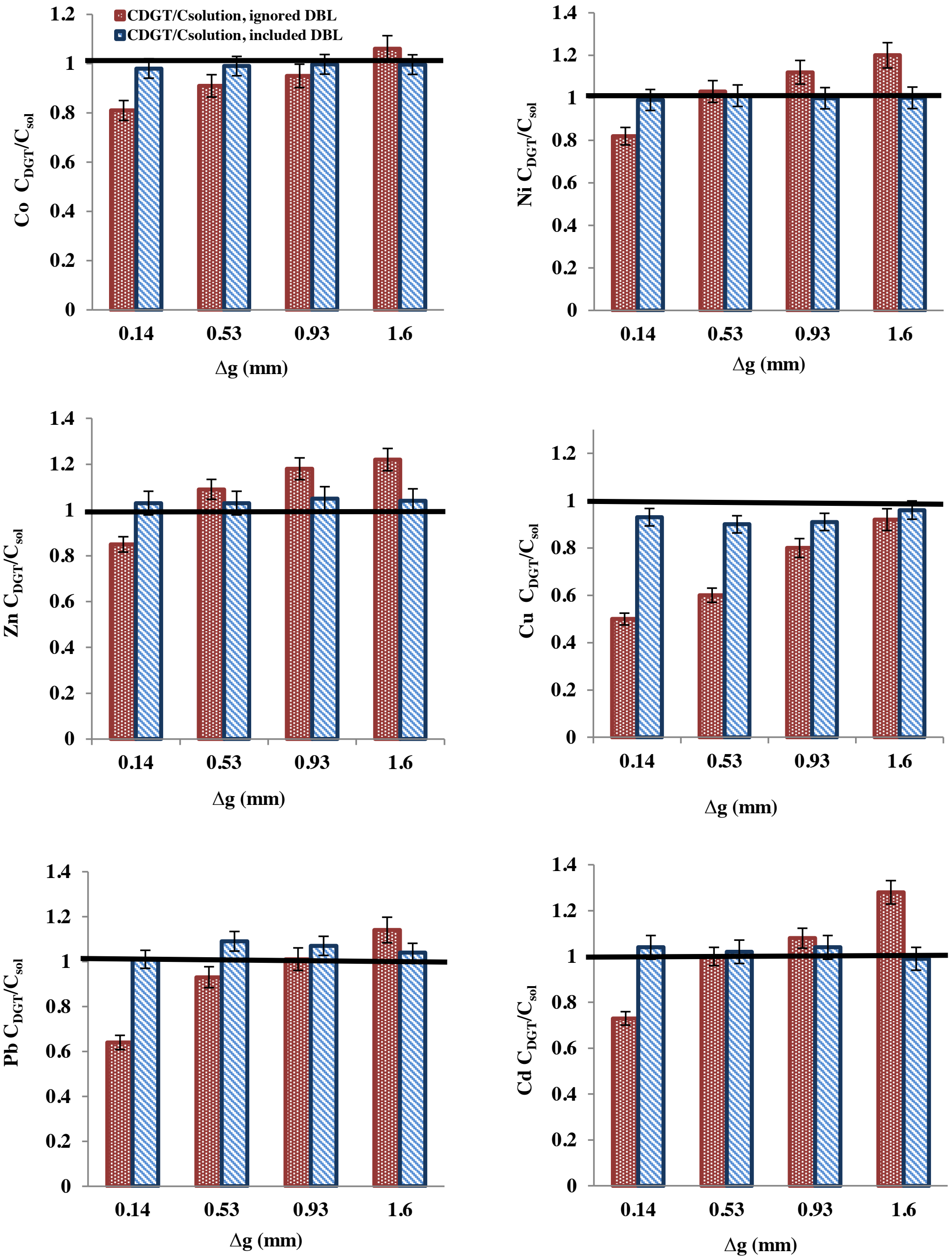
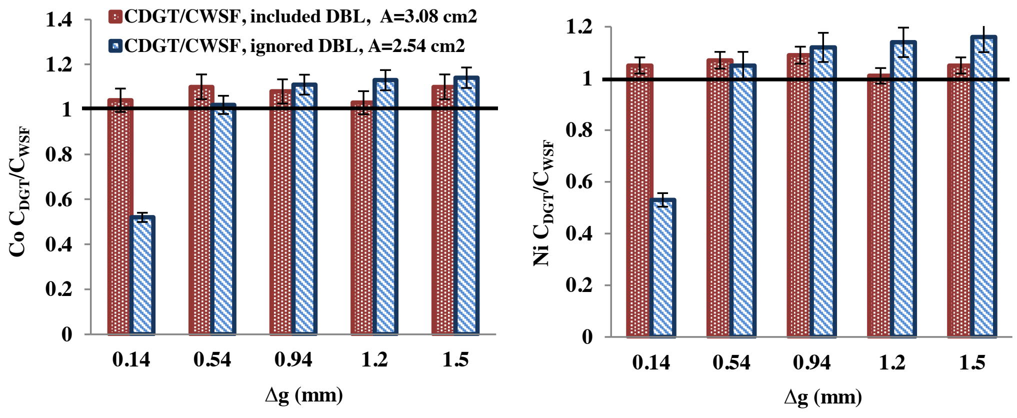


Figure 3.10. The ratio $C_{DGT}/C_{solution}$, calculated where the DBL thickness is ignored and included, 12 h deployment in synthetic solution of 0.5 mol/L NaCl ionic strength contains 50 µg/L of nitrates of (Cd, Cu, Co, Ni, Zn and Pb), at pH ≈ 5.4 and T= 19 °C without oil.

Recalculating C_{DGT}, accounting for the DBL and using an effective area of 3.08 cm^2 using **equation (3.5)** as proposed by Warnken et al. (2006) for all devices deployed. The obtained results were improved with the mean of the theoretical values from (0.93 ± 0.028) (2.8% RSD) to (1.01 ± 0.024) (2.4% RSD) for all studied metals as shown in the **Figure 3.10**. The observations obtained were in good agreement with findings reported by Warnken et al. (2006) and Uher et al. (2013). Ratio of 1 indicates good performance of DGT. The results suggest that DBL can be neglected for calculations of C_{DGT} for Co, Ni, Cd, Zn and Pb when the diffusion layer thickness is above 0.53 mm. For diffusion layer thickness is at 0.14 mm, DBL has a greater effect and it cannot be ignored for the DGT calculations. For Cu, DBL should be considered in all calculations even for thicker diffusion layers.

The results for DGT devices deployed for 24 hours in solution containing 3% OWR oil are shown in **Figure 3.11**. By ignoring the DBL, the mean ratios for C_{DGT}/C_{soln}, ranged between (0.33 ± 0.12 to 1.2 ± 0.13) of (5.4% RSD) for Co, Ni, Zn and Pb and (0.075 ± 0.096 to 0.89 ± 0.17) of (5.87% RSD) for Cd and Cu. Similarly, the results indicate that DBL cannot be ignored for thinner diffusion layer.



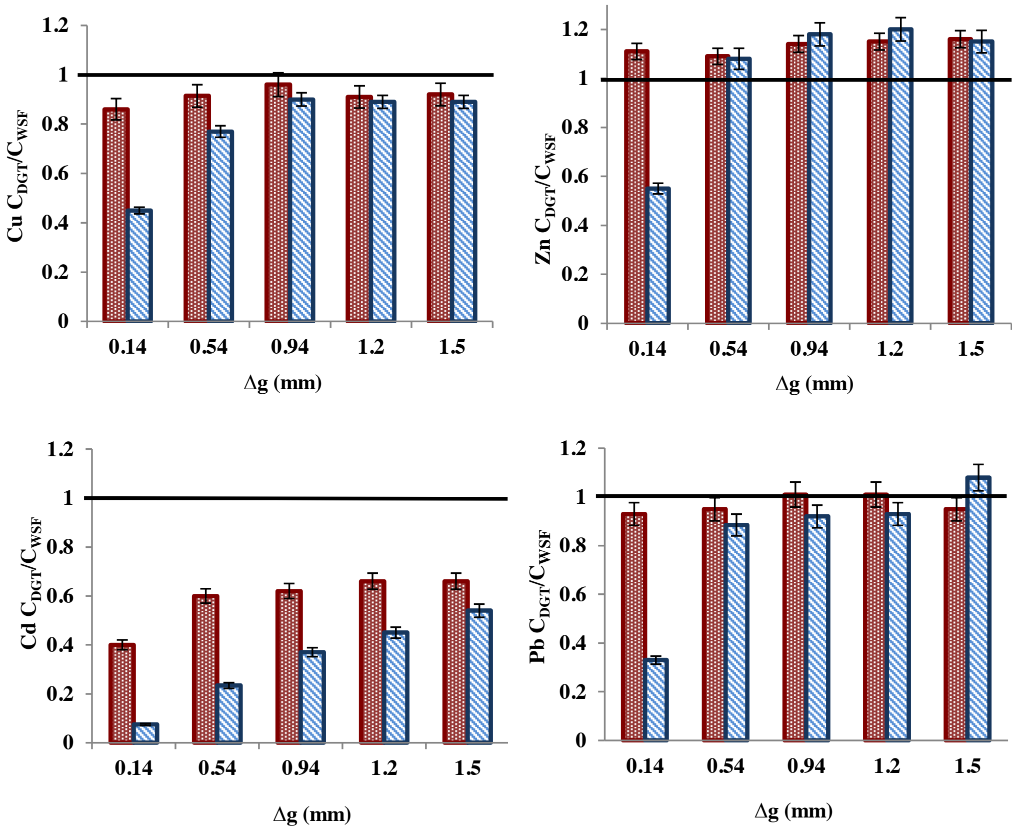
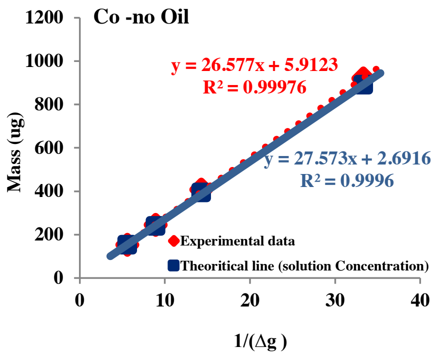
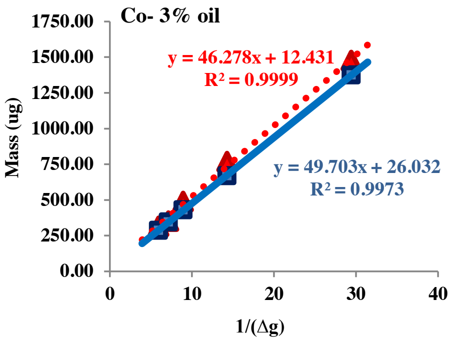


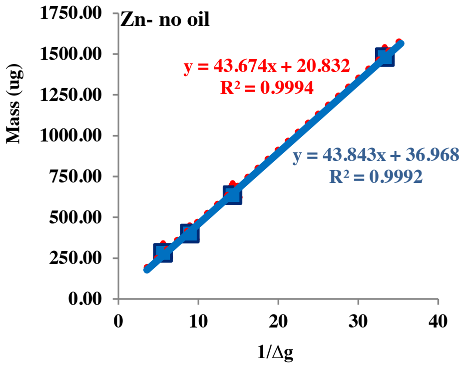
Figure 3.11. The ratio C_{DGT}/C_{WSF} of different diffusion layers, calculated where the DBL thickness is neglected and included using 3.08 cm2 sampling area, for 24 h deployment in a synthetic solution of 0.5 mol/L NaCl ionic strength containing 50 µg/L of nitrates of (Cd, Cu, Co, Ni, Zn and Pb), at pH ≈ 5.4 and T= 19 °C with 3% OWR, w/v.

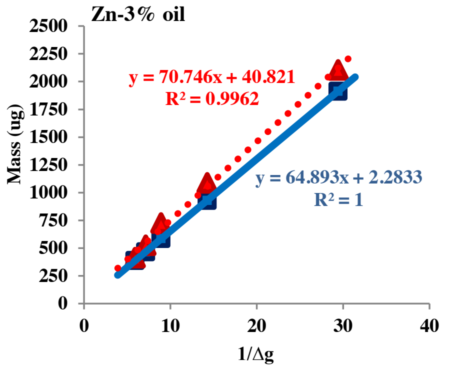
The ratios of C_{DGT}/C_{soln} for Cu were all below 1. This is attributed to the strong complexation of Cu and oil-ligands that is less labile. Much lower ratios (about only 0.5) are observed for Cd. This indicates even stronger complexes that are inert or large complexes that cannot diffuse through the DGT diffusive gel.

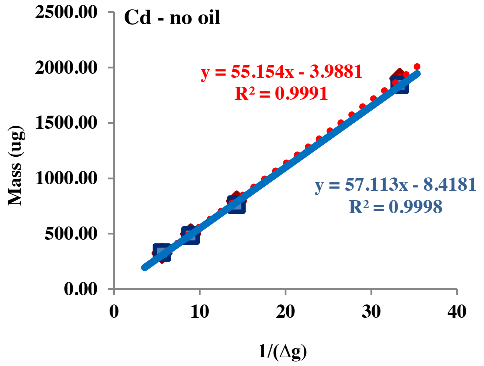
From the above discussion it can be observed that the degree of the metal-DOM dissociation as a function of metal lability in solution with oil can be listed as Zn > Co > Ni > Pb> Cu >> Cd. Results for other metals under the same experiments at varying hydro gel thicknesses are shown in the **Appendix (B)-Figure 1**.

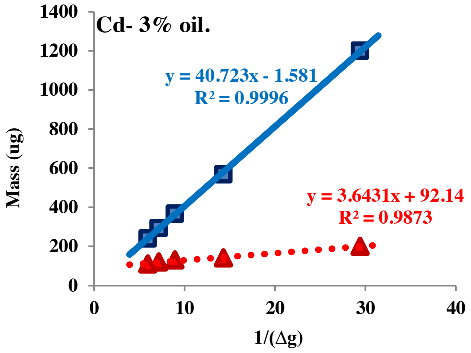

Co -no Oil
y = 26.577x + 5.9123
R² = 0.99976
y = 27.573x + 2.6916
R² = 0.9996
Experimental data
Theoritical line (solution Concentration)
Mass (ug)
1/(Δg)
0
200
400
600
800
1000
1200
0
10
20
30
40

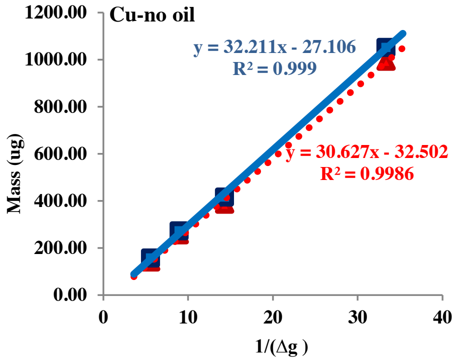

Co- 3% oil
y = 46.278x + 12.431
R² = 0.9999
y = 49.703x + 26.032
R² = 0.9973
Mass (ug)
1/(Δg)
0.00
250.00
500.00
750.00
1000.00
1250.00
1500.00
1750.00
0
10
20
30
40

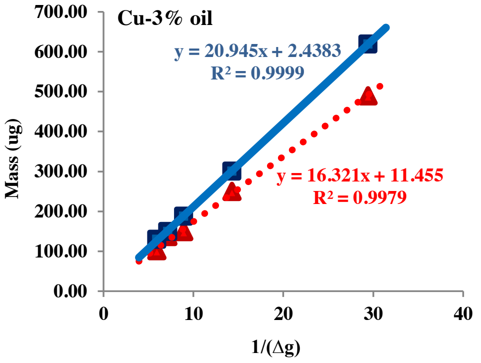

Zn- no oil
y = 43.674x + 20.832
R² = 0.9994
y = 43.843x + 36.968
R² = 0.9992
Mass (ug)
1/Δg
0.00
250.00
500.00
750.00
1000.00
1250.00
1500.00
1750.00
0
10
20
30
40


Zn-3% oil
y = 70.746x + 40.821
R² = 0.9962
y = 64.893x + 2.2833
R² = 1
Mass (ug)
1/Δg
0
250
500
750
1000
1250
1500
1750
2000
2250
2500
0
10
20
30
40


Cd - no oil
y = 55.154x - 3.9881
R² = 0.9991
y = 57.113x - 8.4181
R² = 0.9998
Mass (ug)
1/(Δg)
0.00
500.00
1000.00
1500.00
2000.00
2500.00
0
10
20
30
40


Cd- 3% oil.
y = 40.723x - 1.581
R² = 0.9996
y = 3.6431x + 92.14
R² = 0.9873
Mass (ug)
1/(Δg)
0
200
400
600
800
1000
1200
1400
0
10
20
30
40


Cu-no oil
y = 32.211x - 27.106
R² = 0.999
y = 30.627x - 32.502
R² = 0.9986
Mass (ug)
1/(Δg)
0.00
200.00
400.00
600.00
800.00
1000.00
1200.00
0
10
20
30
40


Cu-3% oil
y = 20.945x + 2.4383
R² = 0.9999
y = 16.321x + 11.455
R² = 0.9979
Mass (ug)
1/(Δg)
0.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
0
10
20
30
40

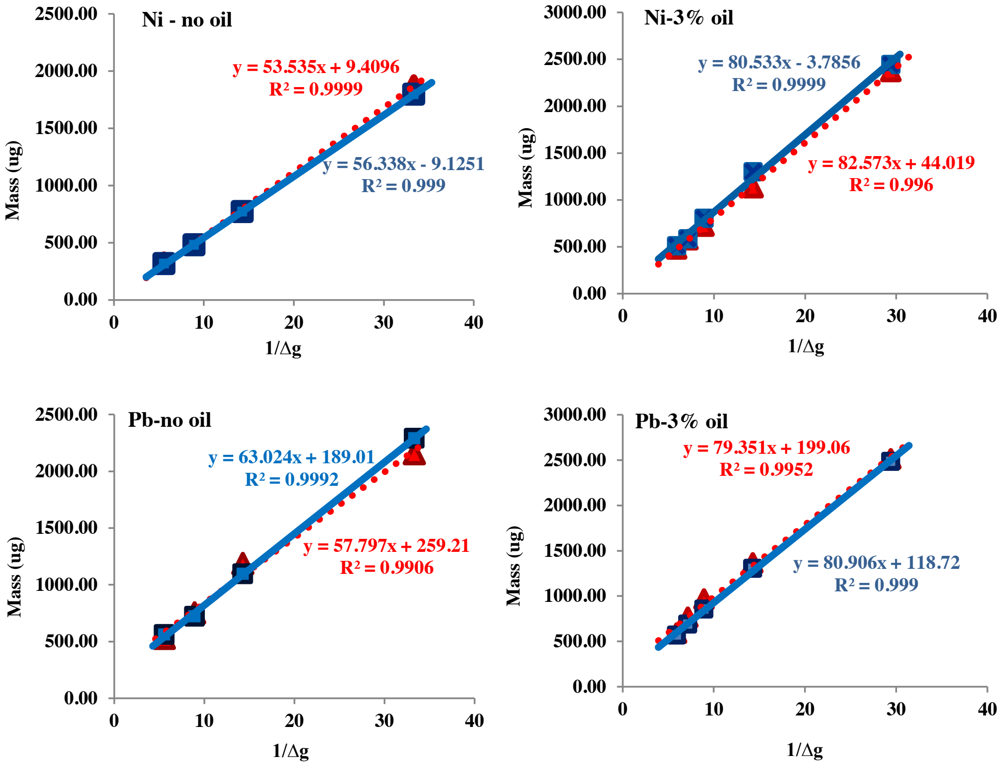


Figure 3.12. The mass of the labile metal fractions accumulated by resin gel in DGT devices as a function of thicknesses (Δg). The DGT units of different thicknesses of hydrogel were exposed to the synthetic solutions with 3% OWR and with no oil, containing ≈ 50 µg/L of Cd, Cu, Co, Ni, Pb and Zn nitrates, pH =5.6 and 0.5 mol/L NaCl ionic strength. Using the measured diffusion coefficients and including DBL and soil device effective sampling area =3.08 cm^2. The solid lines are well fit for the experimental data; the dashed lines are predicted relationships derived from deployment parameters using DGT equation.

The above findings have also been confirmed by the plots of DGT accumulated mass versus 1/Δg, where experiment data were compared with DGT theoretical lines. Slight deviation of Cu and huge deviation of Cd can be observed, in consistent with the conclusions from **Figure 3.10** and **Figure 3.11**.

3.3.9. Comparison of DGT measurements (labile) and resin extraction (WSF)

The concentrations of labile metals measured by DGT were compared with those obtained by the Chelex resin extraction method on the same synthetic solutions at different amount of oil at OWR of 3%, 5% and 25%, w/v. The results of a total eight of laboratory experiments performed in synthetic solutions were presented in **Figure 3.13**.

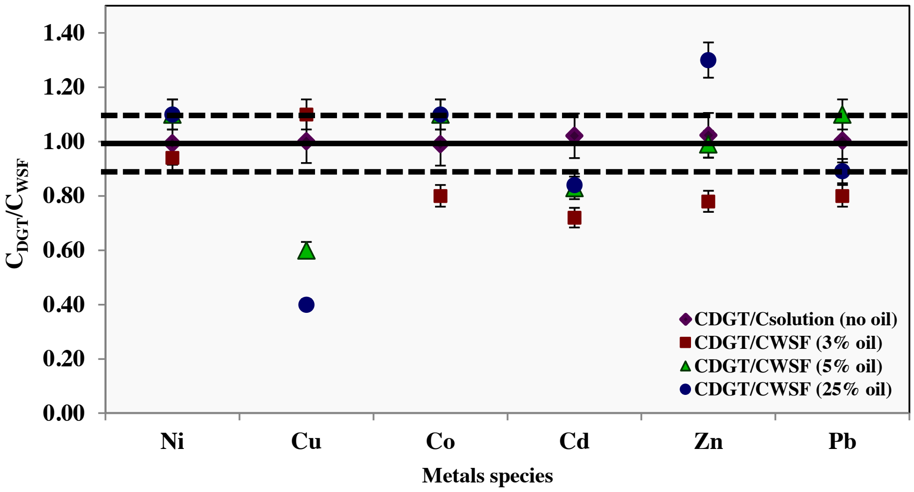


Figure 3.13. C_{DGT}/C_{WSF} of metals Co, Ni, Cu, Zn, Cd and Pb in the synthetic solutions without oil and with varying OWR (3%, 5% and 25%, w/v), containing 50 µg/L targeted metals, pH 5.6 at 0.5 mol/L NaCl ionic strength.

For all trace metals studied, except for Cu at high OWR (5% and 25%), the DGT technique showed similar trends as obtained by resin extraction method. However, the DGT labile metals were generally lower than resin extraction method in the solution with 3% OWR. This was probably attributed to the presence of some large molecular weight ligands in 3% OWR which cannot diffuse through the gel in the DGT devices. It is well established that the oil contains a significant amount of metals that can be dissolved in water, which results in an increase in metal concentrations

(Nduka and Orisakwe, 2009; de Souza et al., 2014). This is the case for Zn at 25% OWR.

For Cu, the DGT measured labile concentration is similar to the WSF measured by resin extraction method in solution with 3% OWR. In solutions of 5% and 25% OWR, DGT labile Cu was much lower than Cu concentrations obtained by resin extraction method. This indicated that Cu in both solutions with 5% and 25% OWR may form large and strong complexes, could not diffuse through the hydrogel or could not dissociate during diffusion (Chakraborty et al., 2009; Kersanach et al., 2009). Combination of DGT and resin extraction methods for trace metals in solutions of different OWR% is useful for understanding the effect of crude oil ligands on trace metal speciation in oil contaminated seawater.

3.4. Conclusion

This chapter demonstrates the potential of DGT technique for determining the labile speciation of trace metals in seawaters polluted with varying concentrations of crude oil OWR% under varying mixing times. DGT performance was validated in synthetic solutions of 0.5 mol/L and 0.7 mol/L NaCl without and with oil at varying concentrations. Using DGT devices containing varying thicknesses of diffusive gel showed that DGT labile species increased as a function of the diffusive layer thickness in synthetic solutions with and without oil. For Cd and Cu, DGT measurements were significantly lower than those measured by resin extraction (WSF) due to complexation with large ligands which cannot diffuse across the hydrogel. The DBLs are influenced by oil ligands (apparent layer) and it is greater than the (physical layer) (δ) explained according to the Eigen mechanism. For all trace metals studied, except for Cu at high OWR (5% and 25%), the DGT technique showed similar trends as obtained by resin extraction method. Combination of DGT and resin extraction methods for trace metals in solutions of different OWR% is useful for understanding the effect of crude oil ligands on trace metal speciation in oil contaminated seawater. The DGT technique was shown to be a reliable and robust procedure for trace metal speciation in crude oil contaminated marine system.

Chapter 4 – Development of DGT technique with different membranes for metal speciation in crude Oil contaminated marine environments

4.1. Introduction

Many research achievements have demonstrated that the standard DGT is an effective dynamic technique for metal speciation measurements in natural waters (Davison and Zhang, 2012). However, it has not been used in oil contaminated seawaters for measuring different metal speciation. Reliable direct measurement of trace metals speciation in crude oil contaminated marine systems is a challenge for analytical method due to their complex chemistry, oil complexes matrix, high salinity and frequent occurrence at low concentrations. More important, however, is the lack of knowledge on trace metals speciation in seawater impacted with crude oil contamination. Therefore, further experimental work needs to be done in developing DGT dynamic technique so that only targeted metals species is to discriminate trace metals species in crude oil contaminated seawater. It is necessary for providing reliable and sufficient information to interpret the reactivity of metals in biological and environmental processes.

In seawaters, trace metal ions may exist in a different chemical forms, categorised by the size, charge and density, all of which account in part for their distribution in the marine systems (Singhal et al., 2006). The trace metals in seawaters are associated with varying sizes of dissolved colloidal inorganic, organic ligands. A variety of filtration and dialysis membranes were applied for trace metals discrimination in seawater on the basis of molecular size. The separation of the dissolved phase of trace metals species can be achieved on the basis of filtration methods, either with conventional filters membrane or the use of numerous ultra-filtration techniques. A single filtration step, through 0.4 µm and 0.45 µm is often employed as a preliminary separation for the dissolved and particulate phases (Harrison et al., 1981). Forsberg et al. (2006) used 0.22 µm membrane filtration in the Baltic Sea immediately after sampling as an on-site fractionation procedure prior the 1kD ultrafiltration and as a stand-alone speciation step. They measured Cd, Cu, Mn, Ni, and Zn species at two sites and the results were compared with DGT measurements. The measured concentrations of Mn, Zn, and Cd in DGT agreed well with those obtained in 1 kDa ultrafiltered samples. The DGT-labile concentrations of Cu and Ni species were lower than ultrafiltered concentrations. All metals in the work were influenced by large organic ligands and phytoplankton activity (Forsberg et al., 2006). However, this separation is complicated by the presence of colloids often results in clogging of the filters membrane during filtration decreases the effective pore size and can cause the retention of increasing amounts of colloids, which then decreasing the concentration of the metals (Mello et al., 2005). Various factors also can affect metals speciation measurements during filtration procedure including (1) type of filter, (2) filtration method, (3) filter diameter, (4) trace metals sorption or desorption from the filter or from retained particles, (6) concentration of organic complexes, and (7) volume of sample used in filter (Gimpel et al., 2003; Forsberg et al., 2006).

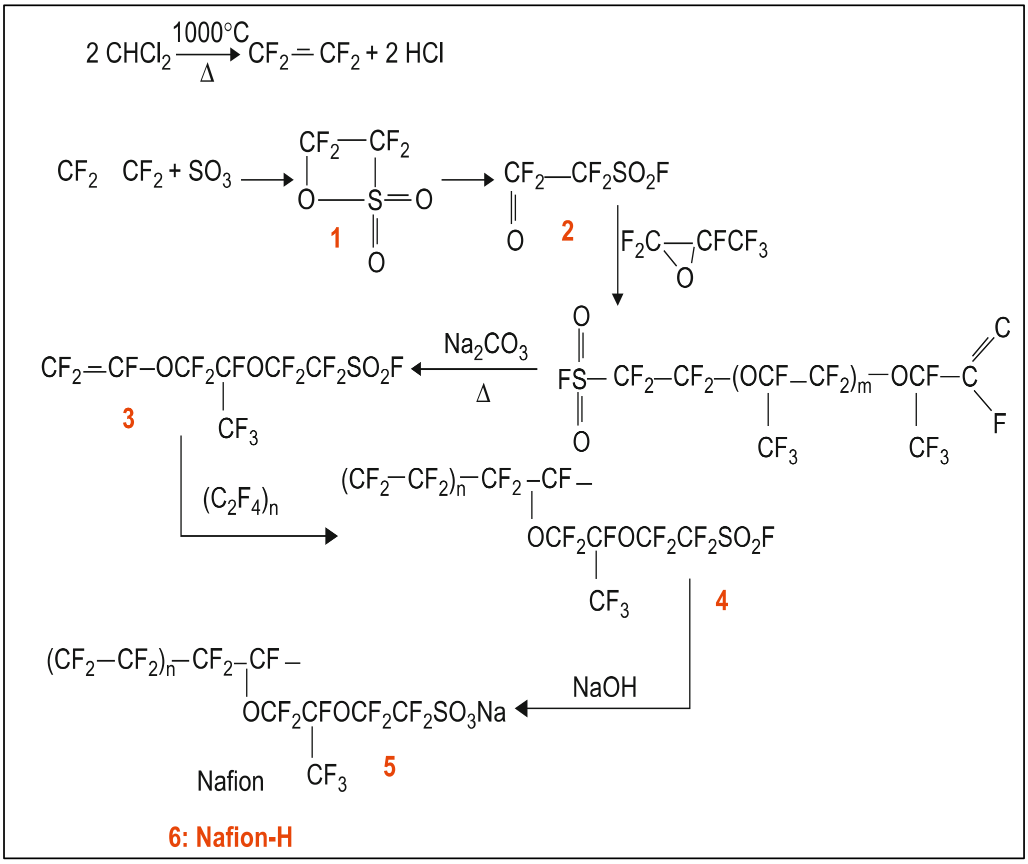
Equilibrium dialysis, for the study of trace metal speciation in seawaters has been used. However, the literature in this area is limited. Dialysis membrane allows the separation of different groups of metals species on the basis of molecular weight (Landner, 1987). Apte et al. (1989) used equilibrium dialysis to study Cd, Ni, Cu and Zn speciation in seawater. Ideally, the dialysis membranes should permeable only to species in true solution, but it has been concluded from other studies some high molecular weight ligands, colloids can pass through membrane (Caroli, 1996; Gimpel et al., 2003).

4.1.1. Nafion membrane properties

Nafion membrane is a unique perfluorosulphonate ionomers separator membrane (Ahmed et al., 2009). It has extensive applications due to its chemical and electrochemical inertness, its insolubility in water, its hydrophilicity, and chemical and thermal stability, which all lead to it possessing almost ideal properties as a chemical modifier (Hurst and Bruland, 2005; Ahmed et al., 2009; Ramkumar, 2012). It has immense possibility for use as a cation exchange membrane for trace metals in the contaminated marine systems owing to its high ion-conductivity (0.083 S/cm/ Nafion-112) and ionic content and shelf life of the membrane (Slade et al., 2002; Ramkumar, 2012). It is a very strong Bronsted acid due to the presence of ($-SO_3^-$) groups attached to the Teflon backbone and Nafion is a very strong proton donor owing to the stabilizing effect enhanced by sulfonic acid in the large polymer matrix (Lim et al., 2009; Ramkumar, 2012). The permeation rate through a membrane is directly related to the thickness (Manea and Mulder, 2002). A higher performance separation and selectivity can be achieved by using a thinner thickness as is applied in this study (Blom et al., 2003). The molecular weight of Nafion is difficult to determine using conventional methods because it is insoluble. It can be described by using equivalent weight or material thickness (Ramkumar, 2012).

4.1.2. The synthesis and structure of Nafion membrane

Nafion membrane made from a precursor co-polymerization of different amount of tetrafluoroethylene (TFE) and unsaturated perfluoroalkyl sulfonyl fluoride as shown in the **Scheme 4.1**. The strongly acidic sulfonic acid group cation exchange site can be easily produced from the hydrolyzation of sulfonyl fluoride group (Ahmed et al., 2009).



Scheme 4.1. Nafion synthesis (Ramkumar, 2012).

The sodium hydroxide NaOH used to convert SO2F group to sodium form SO2Na precursor that can be extruded into sheets of the demanded thicknesses.

Thereafter, the membrane film is soaked in a concentrated acid HNO_3 solution to produce $–SO_3H$ form (Sahu et al., 2009; Ramkumar, 2012).

Nafion is not covalently cross-linked polymer, which makes its solvent welling properties depend on large extent of the hydration characteristics of counter ions and it's pretreatment (Ahmed et al., 2009). Most importantly, the occurrence of transition interphases between hydrophilic cation exchange sites ($–SO_3H$) and hydrophobic fluorinated backbone domains in the same polymer leads to the unique micro-phase separation (Ahmed et al., 2009). The membrane has 40 Å clusters of sulphonate-ended perfluoroalkyl ether groups that are organised as inverted micelles arranged on a lattice as shown in the **Figure 4.1 (a)** (Smitha et al., 2005; Sahu et al., 2009). The size of pores or channels that connect these micelles is 10 Å. When the polymers exposed to the water or other hydrophilic solvents, it tends to segregates in two subphases (Sahu et al., 2009). The hydrophilic subphase formed by water, sulphonate groups and mobile ionic counter region contains absorbed water. Hydrophobic subphase comprising the polymer backbone (perfluorinated polymer backbones) and by the side chains, except of their sulphonate end sites **Figure 4.1 (b)** (Vishnyakov and Neimark, 2001; Sahu et al., 2009; Ramkumar, 2012).

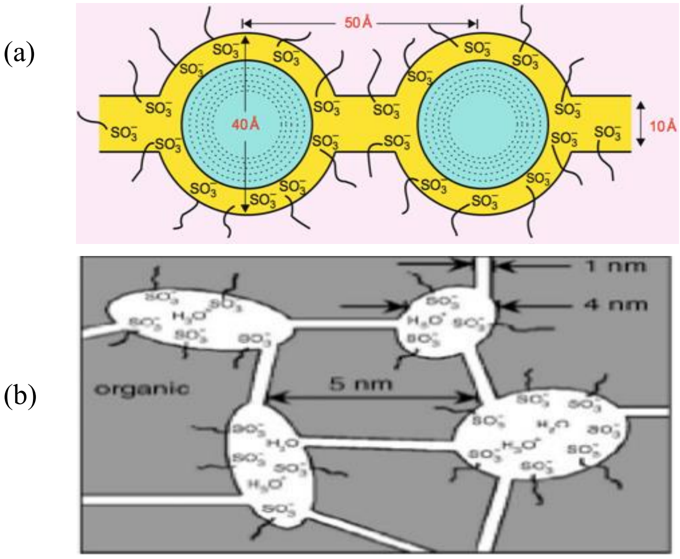


Figure 4.1. Cluster-network model for the interactions between polymer and water in Nafion membrane (Smitha et al., 2005; Ramkumar, 2012).

In this study a thinner Nafion 112 of 0.05 mm thickness and 1100 equivalent weight (EW) was used owing to its high permeation rate, rapid hydration and high conductivity. The EW is defined as the weight of Nafion (in grams) per mole of sulphonic acid group when the membrane is in acid form (Smitha et al., 2005; Ramkumar, 2012). For example, Nafion 112 represents 1100 g EW (amu) and thickness of 0.002 inches or 0.05 mm, which matches to 6.8 % of the Nafion membrane being sulfonate groups by mass (Sahu et al., 2009).

4.1.3. Use of Nafion film for excluding anionic species.

The Nafion polymer as a modifier has been widely and ideally used for analytical purposes and plays crucial roles for analytical methods owing to its chemical and physical properties (Hurst and Bruland, 2005). Nafion, due to its high selectivity and the negatively charged properties, have been employed to prevent diffusion of almost all negatively charged species to an electrode or adsorbent depends on their sizes and affinities for the membrane (Murimboh et al., 2000; Blom et al., 2003; Hurst and Bruland, 2005).

The pK_a of the Nafion ≈ 1 owing to the $–SO_3^-$ groups. At pH 5 of the samples, the $–SO_3H$ groups tend to dissociate and became negatively charged and act as a cation exchange (Murimboh et al., 2000). Nafion-coated electrode has been used for lead (Pb) speciation studies synthetic solution at pH 8 and ionic strength of 0.6 M NaCl. The complexing agents studied were nitrilotriacetic acid, ethylenediamine, oxalic acid (PbOx) and humic acid. At pH 8 Pb-NTA species were non labile and difficult to measurable due to the high stability constant, whereas the observed labile Pb fractions from Pb-EDTA complexes was about 20% and the negatively charged complexes are repelled by Nafion membrane. Although Pb-O complex was partly hindered, it was more labile and small negatively charged Pb-Ox transport to the adsorbent (Dam and Schrøder, 1996).

Nafion coated electrodes have been also widely applied for identifying the biological species at different pH mediums. At pH 5, ascorbic acid occurs in the anionic form and prevented by Nafion film from reaching the electrode surface, whereas uric acid is in the cationic form and can be freely exchanged into the Nafion membrane (Zen, 1998). Above pH 6, uric acid is essentially ionized and Nafion cation exchange polymer eliminated the passage of both anions (ascorbic acid and uric acid) through the membrane to adsorbent in electrode surface (Zen, 1998; Yuan et al., 2005). A passive sampling device similar to DGT consists of a receiving membrane; used a filter membrane coated with Nafion to eliminate transport of M-NOM to chelating membrane. In contrast to the Nafion applications described above, smaller negatively charged complexes M-NTA and oxine-5-sulfonate are permeated Nafion coating membrane to receiving disc (Blom et al., 2003).

4.1.4. Dialysis membranes

The membranes are used for the separation of the smaller hydrated metal cations and soluble inorganic complexes from the larger metal-DOM complexes. Number of studies used anodic stripping voltammetry with dialysis to divide the metal species into different sized fractions. The species that permeates the smallest pore size are generally taken to be free metal ions or small labile complexes (Berggren, 1990; Dewey, 1994; Förstner and Wittmann, 2012). DGT has also been used in conjunction with dialysis to study speciation of trace metals in lake water. Gimpel et al. (2003) used DGT and dialysis in speciation of trace metals in five lakes for characterising accurately the distribution of trace metal species. They found that Zn by dialysis in circumneutral water were slightly higher than DGT measurements, as zinc might be partially complexed by fulvic or humic acid. The substantial differences between dialysis and DGT measurements for Cu were attributed to the complexation by fulvic or humic substances in the studied lakes waters (Gimpel et al., 2003). Pouran et al. (2013 and 2014) applied 1000 MWCO (molecular weight cut off) dialysis in front of DGT diffusive gel for measuring ZnO Nanoparticles in soils. The diffusion of ZnO NPs can be prevented. Recently the Micro Float-A-Lyzer dialysis of different volumes and pore sizes is designed to stand upright on bench-tops during experimental preparation as well as float and self-orient during dialysis **Figure 4.2**. In this work, two types of equilibrium dialysis, 3500 Da and 1000 were used in DGT technique for distinction between free metals and M-DOM metals in synthetic solutions with and without oil matrix. Smaller MWCO dialysis was used to restrict the diffusion of organic complexes through diffusive gel to resin gel. The applicability of DGT technique to determination of trace metals species in synthetic solutions with and without crude oil contamination was examined by comparing the results obtained by Micro Float-A-Lyzer dialysis volume 100 -200µL and1000 MWCO.

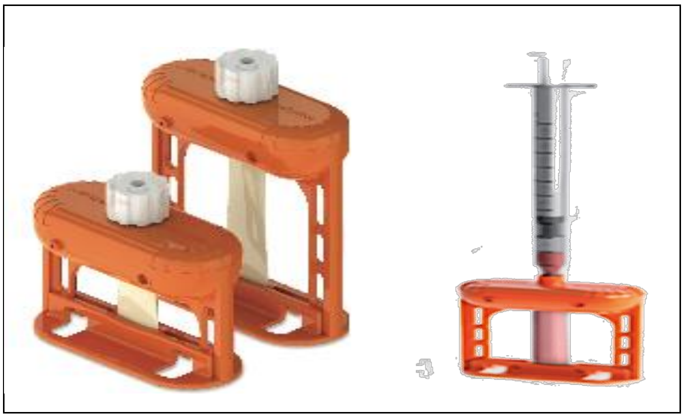


Figure 4.2. Micro Float-A-Lyzer

4.1.5. Objectives of the study

This chapter will focus on the development of a simple and reliable dynamic technique, based on DGT, for speciation measurements of trace metals in crude oil contaminated seawater using different separation membranes. It systemically assesses the influence of the crude oil ligands of various types and sizes on the lability and mobility of targeted trace metals in high ionic strength solutions in the presence of different levels of OWR%. The diffusion coefficients of trace metals through filter membranes and hydrogels with and without dialysis and Nafion112 membranes were measured using diffusion cell.

4.2. Materials and Methods

4.2.1. Reagents, materials and solutions.

Crude oil was provided by Ministry of Oil and Gas in Sultanate of Oman, high purity Milli-Q water (≥ 18 MΩ/cm) was used to prepare all solutions. A 1000 mg/L stock solutions of multielements (Cd, Ni, Zn, Cu, Co and Pb) for experiments were prepared from their nitrate salts by dissolving the salts in Milli.Q water. All experimental components were acid-cleaned in 10% (v/v) HNO_3 overnight and rinsed thoroughly with Milli.Q water before use. The binding layer, chelating resin (Chelex-100, Bio-Rad), the diffusive layers, including open pore (thickness ≈ 0.78 mm), and restricted gels (thickness ≈ 0.76 mm) were prepared in the laboratory following procedure **Chapter 3, section 3.2.1**. The Nafion-112 with thickness of 0.05 mm was provided by Alfa Aesar, 1000 and 3500 MWCO (molecular weight cut off) dialysis membranes (thickness ≈0.05 mm), pore sizes of semi-permeable ≈1.9 nm and 3.3 nm, respectively, and were purchased from Spectrum Biotech. All gels and membranes were soaked in 0.5 M $NaNO_3$ solution before use to take a shorter time to attain equilibrium and eliminate diffusional artifacts present at low ionic strengths. The plastic moldings for the DGT devices were obtained from DGT Research Limited (Lancaster, UK). Micro Float-A-Lyzer dialysis, volume: 100 – 200 µL, concise MWCO's of 1000, were purchased from Spectrum Company.

4.2.2. Nafion preparation

Nafion-112 membrane was soaked in Milli.Q water for 8 days at room temperature, and then cut to 2.5 cm diameter disks using a stainless steel cutter. The membranes disks were washed by soaking in 1.12 mol/L (v/v) HNO_3 (Aristar, BDH) for 24 hours; they were then rinsed in Milli-Q water and stored in a 0.5 mol/L NaCl solution at pH ≈5.6 at room temperature until use. The Nafion membranes can be reused after soaking in Milli-Q water overnight and cleaning in 1.12-mol/L HNO_3.

4.2.3. Float-A-Lyzer dialysis preparation.

The micro dialysis was prepared following the instruction provided by *Spectra/Pro*. First wet the membrane to remove glycerin and achieve maximum membrane permeability. The Micro Float-A-Lyzer device soaked in 10% v/v ethanol (EtOH) followed by thoroughly flushing and soaking in Milli.Q water before dialysis. The cap of Micro Float-A-Lyzer device were removed and loaded with 10% (EtOH) using the provide 1 ml syringe, then place in the same alcohol solution for 15 minutes. Then device removed from alcohol solution and use the 1 ml syringe to remove the alcohol from the sample chamber. The device then rinsed several times with Milli.Q water to flush alcohol out of the sample chamber using 1 ml syringe. Then the device filled with Milli.Q water and placed in the Milli.Q water for 30 minutes to remove alcohol from membrane. The device removed from Milli.Q water and rinsed with MilliQ water several times to flush the sample chamber with water and remove it. Then the sample chamber in the device was loaded with (100 -200 μL) of sample using a rinsed 1 ml syringe. The filled devices (with inside solutions) were placed in the deployment solution using stir bar and magnetic stirrer during dialysis.

4.2.4. Diffusion coefficients measurements

The experiment was carried out to determine the diffusion coefficients of metals ions Cd^{2+}, Co^{2+} Ni^{2+}, Zn^{2+}, Cu^{2+} and Pb^{2+} through hydrogels and filter membranes (0.45μm pore size) with dialysis on the hydrogel using diffusion cell according to the procedure, which is thoroughly described by Zhang and Davison (1999) (**Figure 4.3**).

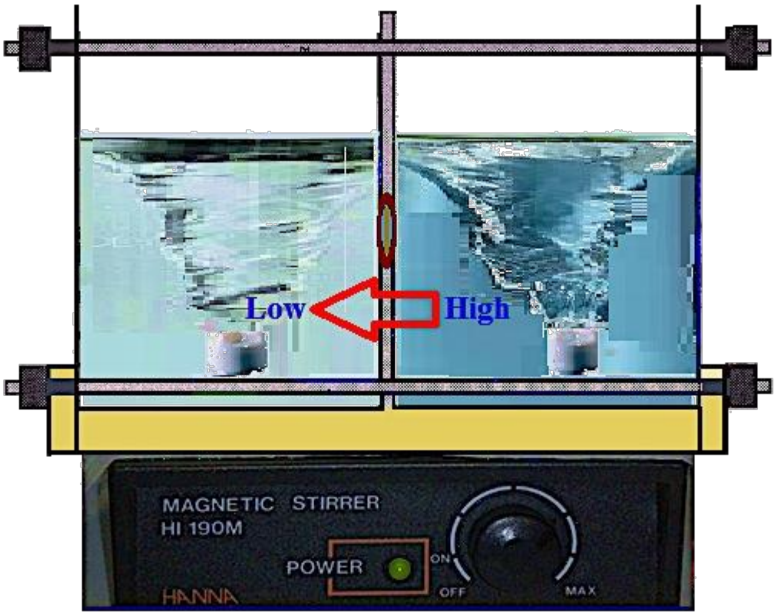


Figure 4.3. Diffusion Cell

The cell comprised of two compartments, each with an interconnecting 2 cm diameter opening. A 2.5 cm diameter disks of filter membrane and dialysis (Δg = 0.005 mm) membrane were placed in the front of hydrogels (Δg = 0.78 mm) between the openings. All measurements were carried out using 100 ml synthetic solutions of 0.5 mol/L NaCl at pH = 5.6 for both compartments (A, source and B, receiving). The carrier solution (A, source) contained 1mg/L of all targeted metals. Both compartments were stirred continuously for 3h and 45min using with magnetic-followers activated by magnetic stirrers to minimize DBL effect. The compartments were covered during experiments to prevent any evaporation.

The diffusion coefficients of the above trace metals were measured, in this way, through hydrogels and filter membranes with Nafion112 on the diffusive layer. The compartment A (source) contained 5 mg/L of (Ni, Zn and Cu) and 1 mg/L of (Cd, Co and Pb) as a carrier solution. Both compartments were stirred continuously for 8 hours using with magnetic-followers activated by magnetic stirrers to minimize DBL effect.

Sub samples of 0.1 ml were taken from each compartment. The sub-samples from compartment (B) were diluted 20 times using Milli-Q water and HNO_3 for ICP-MS analysis. Subsamples from compartment (A) were diluted 50 times using the same matrix (0.1 mol/L HNO_3). The temperature was measured at the beginning, middle and the end of experiments using (thermal thermometer). In total 12 subsamples were taken from each compartment. The measured concentrations of analytes obtained by ICP-MS analysis were used to estimate the mass of diffused analytes to compartment (B). The diffusion coefficients were calculated for the temperatures at which the experiment was achieved following the steps as described in **Chapter 3**.

The diffusion coefficients of metals were also measured, in this way, through filter membrane and hydrogel with Nafion112 membrane. The experiment was carried out for 8 hours.

4.2.5. DGT devices

For preparing and using standard DGT samplers of open pore (OP) and restricted pore (RP) diffusive gels, the procedures as explained in **Chapter 3** were followed. To make DGT sampler using 1000 MWCO dialysis membrane, first a binding layer disc is placed on the DGT base. The diffusive gel disc was then put on the top of the resin gel. Next, 1000 MWCO (molecular weight cut off) dialysis membrane is placed on the diffusive gel. A clean 25 mm diameter and 0.45 μm cellulose nitrate filter membranes of 0.14 mm is placed on the dialysis. The assembly completed by pushing the cap carefully and firmly over the piston and pressed to ensure a good seal between the cap and base. To prevent the formation of air bubbles between gel layers and filter membrane, they kept wet during DGT assembly.

(Nafion112)-DGT and (3500 MWCO dialysis)-DGT devices were assembled by following the above steps using Nafion112 and 3500 MWCO instead of 1000 MWCO dialysis membrane **Figure 4.4**.

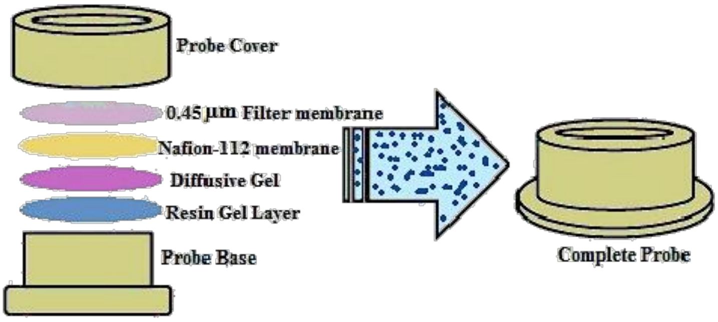


Figure 4.4. Nafion112- DGT assembly

4.2.6. Performance of DGT devices of different diffusive layers in the synthetic solutions with and without crude oil.

The performance of five versions of DGT devices (OP-DGT, RG-DGT, (dialysis 1000Da)-DGT, (dialysis 3500Da)-DGT, (Nafion112)-DGT was investigated in well-stirred 8 L synthetic solution of 0.5 mol/L NaCl, at pH= 5.6 containing ≈ 20 μg/L nitrate salts of Cd, Cu, Co, Pb, Ni, Zn with and without oil. The solution was left on magnetic stirring for two days to equilibrate. The DGT samplers were deployed in triplicates without oil for 17 h except (Nafion112)-DGT were carried out for 24 h.

The influence of oil ligands on the measurement of labile metals species by DGT devices was investigated in 8 L of synthetic solutions of the same ionic strength and pH of the above solution, treated with two different ratios of crude oil: 1 and 4% w/v in two separate containers. The synthetic solutions were stirred slowly 10 L capacity plastic containers for 48 hours. After mixing, the oil water mixture was allowed to stand overnight. The lower phase was collected for DGT deployments. All DGT devices were carried out in well-stirred 8 L of 0.5 mol/L NaCl synthetic solution contain 20 µg/L of Ni, Cd, Co, Cu, Pb and Zn, without oil.

Aliquots of 1 ml of sample were taken from the synthetic deployment solution at the start, middle and end of the experiment for subsequent analysis to estimate total concentration. For solutions with oil addition, also sample 1 ml was taken before oil addition and after. The temperature was measured during taking samples using (thermal thermometer). The accumulated mass, M, is measured in the laboratory. Obtained diffusion coefficient, D, deployment time, t, thickness of the diffusive layer, Δg, and area of the exposure opening, A, the concentration, C, can be calculated:

$$C_{DGT} = \frac{M\Delta g}{DAt} \qquad (4.1)$$

4.3. Micro Float microdialysis of 1000 MWCO

For the microdialysis experiments, Micro Float-A-Lyzer device of 100-200 µL and 1000 MWCO was used. It designed to stand upright on bench-tops during experimental preparation as well as float and self-orient during dialysis. The microdialysis device pretreatment demonstrated in the **section 4.2.3**. To test the efficiency of the device it is equilibrated 1, 2 and 4 days in 3 L synthetic solution of 0.5 mol/L NaCl, pH=5.4, containing 20 µg/L of nitrate salts of Cd, Cu, Co, Pb, Ni and Zn, referred to as the outside solution. Three Float Microdylsis devices were filled with solutions without metals referred to as the inside solutions. The devices in duplicates were immersed in the stirred solution using magnetic stirrers. The equilibrium is reached when the concentrations in the inside and outside solutions are equal after 24 hours.

For the main experiments using synthetic solutions of the same ionic strengths and pH without and with crude oil of 1 and 4 OWR%, Float Microdialysis devices in duplicates were deployed in separate containers for 24 hours. In order to avoid the effects of ionic strength viscosity and the disturbance from metals-ligands binding equilibrium in the sample as a result of metals transport into the inside solutions, all chamber devices in experiments were filled with solutions matching the concentration and pH of the outside solution. Aliquots (0.1 ml) of the samples were taken at the onset and at the end from both inside and outside solutions of all experiments for total metals concentrations analysis. The determined concentrations of inorganic species were used for comparison to those obtained with (dialysis 1000 MWCO)-DGT) in all synthetic solutions with and without oil.

4.4. Results and discussion

4.4.1. Diffusion Coefficients.

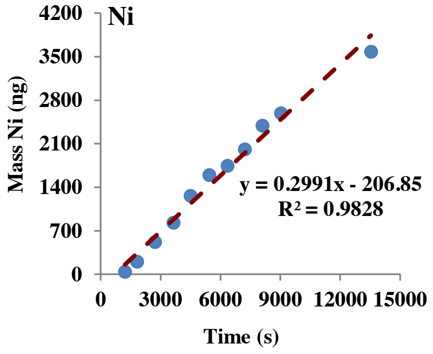
From DGT **equation (4.2)** it can be noted that the calculation of DGT labile concentration is dependent on the diffusion coefficients and it is important factor for the overall accuracy. Very limit work has been reported in literature about the estimated diffusion coefficients of metals ions using Nafion or dialysis membranes. The diffusion coefficients of metals through filter membrane and diffusive gels with and without dialysis and Nafion112 membranes were obtained according to the procedure described above **Table 4.1**.

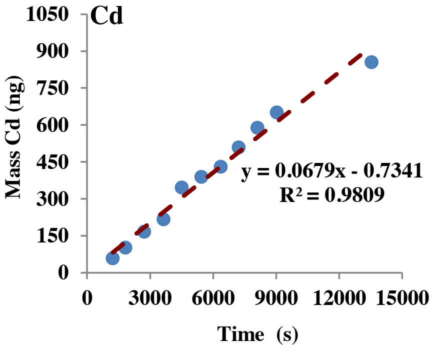
Table 4.1. Diffusion coefficients through filter membrane and diffusive gel with and without dialysis and Nafion112 membranes (pH =5.6, Δg= 0.097 cm; A= 1.77 cm^2)

Metals	D through filter membrane and diffusive gel (D, $\times\ 10^{-6}\ \text{cm}^2\text{s}^{-1}$), T=19 °C	D through filter membrane and diffusive gel with dialysis, (D, $\times\ 10^{-6}\ \text{cm}^2\text{s}^{-1}$), T=21 °C	D through filter membrane and diffusive gel with Nafion112, (D, $\times\ 10^{-7}\ \text{cm}^2\text{s}^{-1}$), 22 °C
Co	**4.7**	**4.5**	**1.2**
Cu	**4.82**	**4.7**	**3**
Cd	**4.8**	**4.1**	**1.87**
Ni	**4.6**	**3.8**	**1.8**
Pb	**6.33**	**4.4**	**1.86**
Zn	**4.76**	**3.5**	**1.3**

4.4.2. The measurements of diffusion coefficients of metal ions using dialysis

Figure 4.5. shows the plot of the masses (ng) of metals diffused and accumulated the receptor compartment (B) vs. time (s). Good linear relationship ($R^2 \approx 0.98$ -0.996) was obtained for all metals.





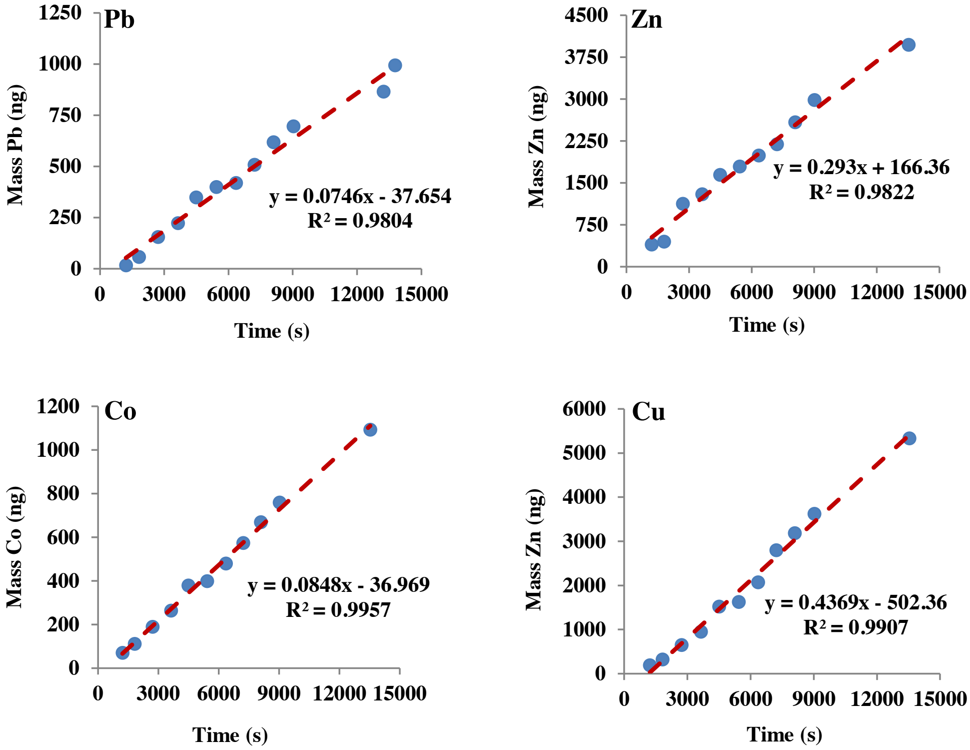
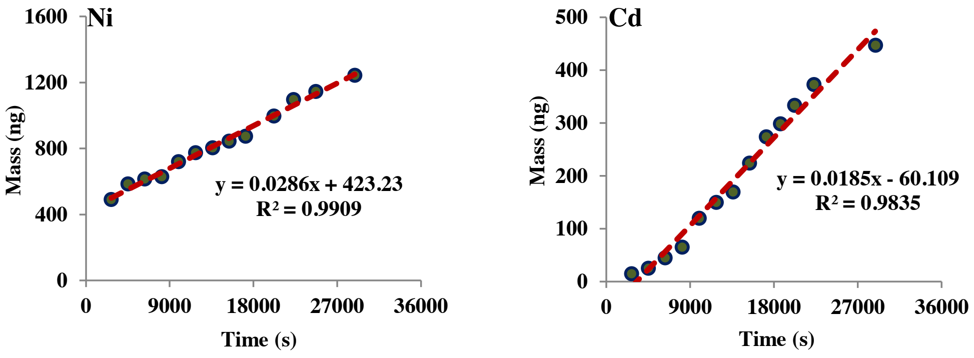


Figure 4.5. Plots of masses of metals ions diffused through filter membrane and diffusive gel with dialysis membrane versus time during 3 hours and 45 minutes diffusion cell experiment at 21 °C and pH = 5.6.

The diffusion coefficients of metals were calculated from the slope of the linear line in **Figure 4.5** and applying **equation (4.1)**. The results were presented in **Table 4.1**. The values of the diffusion coefficients of metals ions measured through filter membrane and diffusive gel with dialysis are slightly lower compared with the D values without dialysis. This may be attributed to the restriction in mobility by the structure of dialysis membrane with smaller pore size. After correcting for temperature, estimated values were 74.8%, 68%, 88%, 64%, 73% and 61.2% of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}, respectively of the calculated diffusion coefficients in water D_w at 25 °C. In the normal applications of DGT devices, DBL layer at membrane interface should be considered using diffusion coefficients of the metal ions in water (D_w). The dialysis membrane thickness can be used as an extension of the total diffusion thickness Δg in the applied DGT equation. Some research groups (Li et al., 2003; Fan et al., 2013) used diffusion cells to measure the diffusion coefficients of Cu, Cd and Pb ions through dialysis membranes of 12000 MWCO in a synthetic solution contained a binding agents as a receptors at varying ionic strengths. They found there was no interaction between the metal ions and the dialysis membrane. Li et al. (2003) reported decreased diffusion coefficients of Cu and Cd with increasing ionic strength. Chen et al. (2011) showed that the diffusion coefficients of Cd through the dialysis membrane immersed in simple inorganic receptor solution without binding agent increased as ionic strength decreased from 1.0 to 0.001M.

Diffusion coefficients of metal ions in Nafion112

Figure 4.6 illustrates the results obtained from the diffusion cell experiment using Nafion112 membrane. It shows the mass of metals diffused into the receptor compartment of the diffusion cell versus time. Reasonably good linearity ($R^2 \approx 0.983$-0.994) was found. The diffusion coefficients of metals ions through filter membrane and diffusive gel with Nafion112 were calculated using slopes of the plots in **Figure 4.6**. The obtained values of diffusion coefficients are presented in **Table 4.1**.



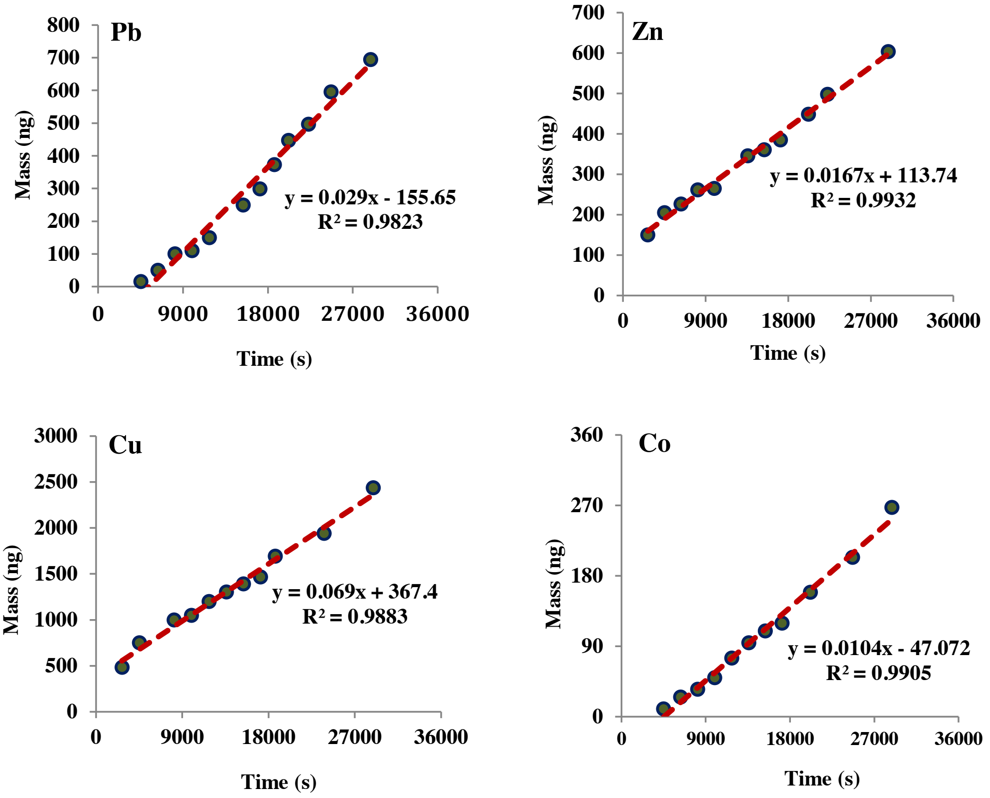


Figure 4.6. Plots of masses of metals ions diffused through filter membrane and diffusive gel plus Nafion112 membrane versus time during 8 hours diffusion cell experiment at 22 °C and pH = 5.6.

The use of Nafion112 in the diffusion cell experiment reduced the diffusion rate of metals due to the negative charges on the membrane and the exclusion of most metal complexes, which carry negative charges. The obtained diffusion coefficients were much lower than those measured through filter membrane and diffusive gel with and without dialysis (**Table 4.1**), 35 to 40 times lower for Co, 20 to 26 times lower for Cu, Cd and Ni, 26 to 35 times lower for Pb and Zn. These results agree with the diffusion coefficients of Cu^{2+} and Ni^{2+} reported by Huang et al. (2003) using Nafion 117 cation exchange membrane. Limited work has been done in this area. Panther et al. (2008) reported the diffusion coefficient of As^{3+} through the Nafion112 membrane with a value of 2.30 ± 0.15x 10^{-7} cm^2/s (pH 5.0, 24.5 ± 0.5 ºC) using diffusion cell. The obtained value was different from diffusion coefficient across a Nafion117. The transport of metals ions through Nafion membrane depends on the thickness, pretreatment and conductivity of the used membrane. The wet thicknesses of Nafion117 and Nafion112 membranes are 215 µm and 58µm, respectively (Slade et al., 2002; Zaidi and Matsuura, 2009). Thus, increasing membrane thickness leads, to decreased metal permeability rate and selectivity. A thinner membrane is usually preferred for higher performance studies (Blom et al., 2003).

The separation of ions and excluding the negative complexes is the main advantage of membrane in its applications (Tant, 1997). Therefore, it is likely that only free metal ions and maybe some positively charged inorganic and small organic complexes could be measured by DGT method. Some metal complexes of such Pb-ligands able to cross Nafion membrane, which are expected of small molecular, neutral or positive charge. Normally Pb-ligands excluded out form the membrane due to the continuum of Pb-ligands of the same stability with heterogeneous, polyfunctional organic complexants like humic substances, which are abundant in contaminated marine systems.

4.5. Influence of crude oil on metal speciation using different types of DGT

Five different membranes were used for the measurements of different labile metal species. The membranes were effectively distinguishing the metals species according to molecular size and diffusions alterations. The effect of crude oil on metal speciation was investigated at two OWR of 1% and 4%. The complicated mixture of ligands of a variety of functional groups often arising from oil refineries and industrial sources form metal complexes varying in stability depending on medium condition and type and composition of oil. The DGT measurements determined by several mechanisms including; exclusion of large species by pore size of diffusive gels and dialysis membranes (Li et al., 2005), anions and negatively charged complexes using Nafiion membrane. The mass transport can be restricted (low diffusion coefficients) during dissociation through diffusion layer to binding layer. Dissociation of the complexes within the time frame required for the species to diffuse across the diffusive layer before they are bound by resin gel (Scally et al., 2003; Li et al., 2005). The obtained results are shown in **Figure 4.7** and **Figure 4.8**.

Figure 4.7 presents the accumulated masses of metals in synthetic solutions without and with different OWR% using five different versions of DGT devices. The accumulated masses of metals were too low in Nafion112-DGT devices at all synthetic solutions. This indicates most of the metals are complex and negatively charged. They were excluded by Nafion membrane, which restricts the mass transport to binding layer.

The masses of metals accumulated by DGT with dialysis 1000 MWCO and DGT with dialysis 3500 MWCO in the three synthetic solutions gave the same results for all metals. It indicates that the determined labile inorganic and organic complexes contributed from the oil are small and may be limited to <1000 MWCO. The masses accumulated by DGT devices with open pore (OP) gels gave the highest values as the diffusive gel has the largest pore size and it allows the large organic ligands and metal complexes diffuse through and to be measured. The masses accumulated by DGT with restricted pore (RP) gel were lower than those of masses by OP-DGT for all metals in all three solutions (no oil, 1% and 4% oil). However, they were higher than those of masses in solution without oil for all metals except Cd, which was very similar. For solution with oil, only the masses of Zn and Pb were higher. These demonstrate that restricted pore (RP) gel has the similar pore sizes as the dialysis membranes used in this study.

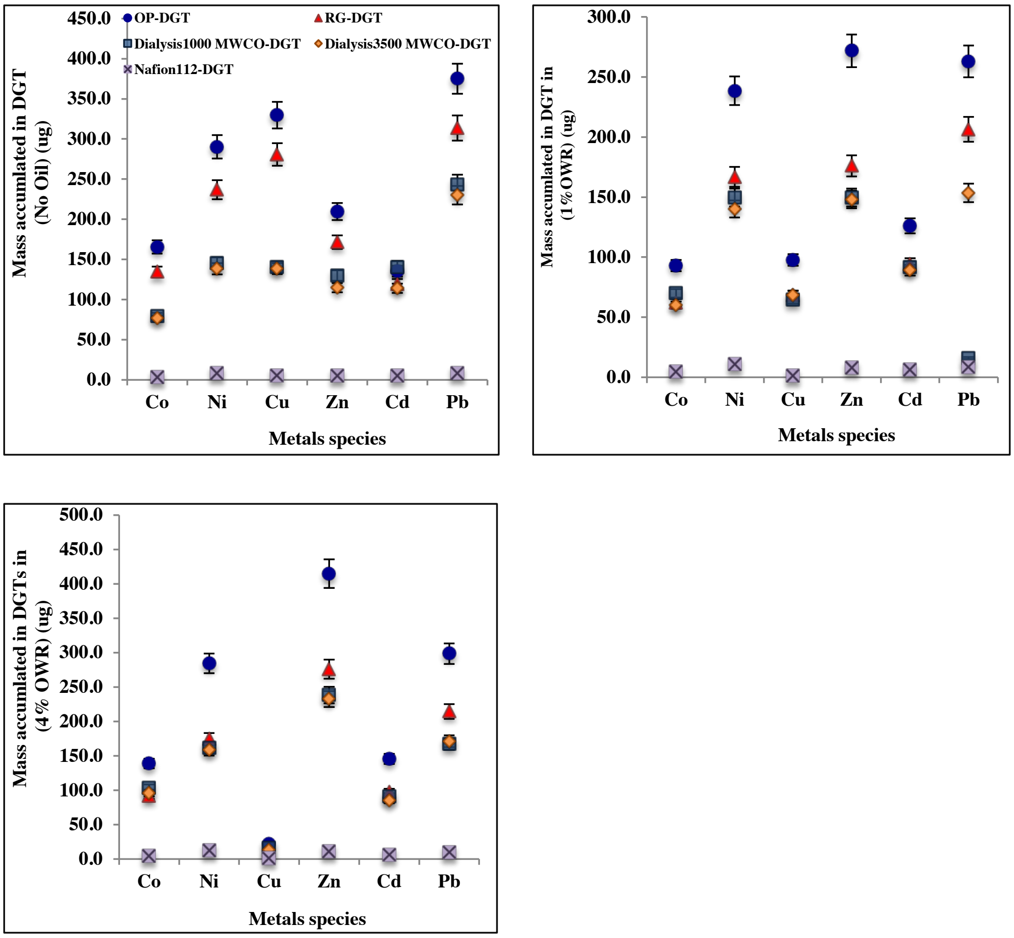


Figure 4.7. The mass of metals accumulated by five types DGT devices with the various ratios of crude oil (1% and 4% w/v) concentrations of metals=20μg/L, pH=5.6, ionic strength = 0.5 mol/L of NaCl, deployment times: 17 hours except (Nafion112)-DGT were carried out for 24h.

All the measured metals ions concentrations (except for the Cu) in synthetic solutions treated with 1% and 4% w/v of oil using OP-DGT, were found with overall averaged recoveries between (94.18 ±1.2% - 102.57 ±3.39% of total dissolved) for the five metals (**Figure 4.8**). This indicates the solubilised lower molecular weight of the constituents' ligands of crude oil that formed labile complexes can dissociate on a time scale during their diffuse through the diffusive gel. The DGT-labile concentrations of Cu were decreased from 61.18±1.4% to 15.57±1.02% in 1% and 4% OWR% of added oil, respectively. This is possibly due to the higher ligand concentrations in solution with 4% oil and larger and stronger Cu-DOM complexes (Gimpel et al., 2003; Guéguen et al., 2011). Zhang and Davison (2000) and Lehto et al. (2006) suggested that RP-DGT permits diffusion of free metals ions with small inorganic species and excludes labile organic species less than 1nm of pore size. It seems clear from **Figure 4.7** that there is a lack of significance differences between OP and RG-DGT labile fractions of dissolved Co, Ni, Zn and Pb in solution of 1% OWR and Co, Ni and Pb in solution of 4% OWR. This could be attributed to the labile complexes in solution containing were smaller than the pore size of the restricted diffusive gel or may due to the release of Co, Ni, Zn and Pb from oil to solution. For Cu, the percentages of labile Cu by RG-DGT in the synthetic solution treated with 1% w/v of oil was 12.2% ± 1.38% and 56.09% ±1.77% in solution spiked with 4% w/v of crude oil. The measured labile Cd fractions by RG-DGT device in the synthetic solutions of 1% and 4%w/v crude oil were 80.04±2.11 % and 86.72±1.2% and respectively. For Zn RG-DGT labile fractions in synthetic solution of 4% w/v oil was 89.26 ±2.74%.

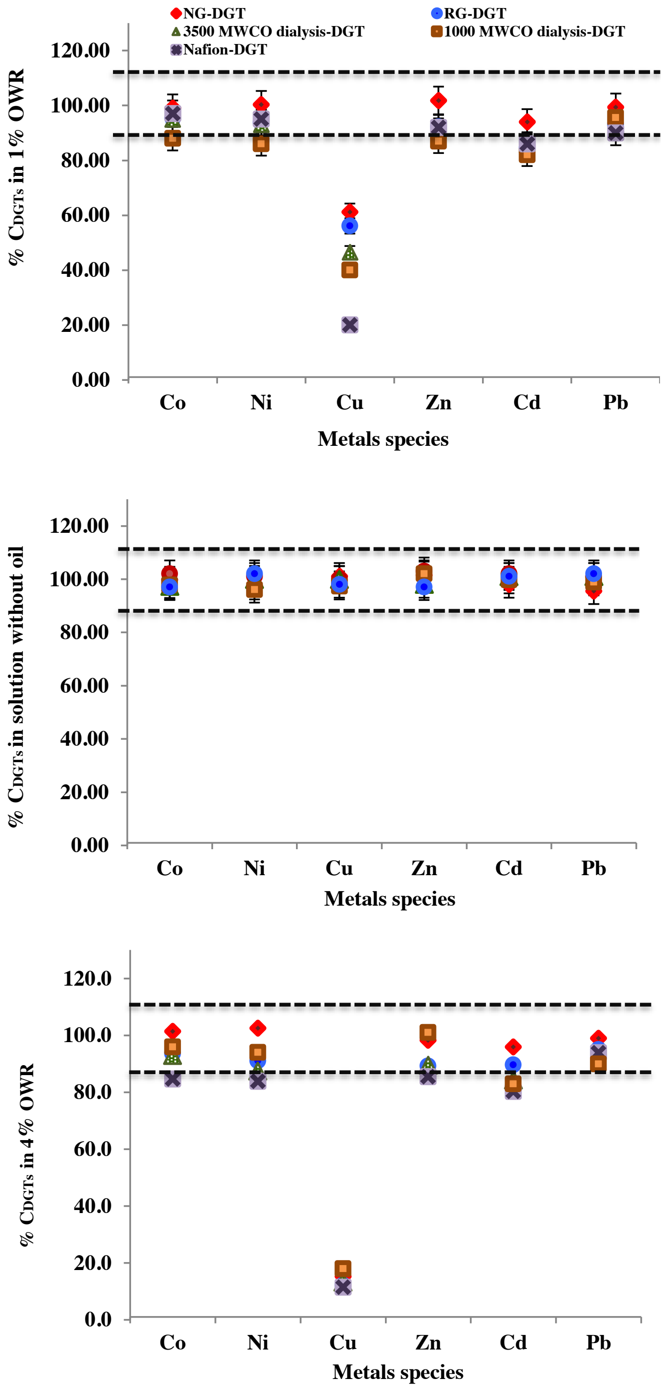
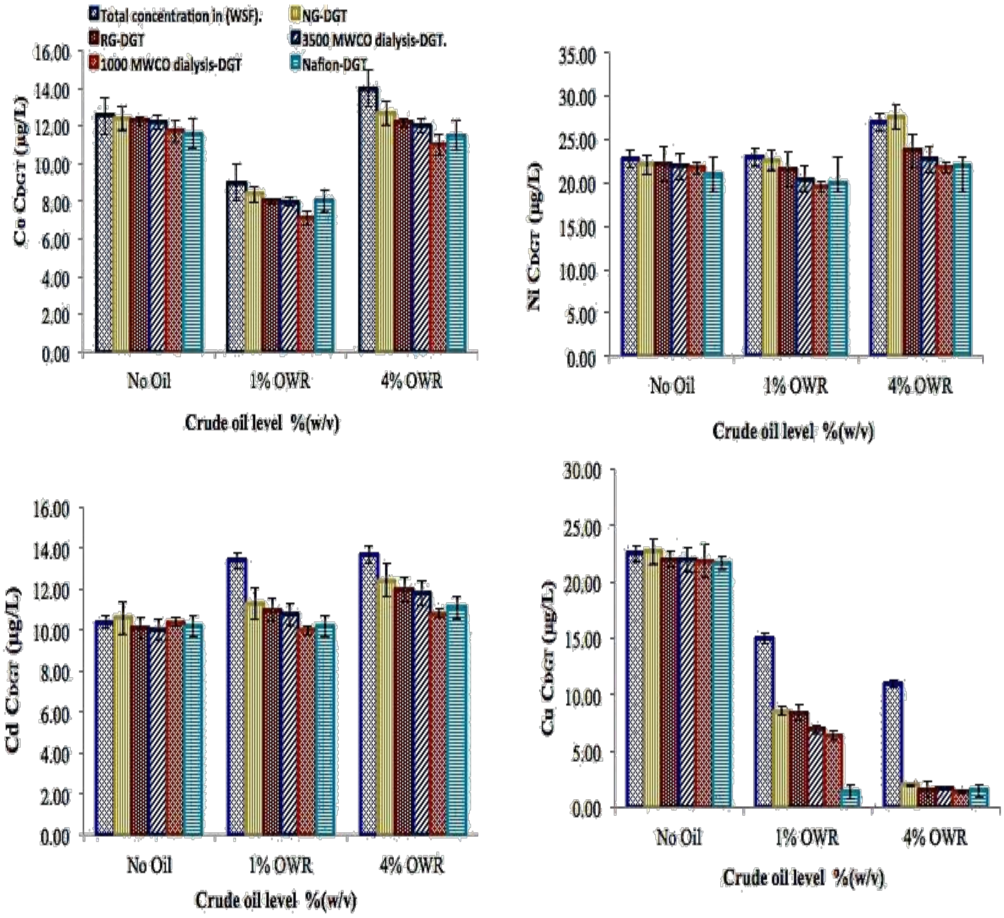


Figure 4.8. Effect of pH on performance of five types used DGT samplers for the measurement of Pb, Zn, Co, Cu, Cd and Ni in well-stirred synthetic solutions containing various ratios of crude oil (0, 1 and 4 w/v%) concentrations of metals=20µg/L, pH=5.6, ionic strength = 0.5 mol/L of NaCl, deployment times: 17 hours except (Nafion112)-DGT were carried out for 24h.

The diffusive permeability of dialysis membranes depends on pore size. Both labile and inert species allowed passing through dialysis except larger metal-DOM and colloids are prevented from diffuse to resin gel. Cu, Zn and Pb did not show any significant difference between the two dialysis–DGT types at both solutions of 1 and 4 % w/v oil. This indicates that small inorganic species of molecular sizes less than a few nm were the predominant DGT-labile forms of metals for Cu, Cd and Pb in the both synthetic solutions with 1 and 4 OWR%, w/v. Metals fractions of Co, Ni and Cd were unable to diffuse through dialysis (1000 MWCO)-DGT represented fractions of 12%, 14% and 19% in synthetic solution of 1% w/v oil and 14%, 17% and 20% in solution treated with 4% w/v oil, respectively (**Figure 4.8**). This is due to the Co-DOM and Ni-DOM complexes in solution, too large to diffuse through the dialysis membrane and not measured by DGT. Non-DGT labile Cu fractions (i.e. colloidal DOM) using dialysis membranes were 60% and 56% in WSF of 1%w/v oil and > 87% at the synthetic solution impacted with 4% w/v oil. This attributed to the presence of highly aromatic DOM substances in solution with increased of OWR% forms highly stable complexes, hence reducing the concentration of free/labile Cu.

The percentages of labile metals fractions using Nafion112-DGT did not show significant trends at any of the solutions with 1% and 4% w/v crude oil for all metals except Cu and Cd. Significantly lower Nafion112-DGT-labile concentrations were found only 15-20% for Cu and 78 -80% for Cd at both synthetic solutions. This may be due to metal complex formation with ligands dissolved from oil could not pass through the Nafion112 membrane in Nafion112-DGT sampler. Organic complexation dominates Cu speciation in both solutions with oil matrix, and a substantial fraction of organically complexed Cu is DGT-labile. Nafion in (Nafion112)-DGT prevented colloids or large and negatively charged metal complexes from diffuse through membrane to resin gel.

Although the accumulated masses showed significant differences when use different gels and membranes, the various in DGT measured labile concentrations are much less marked, except for Cu, when taken into account of diffusion coefficients for different membrane. The results are presented in **Figure 4.9.**



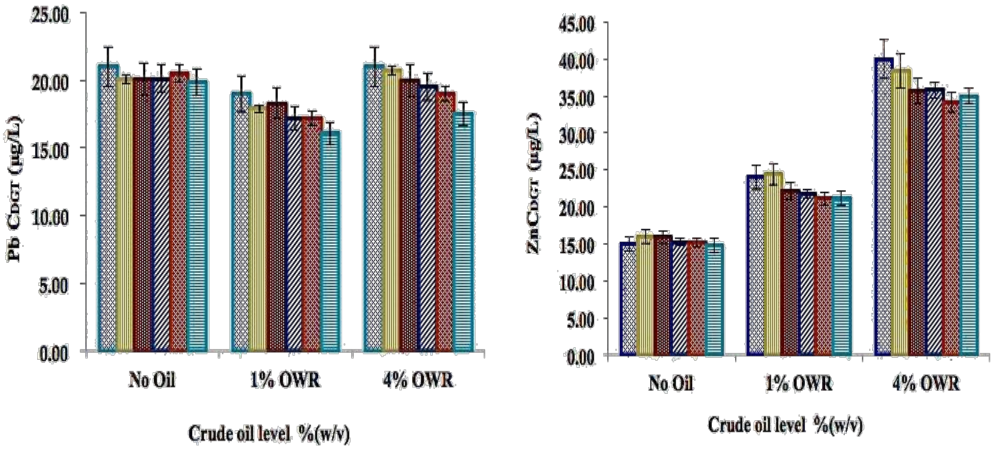


Figure 4.9. Concentrations of metals in five versions of DGT devices in well-stirred synthetic solutions containing various ratios of crude oil (0, 1 and 4 w/v%) concentrations of metals=20µg/L, pH=5.6, ionic strength = 0.5 mol/L of NaCl, deployment times: 17 hours except (Nafion112)-DGT were carried out for 24 h.

For Co and Pb, the labile concentrations measured by all types of DGT devices decreased in the solution with 1% w/v of oil and increased at 4% w/v of OWR%. This can be explained by its association with aromatic organic matters in oil at 1% w/v. At 4%, although complexation still existed, more Co and Pb were released from the oil (Omaka et al., 2011; Pimsee et al., 2014). The labile Cu significantly decreased with increasing oil concentrations due to the presence of strong binding ligand for Cu in oil. This suggests that copper in both synthetic solutions treated with 1% and 4% w/v oil formed Cu-DOM complexes either too large to diffuse through the gels and membranes or too strong to dissociate or both. The labile Cu concentrations measured by Nafion-DGT are similar for both 1% and 4% oil addition, but with big difference for other types of DGT devices (less labile Cu at 4% oil with similar concentration as Nafion-DGT measurement). This suggests that the reduction on labile Cu at 4% oil is mainly for negatively charged complexes and all types of DGT devices were measuring free metal ions plus positively charged complexes. For Cd and Ni, slight increase for all DGT-labile concentrations with increasing oil to water ratios can be observed. This could be due to the release of both metals from the oil. For Zn, the significant increase of labile Zn concentration with increasing of oil w/v% for all DGT measurements and total dissolved, indicating the input of Zn from oil.

This work has demonstrated that DGT is a suitable time integrated dynamic technique for characterising chemical speciation in oil contaminated seawater. In such a dynamic system where metals are continually being complexed and affected by other reactions processes, it is useful to use an *in situ* dynamic technique.

4.6. Comparison of measurements by (1000 MWCO)-DGT and Micro Float microdialysis of 1000 MWCO

The results obtained by (1000 MWCO)-DGT were compared with those obtained by Micro Float microdialysis of 1000 MWCO in the same synthetic solutions. DGT measures labile concentration (species can pass through the dialysis and can be dissociated for uptake) and microdialysis measures total concentration of metal that can pass through the dialysis membrane. The results are shown in **Figure 4.10** for Cd, Co, Cu, Ni, Pb and Zn in three types of synthetic solutions without and with 1 and 4% w/v of oil. The error bars represent the standard deviation of replicate devices for DGT measurements and the instrumental deviation for microdialysis measurements.

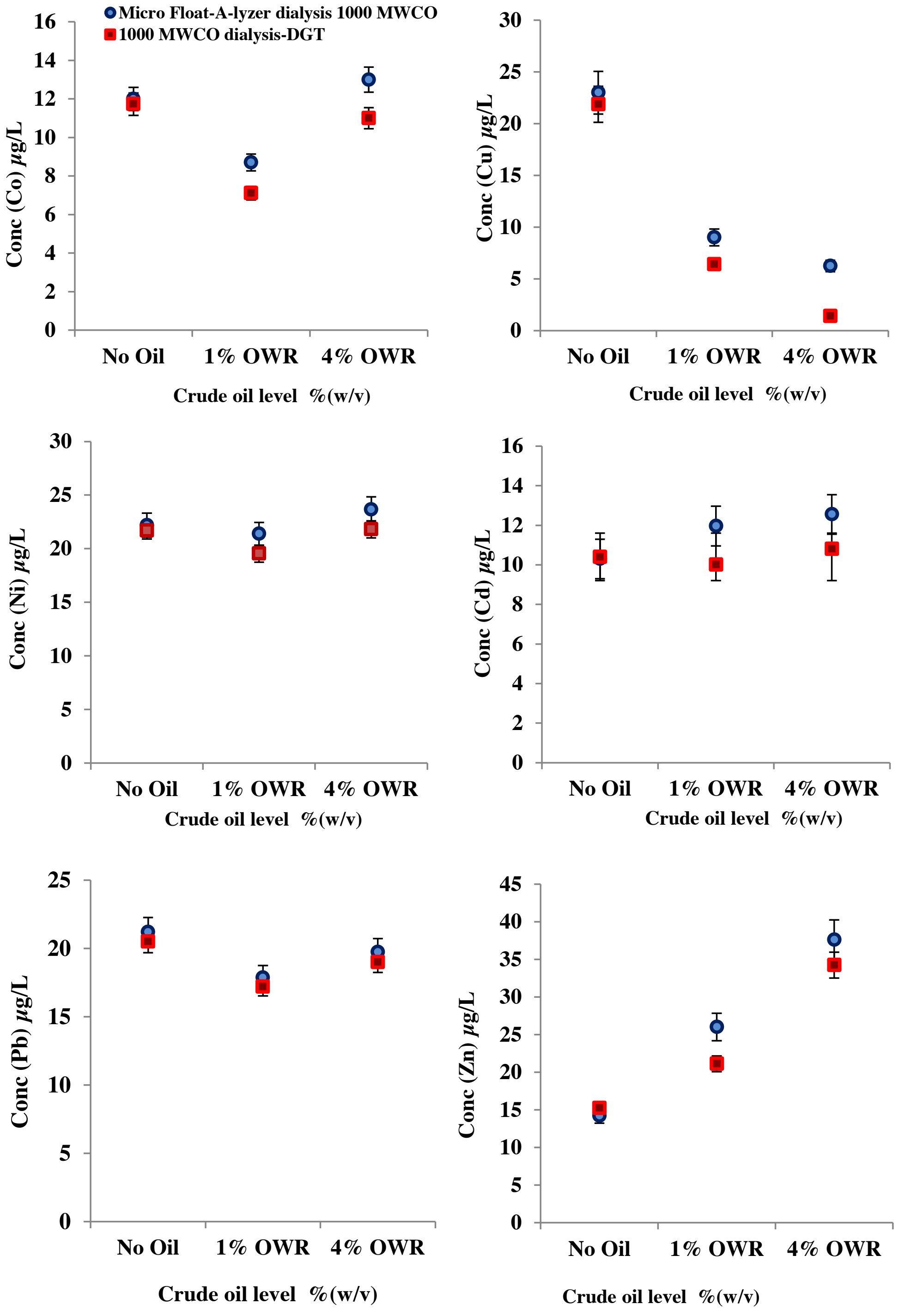


Figure 4.10. Concentrations of Co, Cu, Ni, Zn, Cd and Pb in synthetic solutions with and without oil measured by (Dialysis1000 MWCO)-DGT and Micro Float microdialysis of 1000 MWCO.

Ni and Pb. The measured concentrations of Ni and Pb by two methods were very similar for all three kinds of synthetic solutions with and without oil, especially for Pb (almost the same), indicating all species diffused through dialysis are labile. However, the measured concentrations of Ni in microdialysis were slightly higher than the concentrations that measured in (1000 MWCO)-DGT. It suggests slightly slower dissociation of Ni ligands during transport through hydrogel to binding layer in DGT sampler (Odzak et al., 2002). In contrast to the results obtained in the present study, other work investigated the effect of DOM from mining activities on the trace metals (Omanović et al., 2015) shown that Pb can be strongly complexed with organic complexes and very low DGT-labile concentrations obtained. On the other hand, they found that Ni was predominantly present as a labile, potentially bioavailable fraction (>90%). This indicates that the complexation of trace metals with functional sites in DOM and kinetics alters depending on the environmental conditions and the agreement between the two methods as evident for Pb as for Ni.

Co, Cd, Cu and Zn. The measured concentrations for this group of metals by (1000 MWCO)-DGT samplers were significantly lower than those obtained in (1000 MWCO) Micro Float microdialysis in synthetic solutions with 1% and 4% w/v oil. This shows that the lower molecular weight of Co, Cd, Cu and Zn species are small enough to pass the dialysis membrane but fraction of those are no able to dissociate to be measured by-DGT samplers. Larger portions of the Zn-DOM fractions can be expected more labile for DGT due to the weak Zn bound with oil ligands compared to Co and Cu. The results obtained in this study using (1000 MWCO)-DGT are consistent with those observed by Odzak et al. (2002) indicated that the DGT-labile Zn was around 40% of Zn total concentration. Various studies have shown that Cu can be complexed by organic ligands in marine systems. For both methods the measured Cu fractions showed a significant decrease with the increase of oil concentrations. The lowest concentration in solution containing 4% was reasonable due to higher concentration of crude oil ligands forming strong complexes with Cu that cannot dissociate to be measured. The organic complexes have diffusion coefficients substantially lower than free metal ions. Since diffusion coefficients for free ions are used in the calculations, the DGT-labile concentrations are probably underestimated, contributing to the difference in concentrations measured by the two methods. Dialysis method can essentially be widely applied for environmental analysis as a separation method based on size. However, it suffers from various weaknesses, which may limit its performance and applicability. It is time consuming, often requires days to reach equilibrium. The obtained metals fraction inside solution (dialyzable) does not represent bioavailable fraction. Furthermore, small species of < 1000 MWCO could be inorganic and organic metal complexes and colloids can diffuse through a dialysis membrane (Gimpel et al., 2003). Oil has strong effect on labile Zn concentration. The results in **Figure 4.10** show marked increase on labile Zn and total dissolved Zn with increasing of oil. These findings indicate oil is also a source for Zn pollution in marine system. Similar effect of oil on Cd, but much less pronounced. For the other three metals, Co, Ni and Pb, there was a decrease at 1% oil and then increase at 4%. This indicates complexing process is dominating at low oil concentration and release process is dominating at high oil concentration (4%).

4.7. Conclusions

The diffusion coefficients through filter membrane and hydro gel with Nafioin112 were much lower than those measured through filter membrane and diffusive gel with and without dialysis, 35 to 40 times lower for Co, 26 to 35 times lower for Pb and Zn 20 to 26 times lower for Cu, Cd and Ni, The concentrations of labile metals by all versions of DGT samplers were markedly affected by the presence of oil ligands and showed an increase as well as a decrease in metal concentrations as a result of increased OWR%. Using Nafion112 membrane or/and dialysis membrane in DGT can further understanding metal speciation in solutions of varying OWR%.

Similar concentrations obtained by OP and RG-DGT devices for metals such as Co, Ni, Zn and Pb in the presence of oil suggesting the complexes were smaller than the pore size of RG gel and they are all labile. No significant differences between the (Dialysis1000 MWCO)-DGT and (Dialysis3500 MWCO)-DGT in the accumulated masses of metals also suggests that small, possibly inorganic species (<1000 MWCO) were the predominant DGT-labile forms of metals in the solutions.

The measured concentrations of Co, Cd, Cu and Zn in (Dialysis1000 MWCO)-DGT samplers were lower than those determined in 1000 MWCO Micro Float microdialysis concentrations. This attributed to the existence of low molecular weight Co, Cd, Cu and Zn species, small enough to pass through the 1000 MWCO- Micro Float microdialysis but not labile enough to be retained in the (Dialysis 1000 MWCO)-DGT samplers. This study represents a benchmark for future metal speciation assessment in the Sultanate of Oman marine systems around large economic harbours with industries and refineries.

Chapter 5 – Investigation the effect of crude oil on metal availability in soils and aging processes

5.1. Introduction

Soils are geochemical sinks for a wide range of chemical substances produced by various anthropogenic activities, and act as a natural buffer that governs the transport of contaminants to aquatic environments and the terrestrial food chain (Rocha et al., 2011). Soil sampling and analysis have been carried out by scientists and regulators to assess crude oil contamination around refinery industries or commercial ports. It is crucial to evaluate the environmental impact of oil contaminated soils. There is a need for simple, reliable and low cost technique that determine the influence of oil ligands on chemical speciation and availability in soils (Relić et al., 2005). Economic development plays an important role in the distribution and migration of metals and oil related chemicals in the soils associated with industrial activities, crude oil extraction processes, and refineries, all of which threaten the soils quality. Numerous studies have shown that crude oil contamination strongly influences the mobility and bioavailability of trace metals in soils around oil production and refining facilities (Zhang et al., 1998; Iwegbue, 2011; Omaka et al., 2011; Rocha et al., 2011; Fu et al., 2014). Assessment of the effect of crude oil contamination on the soils quality and the need of remediation can be hampered by a poor understanding of chemical speciation in these soils. When trace metals are introduced into the soils, they interact with inorganic and organic ligands and colloids depend on the affinity (Guéguen et al., 2011). Trace metals availability in soils varies with soil properties which influence the partition with resupply from solid phase through adsorption/desorption and dissolution/precipitation processes (Zhang et al., 1998). To sufficiently understand the above processes, it is worth proposing a simple and robust technique for the simultaneous determination of trace metals chemical forms in soils impacted with crude oil, rather than measuring the total concentrations. Various sampling and measuring techniques were widely used for determining concentration of metals in soils such as chemical extraction, either partial or sequential extraction (Fernández et al., 2004; Katana et al., 2013; Fu et al., 2014). All these extraction techniques are broad in scope but varied in findings. The selective extraction techniques have been shown to be better and more efficient than measuring total metal content using acid digestion (Venn, 2008). However, these extraction methods using unrealistic volume and concentration of chemicals and they really represent the available metals in soils. Batch extraction methods using ion-exchange resin were used for metals speciation in soils. A certain amount of soil and resin (beads or membranes can be used as a membrane or capsules resin had a uniform spherical shape), are mixed in a sufficient amount of water and shaken for suggested periods then the resin capsulated or membrane separated for elution. The obtained results from this method are strongly governed by resin/soil/solution ratios, shaking time temperature and type of resin (McLaughlin et al., 1993; Dobermann et al., 1994; Qian and Schoenau, 2002). However, they cannot provide detailed information on the transportation of ions from the soil to the resin sink, which is important for assessing bioavailability.

Metal bioavailability has been associated to the activity of metal ions in soil solution and the metal species exchange (Antunes and Kreager, 2009). However, there is still no general consensus in the scientific literature regarding the definition of bioavailability measurements. This probably due to the many inconsistencies between the bioavailable species measured and the retain of metals by plants and various processes that may governing bioavailability existing in the rhizospher (Van Hees et al., 2004; Başar, 2009). Numerous attempts have been performed to find suitable experiments for determining metal bioavailability in soils and varied from concentrations measurements of the directly bioavailable metal to also including estimates of capacity of the soil to re-supply the metal species concentration as it is removed from the soil solution (Riechaman, 2002). Measurements using conventional chemical extraction methods, generally applied with chemical extraction reagents including complexing agents, such as dilute acid HNO_3 and HCl and salt solutions 0.1M $NaNO_3$, 0.1M $CaCl_2$ (Houba et al., 1996). Strong acids, such as HF, $HClO_4$, HNO_3 and aqua regia (HNO_3/HCl) are usually used to extract the 'total' metal in a soil. Various researches into the literature shows that there is a connection between the crude oil contamination and increase or decrease in trace metal concentration, with higher concentrations near crude oil refineries in Nigeria (Anglin-Brown et al., 1995; Omaka et al., 2011).

Extraction by chelation methods comprising aminopolycarboxylic acids such a diethylene-triaminepenta-acetic acid (DTPA) and ethylene-diamine-tetra-acetic acid (EDTA) have been applied widely to determine the availability of metals in soils. However, they were designed to study soils containing low concentrations of organic matter. The metals levels in the soils often exceed the capacity of chelating of the compound; using EDTA requires the compound to control pH sometime to 6, which could affect the solubility of metals especially Cd and Zn (Stevenson et al., 1984; Huang et al., 2011).

Weak and neutral salts for extraction such as $CaCl_2$, and $NaNO_3$ have been assessed in various studies with promising findings. Menzies et al. (2007) reviewed different types of extractants applied to determine metals species. The review showed that neutral salt solutions can provide a good relationship between metals concentration in extracts and concentration in plant tissues.

Metal species in soil solution has been considered available for uptake. Ivezić et al. (2013) used water extraction (soil solution) technique to predict plant uptake of (Cd, Cu, Fe, Mn and Zn). The results were compared to those obtained by aqua regia extraction, HNO_3 extraction and EDTA extraction methods (Ivezić et al., 2013). Water extraction (soil solution) was in good correlation with plant uptake.

Although, the above extraction methods allow better understanding of metal bioavailability, they are still unrealistic and cause great perturbation to soil system and there is no information on kinetic resupply from solid phase to solution, which are crucial for plant uptake. A dynamic in situ technique, DGT, has been developed and applied in soils to quantitative measure the labile metal resupply and bioavailability (Dočekalová et al., 2012; Senila et al., 2012; Garrido Reyes et al., 2013).

5.1.1. DGT in soils

Diffusive gradients in thin films (DGT) have recently been used in soils to measure labile metals and the flux of available species resupplied from solid phase to solution (Davison and Zhang, 1994; Zhang and Davison, 2001). It has been used successfully for speciation measurements in soils, groundwaters, and sediments, as described previously in **Chapter 2**, **sections 2.11-2.13**.

When DGT is deployed in soil, it removes metal from soil solution by accumulating it on the binding layer of the DGT device. The metal must first diffuse through the filter membrane and the layer of diffusive gel, which sets a maximum possible flux to the DGT devices. DGT continuously removes and accumulates metal and so supply processes from the soil must be considered dynamically. In response to the removal, the concentration of metal in soil solution adjacent to the device is lowered. Metal will therefore dissociate from complexes in solution to try to re-establish the equilibrium state that has been perturbed. Consequently, all species that are labile, that is able to dissociate sufficiently rapidly to contribute to the flux to the device, will be measured (Zhang and Davison, 2000). However, there is also a dynamic exchange of metal between solution and solid phase. Local depletion of metal in soil solution will induce release of metal from the solid phase at the site of depletion. As for release from complexes in solution, the extent of this supply of metal from the solid phase will depend on its rate of release.

Figure 5.1 illustrates how the extent of depletion in soil solution depends on the rate of release of metal from the solid phase. When the rate of release is very fast, the supply from the large pool of metal in the solid phase effectively buffers the metal concentration in soil solution so that very little depletion occurs. The rate of metal uptake is then controlled by the DGT device. Depletion of metal in solution will eventually occur, even when there is fast release, because the metal in the solid phase adjacent to the device will gradually be used up. If the rate of release from the solid phase is very slow, there will be little supply from this source, and metal supply will depend on diffusion of labile species in solution. The metal in solution adjacent to the device is quickly depleted with time, causing the flux of metal to the DGT device to decline quite rapidly. The intermediate case occurs when metal is released from the solid phase at an appreciable rate, but it is insufficient to sustain fully the concentration in solution adjacent to the device.

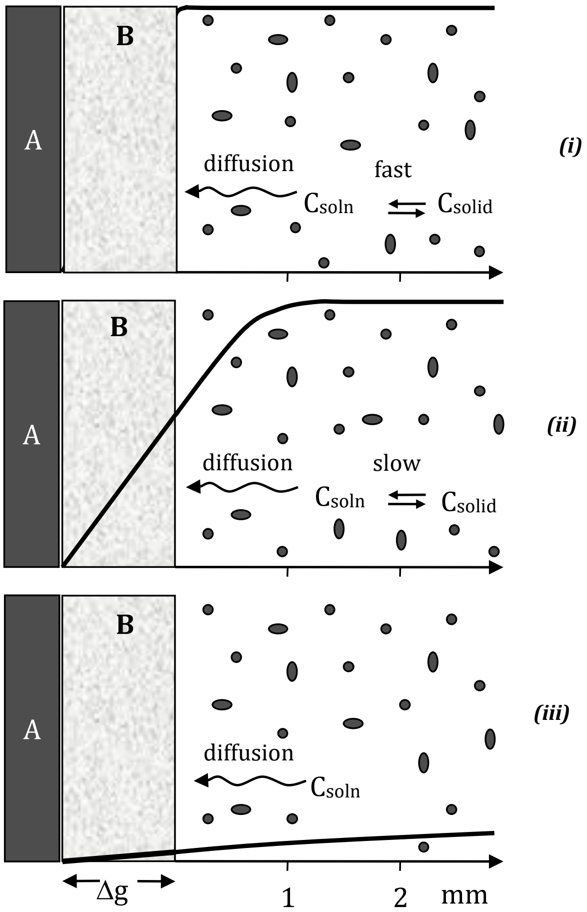


Figure 5.1. Schematic representation of the concentration of metal in solution in DGT and the adjacent soil after 24 hours, for three cases: (i), very fast release from solid phase; (ii), fairly slow release; (iii), no release. Layer A is the resin gel and layer B is the diffusion layer. (Taken from Zhang and Davison, NATO book chapter)

The above processes can be quantified by modeling simultaneously and dynamically the supply of metal by diffusion and its release from the solid phase (Harper et al., 1998). A one dimensional version of this model, known as DIFS (DGT-induced fluxes in soils) has been developed by Harper et al. (2000). A full two dimensional version, which more accurately reflects the diffusional supply, has been developed by Sochaczewski et al. (2005).

As the DGT device continuously takes metals out of the soil system during deployment, it is inevitable that for most cases some depletion of the concentration of metal in soil solution at the interface of the DGT device and soil will occur (Ernstberger et al., 2002). The extent of the depletion is indicated using the (*R*) value of C_{DGT} to the independently measured initial concentration of metal in the soil solution (C_{soln}): The value of R is affected by the solid-phase labile pool size and the response time of the soil to the depletion ($\underline{T}$c) (Harper et al., 1998).

The DIFS model uses the partition coefficient for labile species (K_{d}) to calculate the labile pool size in the solid phase and quantifies the relationship between *R*, *K*d, and *T*c. As *T*c is directly related to the rate constant of the supply process from solid phase to solution (*k*-1), it can be obtained if R and *K*d are known.

Input parameters of particle concentration (*P*c), soil porosity (φ), and the diffusion coefficients of metals in the soil (*D*s) were calculated using **equations (5.1-5.3)** (Harper et al, 1998, Boudreau, 1996):

$$P\mathrm{c} = m/V \tag{5.1}$$

$$\varphi = d\mathrm{p}/(P\mathrm{c} + d\mathrm{p}) \tag{5.2}$$

$$D\mathrm{s} = D\mathrm{o}/(1 - \ln\varphi^2) \tag{5.3}$$

Where *m* is the total mass of all soil particles; *V* is the porewater volume in a given volume of total soil; *D*o is the diffusion coefficient in water; and *d*p is the density of the soil particles, which is commonly assumed to be 2.65 g cm-3 in soils (Bielders et al., 1990).

5.1.2. Objectives of the Study

The present work has been undertaken in order to:

(1) Assess the effects of crude oil contaminated soils on the studied trace metals speciation in soils solutions, as well as the changes in soil properties using DGT dynamic sampler.

(2) Investigate the aging effect on fractionation and lability of targeted trace metals in soils.

(3) To investigate the correlation of extracted trace metals in $CaCl_2$ solutions to C_{DGT}-labile species.

5.2. Methods and Materials

5.2.1. Reagents, chemicals and solutions

Crude oil was provided by the Ministry of Oil and Gas in the Sultanate of Oman, and high purity Milli-Q water (≥ 18 MΩ/cm) was used to prepare all solutions. A stock solution of 1000 mg/Lmixed metals using nitrate salts and Milli.Q water was prepared for spiking soils. All containers DGT mouldings, and glass plates and spacers for making gels were acid washed in 10% (v/v) nitric acid, (BDH), for at least 24 hours, and rinsed thoroughly with M.Q water before use. Nitric Acid BDH ARISTAR® ULTRA, a high purity acid for quantitative trace metals analysis, was used for elution. The Chelex 100 resin for making DGT binding layer was from Bio-Rad.

5.2.2. Preparation of DGT devices

The procedures for preparing and using DGT samplers have been explained in detail by Zhang and Davison (1995) and Zhang et al. (1998). DGT plastic mouldings with a sampling window area of 2.54 cm^2 were supplied by DGT Research Limited, Lancaster, UK. A diffusive gel layer (0.8 mm thick) and binding layer (Chelex 100 resin, 0.4 mm thick) were used in all experiments.

5.2.3. Soil amendments and soil sampling

Three soil types (surface samples, 0-20 cm depth) with a different pH and organic content were collected from three allotments in Birmingham area in UK: Coney Green, Gibson, and Knowle Road. Soils were air dried at room temperature and passed through a 2 mm sieve, then stored in plastic containers. Soil pH, OM%, and water holding capacity (MWHC), were measured as described in the following sections. For all collected soils, each soil of 2 kg was spiked with different concentrations of the metals in solution to achieve the final metal concentration in soils as 2 mg/kg Co, 2 mg/kg Cd, 30 mg/kg Ni; 30 mg/kg Cu, 30 mg/kg Pb, and 100 mg/kg Zn. The solution and soil ratio for spiking was 10ml:100g. The solution was added to soil drop by drop and mixed thoroughly. They were divided into three parts, about 600g of each. They were left for 2 days before being amended with a crude oil matrix. Soils then were treated with two levels of crude oil: 0, 2 and 8% w/w, representing slightly and highly contaminated soils.

All soil samples with and without oil were left to equilibrate for two days prior to the metals measurements by DGT, soil solutions and extraction in 0.01 M $CaCl_2$ solutions. The same measurements were carried out at different times: 1 day, 4 days, 8 days, 2 weeks, 4, 6, and 8 weeks after spiking. Aliquots of soil samples were taken for DGT measurements and extraction.

5.2.4. Soil pH and organic matter content

The soil pH was measured at 1:5 soil:0.01M $CaCl_2$, by adding 10 g of 0.01 M CaCl2 solution to 2 g of dried soil in a 50 ml polyethylene beaker, and shaken for 1 hour. This was then left to stand for 30 minutes. The pH of the solutions was determined using a pH meter, and making sure to avoid the settled soil particles coming into contact with the electrode.

The organic content (OM%) of selected soils was measured by loss on ignition (LOI). The OM% of selected soils was estimated as the mass of the oven-dried soil lost as a proportion of the mass of ignited soils. The obtained pH and OM% values of the three studied soils are shown in **Table 5.1**.

Table 5.1. The pH values and OM% of the three soils.

	Soil 1	**Soil 2**	**Soil 3**
Selected sites	Coney Green	Gibson	Knowle Road
Soil pH	6.9	5.65	7.43
OM proportion	2.02%	2.45%	3.54%

5.2.5. DGT deployment and retrieval

The water holding capacity (MWHC) of the soils was measured previously in other studies. The values were 62.8%, 50.03%, and 54.89% for Coney Green, Gibson, and Knowle Road, respectively. For DGT deployment, a subsample of 60 g soil was weighted in a clean beaker, and then mixed well with Milli-Q water in order to achieve soil moisture content of about 80% MWHC. The amounts of Milli-Q water added to each soil were 26.38 g for Coney Green, 23.05 g for Gibson, and 21 g for Knowle Road. They were all well mixed and then equilibrated for 24 hours. Each soil sample was then averagely divided into three clean pots. DGT devices were gently pushed into the surface of the paste to ensure that the filter membrane of the DGT window made good contact with the soil, and then they were loosely covered with a plastic sheet to prevent water evaporation. The DGT deployment were carried out on day 1 for 22 hours at a temperature of 17 ± 2 ºC, and then retrieved from soils and rinsed thoroughly with Milli-Q water to wash off any soil particles. The binding layers were transferred from devices to clean 1.5 ml centrifuge tubes using clean tweezers and eluted with 1 mL of 1 M HNO_3 acid for 24 h prior to ICP-MS analysis. The above steps were repeated on day 4 and 8, and week 2, 4, 6, and 8, at different temperatures, as indicated in **Table 5.2**.

Table 5.2. Soil deployment temperatures for each sampling period.

Sampling time	Day 1	Day 4	Day 8	Week 2	Week 4	Week 6	Week 8
Temperature (°C)	17	17	19	19	18	21	26

5.2.6. Soil solutions measurement

Following each DGT deployment, the remaining soils were carefully transferred to 50 mL centrifuge tubes, and then centrifuged at 3000 rpm for 10 minutes to complete the soil solution extraction. The soil solution was then filtered through a syringe-filter (0.45 µm) into a clean 1.5 ml centrifuge tube. From each filtered soil solution sample, 900 µl was put into a centrifuge tube and acidified by adding 100 µl 1 M HNO_3 prior to ICP-MS analysis.

5.2.7. Extraction using 0.01M $CaCl_2$

The concentrations of extractable metal species in soils were obtained by weighting 2 g of air-dried soil into a clean 50 ml centrifuge tube, and then adding 20 ml of 0.01 M $CaCl_2$ solution. The mixtures were shaking for 2 hours. Following this, a 1.5 ml aliquot was pipetted into a clean 1.5 ml centrifuge tube and centrifuged at 6000 rpm for 10 minutes. The samples were filtered using syringe-filters (0.45 µm, Acrodisc) into a clean 1.5 ml centrifuge tube. Finally, 900 µl of filtered solution were put in the 1.5 ml clean centrifuge tube and acidified by adding 100 µl of 1 M HNO_3, for subsequent ICP-MS analysis.

5.2.8. Quality control and quality assurance

The quality assurance (QA) and quality control (QC) were used in the experiments for reducing the errors of data analysis (Zhang, 2007). Blanks were assessed during all experiments. For each DGT deployment, three devices were kept as blanks. Acid blanks and reagent blanks were also measured for each experiment. Internal standard and QC samples were used for ICPMS analysis.

5.2.9. Samples analysis and calculations

After 10 times dilution using 0.1 M HNO_3 followed by adding 20 µl of internal standard (Rh) in to 1ml of samples, they were analysed by inductively coupled plasma-mass spectrometry (ICP-MS).

The concentrations of labile metals measured by DGT (C_{DGT}) were calculated using the following equation (Liang et al., 2014):

$$C_{DGT} = \frac{M\Delta g}{DAt} \tag{5.4}$$

Where M is mass of metal accumulated in the resin gel, Δg is the thickness of the diffusive gel (0.078 cm) and the filter membrane (0.014 cm); A is the surface area of DGT window (2.54 cm^2), t is the time of deployment, and D is the diffusion coefficient of metals in gel.

The R value, representing the degree of the depletion at the interface of the DGT device and soil, can be calculated using **equation (5.5)**.

$$R = C_{DGT}/Csoln \tag{5.5}$$

The C_{soil} is a total dissolved metal concentration in in soil solution. The R values can be used to evaluate the capacity of the solid phase for resupplying the soil solution. It is strongly dependent on the deployment time, and the quantity of metals resupplied from the solid phase, and the degree of this resupply (Harper et al., 2000).

5.2.10. Using Two-Dimensional DGT-Induced Fluxes in Soils (2D-DIFS)

DIFS model can be downloaded freely from the following website:

http://www.es.lancs.ac.uk/wdgroup/difs.htm.

It can be used to estimate response time to perturbation of metal removal (T_c), and dissociation rate constant (k_{-1}), provided the R value and Kd are known. The distribution coefficient (K_d) is usually defined as the ratio of labile concentrations in the solid phase and in solution, it represents the adsorbed species to the solid phase that are able to desorb and accumulated in DGT (Harper et al., 2000; Di Bonito et al., 2008). T_c represents the inverse of a dissociation rate and thus embraces the capacity of the labile metals species on the solid phase and its rate of release. The rapid resupply kinetics ($R \geq 0.95$) can be achieved at large K_d (high proportion in soil solution) during the depletion process (very low Tc, ≤ 1 s, and large k_{-1}) (Zhang et al., 1998; Harper et al., 2000). The dissociation rate constant k_{-1} can be estimated by using the following equation (Harper et al., 2000).

$$k_{-1} = 1/((1 + K_d P_c) T_c) \qquad (5.6)$$

These kinetic parameters are obtained in this study to estimate the rate exchange of labile metals between solid phase and solution phase of the soil and to assess the resupply of metals from soil particles to solution.

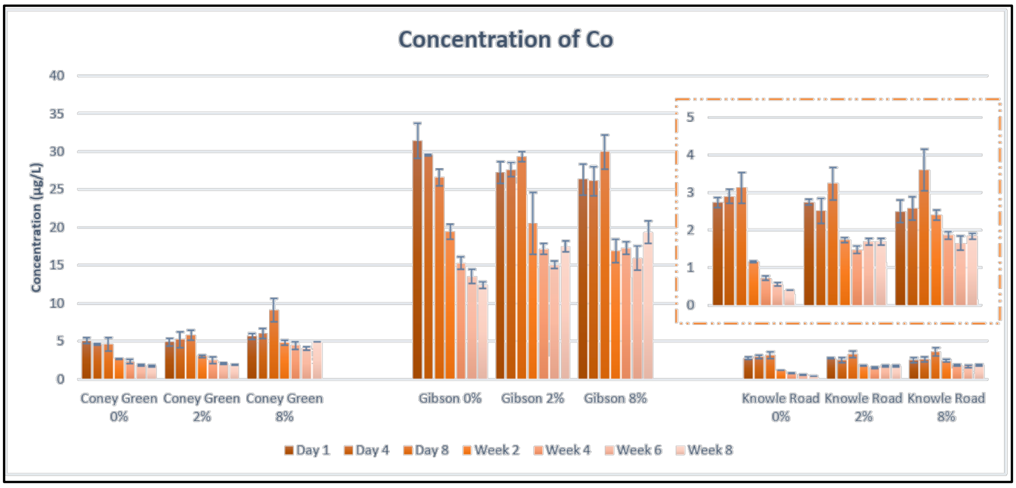
5.3. Results and Discussion

Crude oil ligands in soils can form stable complexes with trace metals cations at varying ratios. Aromatic hydrocarbons and phenolic substances play a crucial role as the main oil constituents for trace metals distribution and fractionation (Omaka et al., 2011; Fu et al., 2014). They can form stable metal-ligands and make metals species have less lability in solid phase and soil solutions. However, organic matter in soil may have a strong competition with oil ligands to form meta-ligand with trace metals at varying stability and different capacities of resupply metals species from solid phases (Conesa et al., 2010). The DGT sampler was carried out in three different soils of different properties treated with varying crude oil content (0%, 2%, and 8% w/w) and aging time. Based on the study performed by Scally et al. (2003) and Garrido Reyes et al. (2013), the obtained results will be interpreted by the lability of the complexes formed between a metal and a ligand that pass through hydro gel accumulated in the binding layer.

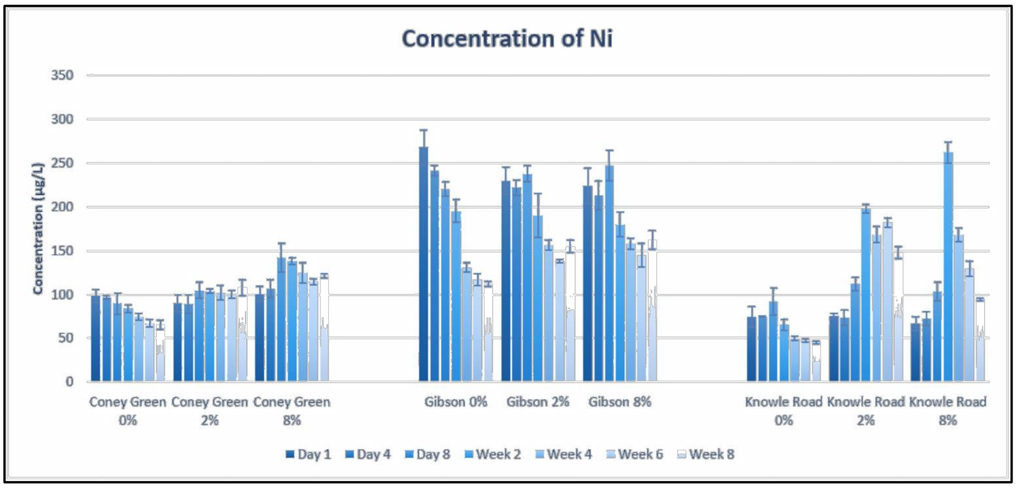
5.3.1. DGT measured concentrations

The measured C_{DGT} labile species of studied metals reflect the flux of metal species supplied from solid phases to soil solution. It measures concentrations of metals species in soil solutions (water-soluble), labile pool in the solid phase (C_{DGT} and R value) and kinetic exchange between the two (dissociation rate, k_{-1}) (Liang et al., 2014).

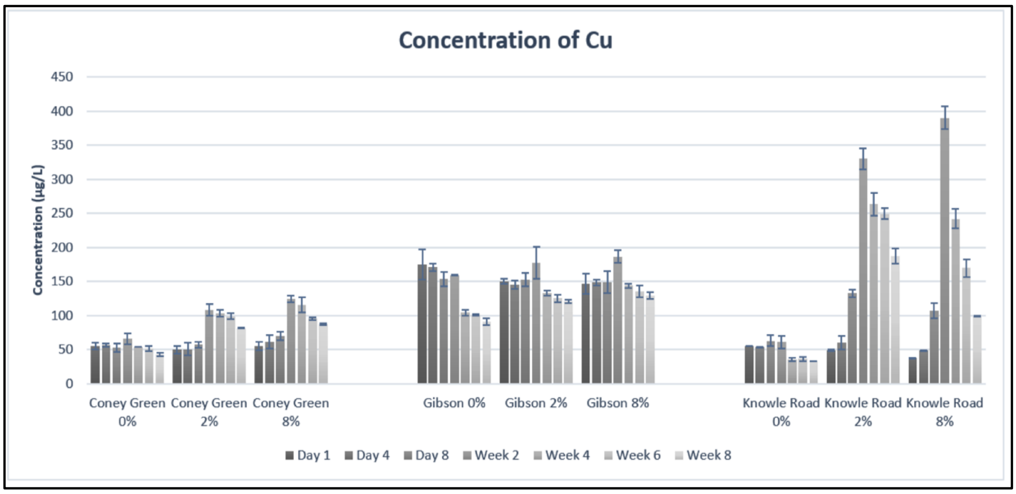
(A)


Concentration of Co
Concentration (µg/L)
0
5
10
15
20
25
30
35
40
0
1
2
3
4
5
Coney Green 0%
Coney Green 2%
Coney Green 8%
Gibson 0%
Gibson 2%
Gibson 8%
Knowle Road 0%
Knowle Road 2%
Knowle Road 8%
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8

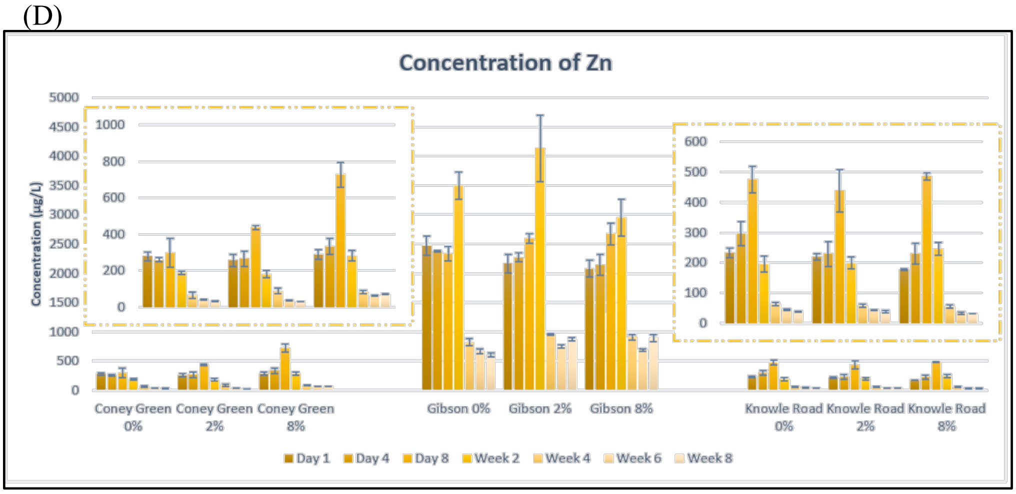
(B)


Concentration of Ni
Concentration (µg/L)
0
50
100
150
200
250
300
350
Coney Green 0%
Coney Green 2%
Coney Green 8%
Gibson 0%
Gibson 2%
Gibson 8%
Knowle Road 0%
Knowle Road 2%
Knowle Road 8%
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8

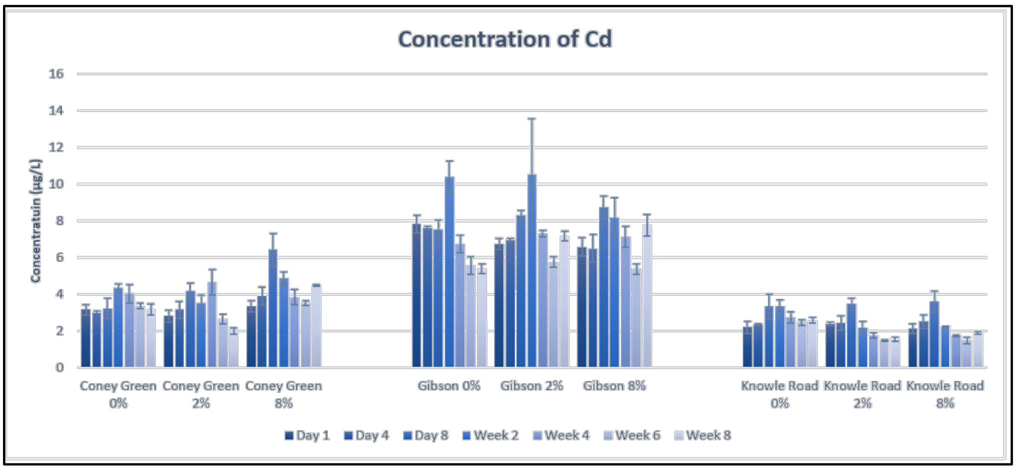
(C)


Concentration of Cu
Concentration (µg/L)
0
50
100
150
200
250
300
350
400
450
Coney Green 0%
Coney Green 2%
Coney Green 8%
Gibson 0%
Gibson 2%
Gibson 8%
Knowle Road 0%
Knowle Road 2%
Knowle Road 8%
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8

(D)



(E)



(F)

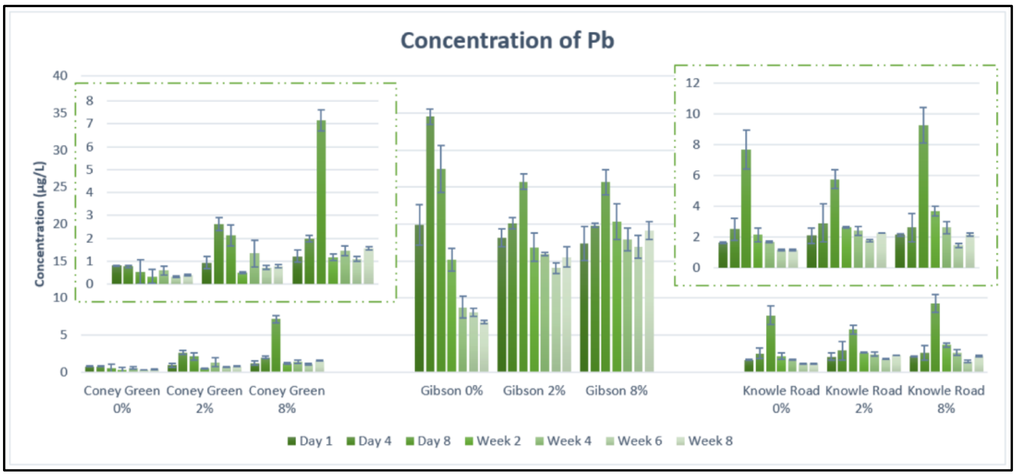


Figure 5.2. Determinations in C_{DGT}-labile species of Co, Ni, Cu; Zn, Cd, and Pb in three soils treated and untreated with crude oil during aging time.

Cobalt (Co). The measured C_{DGT}-labile species of Co showed no significant difference in three studied soils with increasing of crude oil amendment (0, 2 and 8 %w/v) as shown in **Figure 5.2-(A)**. This is may be attributed to the low concentration of Co in crude oil.

It can be observed that, gradual decreases in C_{DGT} of labile Co species with incubation period, suggesting that labile metals changed to non-labile with aging (Liang et al., 2014). This also could be explained by the complexation of metals with colloidal organic ligands in soils, which are maybe increased due to microbial oxidation with aging (Martínez and McBride, 1999).

Nickel (Ni). A gradual increase of C_{DGT}–labile species of Ni was observed with increasing of crude oil contamination in three soils with average range between 81.3 µg/L and 105 µg/L in Coney Green soil, 183.2 µg/L to 191 µg/L in Gibson soil and 64.15 µg/L and 128.1 µg/L in Knowle Road soil, this is probably due to the release of Ni from oil to soils.

A declining trend of Ni C_{DGT} was observed in three selected soils with no oil during aging, due to Ni complexation and adsorption with organic matters sites in soils during incubation time (Sabir et al., 2008). The C_{DGT}-labile species of Ni in Coney Green and Knowle Road soils treated with 2% and 8% w/v were increases at first two weeks, and then showed a slow decrease at the rest of incubation time **Figure 5.2-(B)**. It is likely that the proportions of Ni species at first two weeks associated with the weakly bound ligands and available from solid phase to solution. With aging, more stable and stronger binding oil ligands formed and reduce the availability (Jalali and Khanlari, 2008). For Gibson soil with and with no oil, the C_{DGT}-labile species of Ni showed a markedly decrease during the incubation time, possibly the Ni species could be rapidly adsorbed on solid phase surfaces and precipitated. The organic ligands in oil-amended soils also maybe contributed to OM in soils for inducing a rapid decrease in C_{DGT}-labile Ni species (Relić et al., 2005; Ma et al., 2013).

Copper (Cu). The C_{DGT} of Cu in three soils showed a general increase with increasing quantity of crude oil treatments at average range from 54.1-87.13 µg/L for Coney Green soil, 136.4-148.5 µg/L for Gibson soil and 48.3-156.4 µg/L for Knowle Road soil. This is may be because Cu was most strongly associated with ligands in unamended soils, and weakly associated to organic complexes in oil-amended soils; in the latter, maybe the strongest sites of organic complexes were completely saturated. Moreover, the soluble organic ligands could be adsorbed by iron oxides (Martínez and McBride, 1999; Twiss and Moffett, 2002).

The C_{DGT} of Cu in Gibson soil with no oil showed a slow decrease with incubation time. This is maybe Cu was most strongly associated with ligands in unamended soils and became more stable with aging time. At amended soil with 2% and 8% v/w oil, C_{DGT} gradually increased at first two weeks then decreased at the reminder of aging time, this is probably at first two weeks Cu weakly associated to organic complexes in oil-amended soils due to the competition between OM in soils and oil's ligands then became non-labile with rest of aging time. Moreover, the soluble organic ligands could be adsorbed by iron oxides (Martínez and McBride, 1999; Twiss and Moffett, 2002).

The lability of Cu in Coney Green and Knowle Road soils steadily increased from day (1) to week (2), and then significantly decreased during the rest of aging time. This may be attributed to the strong competition of oil organic ligands with organic complexes in soils. At first two weeks Cu could bound with inorganic ligands and weakly associated to organic ligands and then tend to form more stable complexes with aging time (Jalali and Khanlari, 2008; Ma et al., 2013; Liang et al., 2014).

Zinc (Zn). The C_{DGT}-labile species of Zn species showed a substantial variation in three soils with increasing of crude oil amendment, which is maybe attributed to the variation in redox processes in soils or due to varying stability of OM contributed by metals and oil amendments (Jalali and Khanlari, 2008; Sabir et al., 2008).

As shown in **Figure 5.2-(E)**, the C_{DGT}-labile species of Zn species slowly increased at first two weeks incubation times for Coney Green and Knowle Road soils after which the lability of Zn species continually decreased during the rest of aging time, and changed to more stable forms. For Gibson soil, the C_{DGT} slowly increased at the first two weeks then decreased during the rest of the incubation time. This is probably attributed to the Zn being weakly bound to organic ligands, and inorganic complexes at first 8 days. The Zn species then changed into less available forms, possibly into the forms associated with large stable organic ligands which increased substantially after week 2 due to microbial activity with incubation time (Ma and Uren, 2006; Antoniadis et al., 2007).

Cd and Pb. The concentrations of Cd and Pb for all three studied soils were the lowest compared to the other five metals species during incubation time. The measured C_{DGT} of Cd in Coney Green, Gibson and Knowle Road soils were ranged between 3.0 μg/L to 4.0 μg/L and 5.4μg/L to 10.4 μg/L and 2.2 μg/L to 3.4 μg/L, while the concentrations of labile Pb species were in the range between 0.2-0.8, 6.8-34.5 and 1.16-7.7, respectively **Figure 5.2-(E)** and **Figure 5.2-(F)**. This is probably attributed to the present of humic matter and iron oxides in minerals in soils can form strong complexes with both metals or may be due to low content of metals in soils. It can be noted that the C_{DGT} of Cd and Pb species in Coney Green and Knowle Road soils are the smallest comparing to those in Gibson soil, due to their strong fixation onto soil organic ligands and their affinity for Mn and Fe (hydr) oxides from soils and oil (Trakal et al., 2011). The measured concentrations of Cd and Pb in DGT showed no significant differences with increasing of crude oil treatments. This is probably due to formation of stable organic complexes with oil ligands of similar range (Trakal et al., 2011).

The measured concentration in DGT of Cd in three soils with and with no oil showed no significant changes may due to the mutual competition with the metals in soils.

For Pb, the C_{DGT} of Pb in Cony Green and Knowle Road soils with and with no oil was not significantly changed during aging time possibly due to the decrease in organic matter content stability in soil with increasing of oil amendments (Sabir et al., 2008).

The concentration of labile Pb in Gibson soil with no oil was gradually decreased with aging time probably due to the conversion of organic ligands in soil into more stable form that could bind more Pb during incubation period. However, for the oil-amended Gibson soil, the C_{DGT} of Pb was varying with incubation period, which could be attributed to varying stability of organic matter in soil contributed by aging and oil amendments (Martínez and McBride, 1999).

5.3.2. Soil solution concentrations

The overall distribution of studied trace metal concentrations in soil solutions **Figure 5.3-(A-F)** mirroring the DGT-measured concentrations **Figure 5.2-(A-F)**, although total dissolved concentrations of metals species in the soils solutions are often higher than DGT values. Crude oil amendments significantly affected soil-dissolved Ni, Cu and Zn concentrations after incubation period as shown in **Figure**

5.2-(A-F). Total dissolved Co, Cu, Co, Ni, Zn, Pb and Zn concentrations in Gibson soil generally greater than in Coney Green and Knowle Road soils. This is probably attributed to the low pH value of 5.64 in Gibson soils prohibited the dissociation of organics ligands (carboxyl and phenolic-OH groups) and chemically inactive in complex reactions (Tan, 2010).

Cobalt Co. For Coney Green soil, the Co dissolved concentrations showed no significance different with 2% w/v oil-amended soil; however, it increased by ≈ 39.4% at 8% oil amended soils. In the Gibson and Knowle Road soil-dissolved Co concentrations generally increased with increasing quantity of crude oil treatments with average ranged from 43.6 µg/L to 53 µg/L and 4.0 µg/L to 6.5 µg/L respectively **Figure 5.3-(A)**.

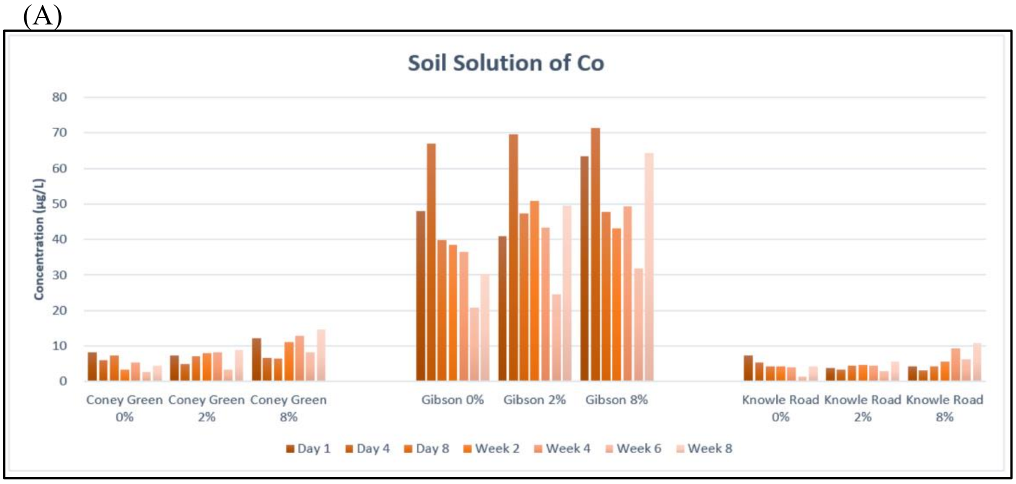
During (8) weeks aging time, the Co dissolved concentration in the Coney Green and Knowle Road soils with no oil was slowly decreased from 8.3 µg/L to 4.6 µg/L and 7.4 µg/L to 4.2 µg/L respectively. The dissolved concentration in unamended Gibson soil was increased from day (1) to day (2) from 48 µg/L to 67 µg/L then showed a general decrease during the rest of the incubation time to 30 µg/L.

Clearly, it can be seen that the dissolved concentrations of Co in three studied soils with 2% and 8% v/w oil amendments generally exhibited a significant variation with aging. This is probably attributed to the variation of competitive ability between chelating of crude oil ligands and adsorption of soil with incubation period (Jiang et al., 2012).

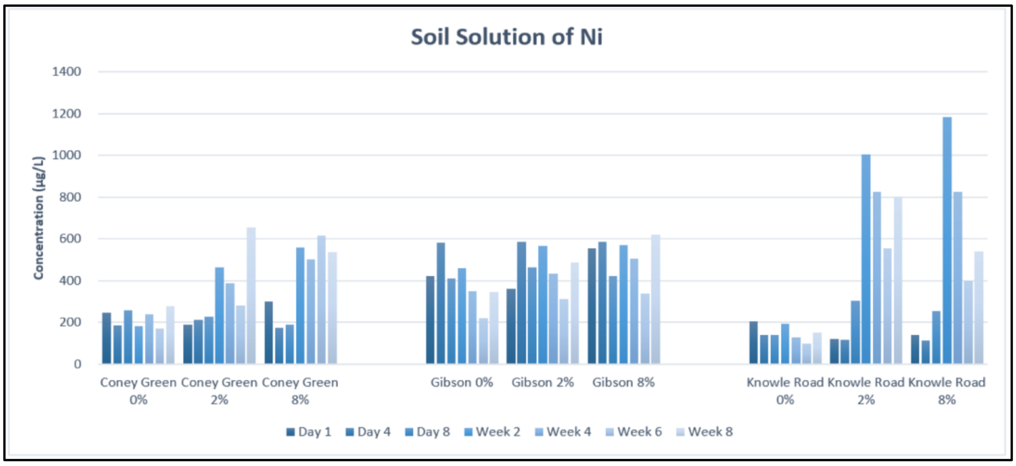
Nickel (Ni). In the Coney Green soil-dissolved Ni concentration at day (1) and day (2) showed a significant variation with increasing oil addition. The 2% and 8% crude oil amendments increased total dissolved Ni concentrations in Coney Green soil by 46% and 84%, respectively, compared with that of control (soil with no oil) due to Ni release from crude oil to soil. Total dissolved concentration in Gibson soils showed no significant different with increasing crude oil treatments may due to the naturally occurrence of high Ni in soil. In the Knowle Road soil-dissolved concentration varied with oil treatments, which could be attributed to varying stability of organic ligands contributed by oil amendments. However, general increase in total dissolved Ni concentrations in three selected soils with and with no oil considerably varied with incubation time, which probably attributed to varying decomposition/oxidation of organic complexes by soil microorganisms during aging time (Wuana et al., 2015).

Copper (Cu). Total dissolved Cu concentrations in three soils exhibited a substantial variation with both increasing quantity of crude oil amendment and aging time **Figure 5.3-(C)**. This is may be due to the competition among multiple and mixed solid phases for Cu retention with oil addition and aging time (Martínez and McBride, 1999).

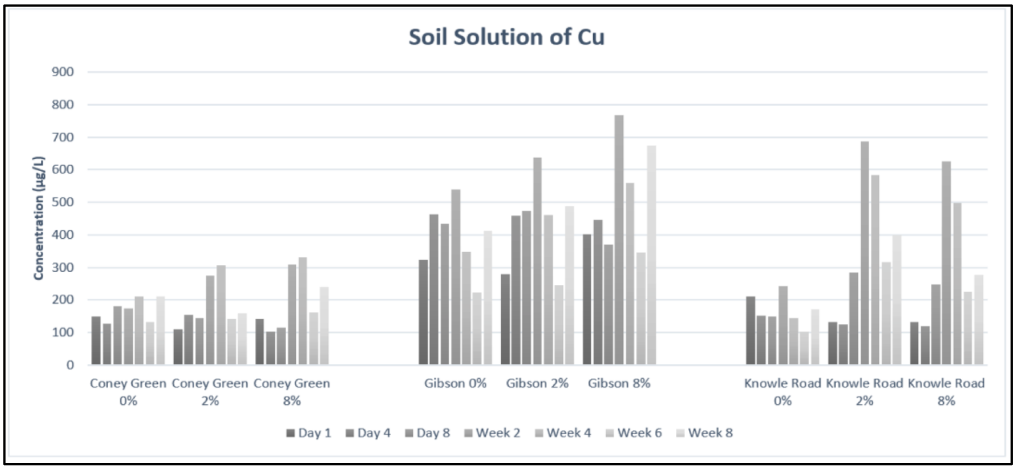
(A)


Soil Solution of Co
Concentration (µg/L)
80
70
60
50
40
30
20
10
0
Coney Green 0%
Coney Green 2%
Coney Green 8%
Gibson 0%
Gibson 2%
Gibson 8%
Knowle Road 0%
Knowle Road 2%
Knowle Road 8%
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8

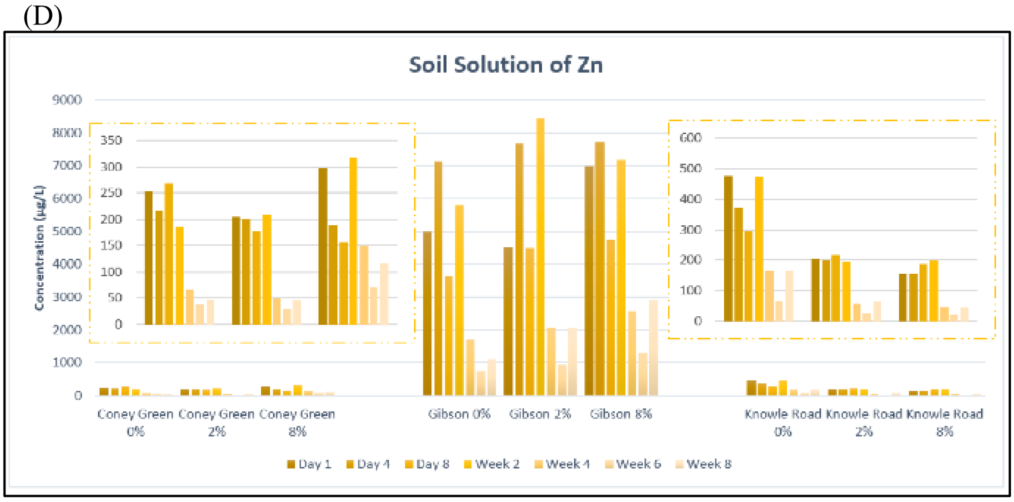
(B)


Soil Solution of Ni
Concentration (µg/L)
1400
1200
1000
800
600
400
200
0
Coney Green 0%
Coney Green 2%
Coney Green 8%
Gibson 0%
Gibson 2%
Gibson 8%
Knowle Road 0%
Knowle Road 2%
Knowle Road 8%
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8

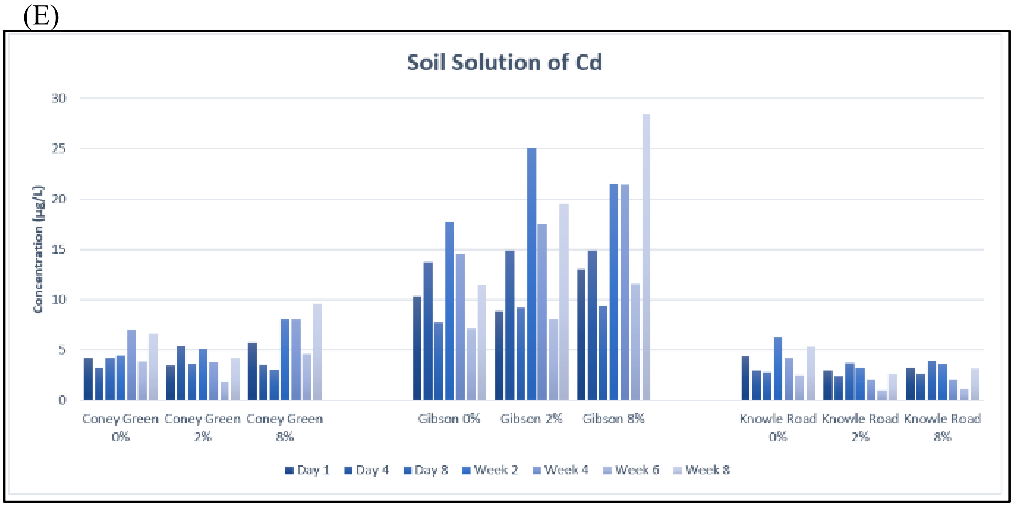
(C)


Soil Solution of Cu
Concentration (µg/L)
900
800
700
600
500
400
300
200
100
0
Coney Green 0%
Coney Green 2%
Coney Green 8%
Gibson 0%
Gibson 2%
Gibson 8%
Knowle Road 0%
Knowle Road 2%
Knowle Road 8%
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8

(D)



(E)



(F)

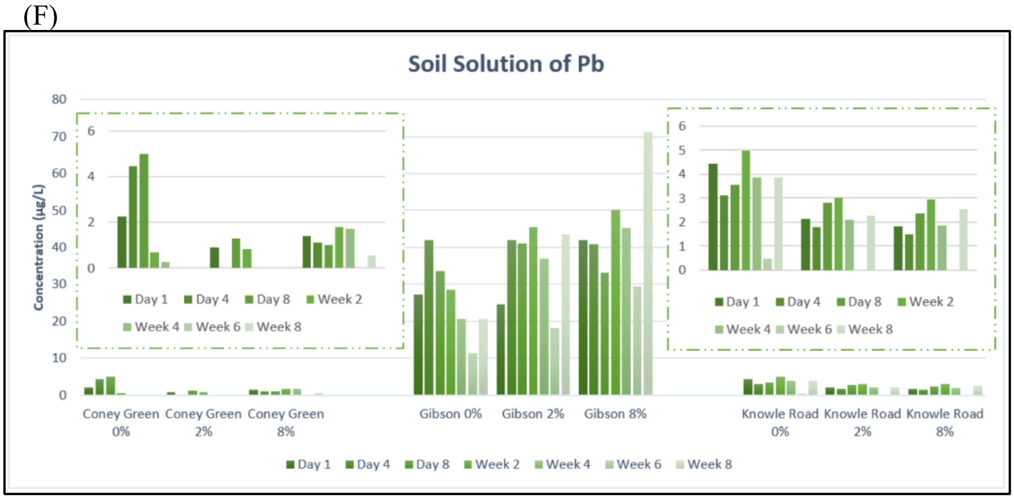


Figure 5.3. (A-F). Determinations of total dissolved concentrations in soil solutions of Co, Ni, Cu, Zn, Cd and Pb in Coney Green, Gibson and Knowle Road soils treated and untreated with crude oil (0%, 2% and 8% w/w) and incubated.

Zinc (Zn). At both crude oil treatments of Coney Green and Gibson soils, total dissolved Zn showed a general increase varied with increasing quantity of crude oil application due to varying stability of organic complexes contributed by amendments (Sabir et al., 2008).

With incubation periods, the total dissolved Zn concentrations in three soils with and with no oil showed a general decrease with a slight variation due to changes in redox and decomposition condition with aging.

Cadmium (Cd) and Lead (Pb). The total dissolved concentrations of Cd and Pb in soil solutions of three selected soils with and with no oil were low and not substantially different with incubation time as shown in **Figure 5.3-(E)** and **Figure 5.3-(F)**. This is probably attributed to the stable organic ligands in soils associated with both metals in the presence of oil and during aging or to the presence of low content of this metal in soil's solid and soil phases (Ford et al., 1997; Lock and Janssen, 2003; Jalali and Khanlari, 2008). The measured concentrations in soil solutions of Pb often were effectively at or below the detection limit. This is possibly due to extracting insufficient quantity of soil solutions for analysis.

5.3.3. Effect of oil and aging on R values

Tables 5.3-5.5 show the obtained R values of the concentrations measured by DGT to that in soil solutions, (C_{soln}), for studied metals in three selected soils with and with no oil. The R value C_{DGT}/C_{soln} ($0 < R < 1$) indicates the capacity of the solid phase in soil to resupply metals into soil solutions. When $R > 0.95$, the metal is present as mobile and kinetically labile species in the solid phase and the capacity of the solid phase to resupply the pore water is high. If C_{DGT}/C_{soln} approaching (0) indicates very limited or no metal resupply from solid phase into soil solution (Senila et al., 2012).

Cobalt (Co). The R values for Co in soil with no oil ranged between 0.37 - 0.77 (average 0.57), while in the 2% and 8% oil mended soils ranged between 0.30 - 1.04 (average 0.67) and 0.2 - 0.89 (average 0.55) respectively **Table 5.3**. This indicates in general an intermediate capacity for Co resupply from the solid phase to soil solution. Soil amendment with crude oil generally decreased R values for Co except at day (4) and day (8), R values were higher may be due to the release of Co from oil in these two periods. If the metal in the soil is significantly complexed stable organic ligands, DGT will capture only a proportion of the labile metal species in soil solution (Zhang et al., 2006). With incubation time R values for Co in Coney Green soil with and with no oil showed a gradual decrease may be due to the conversion of organic complexes into more stable form that could bind more Co (Martínez and McBride, 1999).

Table 5.3. (R) Values for studied metals in Coney Green soil with and without crude oil.

		Co			Ni			Cu			Zn			Cd			Pb		
Soils	Aging time	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w
Coney Green	Day 1	0.61	0.66	0.46	0.39	0.47	0.33	0.37	0.45	0.39	1.11	1.26	0.97	0.75	0.82	0.59	0.35	1.01	0.87
	Day 4	0.77	1.04	0.89	0.52	0.42	0.61	0.44	0.33	0.60	1.20	1.32	1.76	0.94	0.60	1.11	0.16	-0.50	1.77
	Day 8	0.61	0.82	0.67	0.35	0.46	0.74	0.29	0.40	0.61	1.11	2.45	1.80	0.77	1.16	2.10	0.08	1.63	7.04
	Week 2	0.77	0.38	0.43	0.46	0.22	0.25	0.38	0.39	0.40	1.02	0.86	0.89	0.97	0.69	0.60	0.42	0.58	0.65
	Week 4	0.42	0.30	0.34	0.31	0.26	0.25	0.26	0.34	0.35	0.99	1.84	0.57	0.57	1.24	0.48	0.80	-22.17	0.84
	Week 6	0.65	0.60	0.49	0.39	0.35	0.19	0.39	0.70	0.59	1.05	1.31	0.90	0.87	1.43	0.76	-0.22	-0.58	-1.86
	Week 8	0.37	0.30	0.24	0.24	0.19	0.18	0.20	0.52	0.37	0.70	0.64	0.61	0.47	0.48	0.47	-0.42	-0.96	2.77

Table 5.4. (R) Values for studied metals in Gibson soil with and without crude oil.

		Co			Ni			Cu			Zn			Cd			Pb		
Soils	Aging time	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w
Gibson	Day 1	0.65	0.67	0.41	0.63	0.64	0.40	0.54	0.54	0.37	0.49	0.48	0.30	0.76	0.76	0.50	0.73	0.74	0.41
	Day 4	0.44	0.40	0.37	0.41	0.38	0.36	0.37	0.32	0.33	0.33	0.30	0.28	0.55	0.47	0.43	0.82	0.48	0.49
	Day 8	0.67	0.62	0.63	0.54	0.51	0.59	0.35	0.32	0.40	0.64	0.58	0.56	0.97	0.91	0.93	0.82	0.63	0.77
	Week 2	0.50	0.40	0.39	0.43	0.34	0.32	0.30	0.28	0.24	0.60	0.49	0.41	0.59	0.42	0.38	0.53	0.37	0.41
	Week 4	0.42	0.40	0.35	0.37	0.36	0.31	0.30	0.29	0.26	0.49	0.45	0.35	0.46	0.41	0.33	0.42	0.43	0.40
	Week 6	0.65	0.61	0.50	0.53	0.44	0.43	0.45	0.51	0.39	0.89	0.79	0.53	0.78	0.71	0.47	0.71	0.77	0.58
	Week 8	0.41	0.35	0.30	0.32	0.32	0.26	0.22	0.25	0.19	0.55	0.42	0.31	0.47	0.37	0.27	0.33	0.38	0.27

Table 5.5. (R) Values for studied metals in Knowle Road soil with and without crude oil.

		Co			Ni			Cu			Zn			Cd			Pb		
Soils	Aging time	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w	0% w/w	2% w/w	8% w/w
Knowle Road	Day 1	0.37	0.70	0.59	0.36	0.62	0.47	0.26	0.37	0.28	0.49	1.08	1.13	0.50	0.81	0.67	0.37	0.97	1.17
	Day 4	0.55	0.75	0.83	0.53	0.63	0.63	0.35	0.48	0.41	0.79	1.14	1.48	0.81	1.04	0.97	0.81	1.61	1.73
	Day 8	0.72	0.71	0.82	0.65	0.37	0.40	0.42	0.47	0.43	1.61	2.03	2.59	1.22	0.95	0.92	2.15	2.05	3.92
	Week 2	0.27	0.36	0.43	0.34	0.20	0.22	0.25	0.48	0.62	0.41	1.01	1.24	0.53	0.68	0.62	0.43	0.86	1.24
	Week 4	0.18	0.33	0.20	0.39	0.20	0.20	0.25	0.45	0.49	0.39	1.01	1.17	0.66	0.84	0.83	0.44	1.13	1.41
	Week 6	0.37	0.58	0.27	0.49	0.33	0.32	0.36	0.79	0.75	0.68	1.70	1.39	0.98	1.36	1.28	2.46	-5.67	-8.43
	Week 8	0.10	0.31	0.17	0.30	0.18	0.22	0.19	0.47	0.36	0.23	0.60	0.71	0.48	0.59	0.61	0.30	1.00	0.85

For Gibson and Knowle Road soils, R values for Co ranged between 0.1-0.83 (average 0.47), indicating an intermediate capacity for Co resupply from the solid phase **Table 5.4**. The R values for Co in both soils with and with no oil exhibited fluctuations decreases during aging time may be due to the varying stability of organic complexes with incubation periods (Martínez and McBride, 1999).

Nickel (Ni). The R values in three soils with and with no oil ranged between 0.18-0.74 (average 0.46), indicating in general a poorer capacity re-supply of Ni from solid phase to solution **Tables (5.3-5.5)**. With increasing of crude oil treatments and incubation time for three soils, R-values showed a general decrease compared with that of control soils probably due to Ni formation of organic and inorganic complexes from oil that adsorbed to solid phase (Sabir et al., 2008; Wuana et al., 2015).

Copper (Cu). The R values of Cu in three soils sensibly ranged from 0.19 - 0.79 (average 0.49), indicating poor buffering from solid phase re-supply of the Cu in soil solution. For Coney Green and Knowle Road soils, R values exhibited a general increase with increasing of crude oil amendments compared with that for control. This is may be Cu was most strongly associated with ligands in unamended both soils, and weakly associated to organic complexes in oil-amended soils; in the latter, maybe the strongest sites of organic complexes were completely saturated. On the other hand, the soluble organic ligands could be adsorbed by iron oxides from oil (Martínez and McBride, 1999; Twiss and Moffett, 2002). For Gibson soil, the R values for Cu showed a gradual decrease with increasing of oil amendments compared with that of control soil. This may be Cu less affected by competition with OM in soil of low pH and form more stable complexes increasing of oil ligands (Torri and Corrêa, 2012). The R values in three soils decreased with slight fluctuations during incubation times due to the varying competition between OM in soils and oil ligands.

Zinc (Zn). The R values for Zn in the three soils with and with no oil were slightly higher than those in soils with no oil (control); this may be due to the release of Zn species from the oil into the soils. In Coney Green and Knowle soils, the R values are greater than 1, which is not possible. This only means contamination of Zn during DGT assembly, sample treatments or analysis. Therefore, those data cannot be used and interpreted.

The R values for Gibson soil showed a gradual decrease with increasing oil treatments compared to that for control, due to complexation of Zn with oil ligands **Table 5.4**. During aging time the R values for Zn in Gibson soil with and with no oil showed a substantial variation again due to the varying stability of ligands with incubation time.

Cadmium (Cd). The R values for Cd in three studied soils were ranged between 0.27-1.28 (average 0.80), indicating high capacity of solid phase to resupply Cd species concentrations into soil solution (**Table 5.3-5.5**). There was a significant variation of R values for Cd in three soils with and with no oil during aging period. The often overestimated Cd in Coney Green and in Knowle Road could be attributed to the contamination of samples and handling during extraction step.

Lead (Pb). For Gibson soil, the R values of Pb were ranged between 0.27-0.77 (average 0.52), indicating an intermediate and partial resupply from solid phase to soil solutions. The R values for Pb in Gibson soil showed a general decrease with increasing of crude oil amendments and varied during incubation time. The often overestimation and underestimation of R values for Pb in Coney Green and Knowle Road soils attributed to the contamination of samples and handling during extraction step.

5.3.4. $CaCl_2$ extractable concentrations

Figures 5.4-(A-F) show the measured $CaCl_2$-extractable of studied trace metals contents in the three selected soils with and with no oil. The concentrations of studied trace metals measured as $C_{solution}$ and C_{DGT} were substantially lower than those extracted in 0.01 M $CaCl_2$ because $CaCl_2$ was in direct contact with the solid phase (Garrido Reyes et al., 2013).

Co. A slight increase in $CaCl_2$-extractable Co for Coney Green and Gibson soils was observed with increasing of crude oil amendment compared with that of control, ranged from 25.7-31 µg/Kg and 29-33 µg/Kg respectively. This may be attributed to the release of Co from crude oil and due to the present of organic ligands with saturated sites with adding oil. The $CaCl_2$-extractable Co in Knowle Road soil showed a slight decrease with increasing crude oil ranged from 22 µg/Kg -10 µg/Kg probably due to the complexation of Co with oil organic ligand.

A general decrease in $CaCl_2$-extractable Co for both three soils with and with no oil was observed with aging time **Figure 5.4-(A).** This is probably due to the conversion of organic ligands into more stable form that could bind more Co with incubation time (Qin et al., 2004; Sabir et al., 2008)**.**

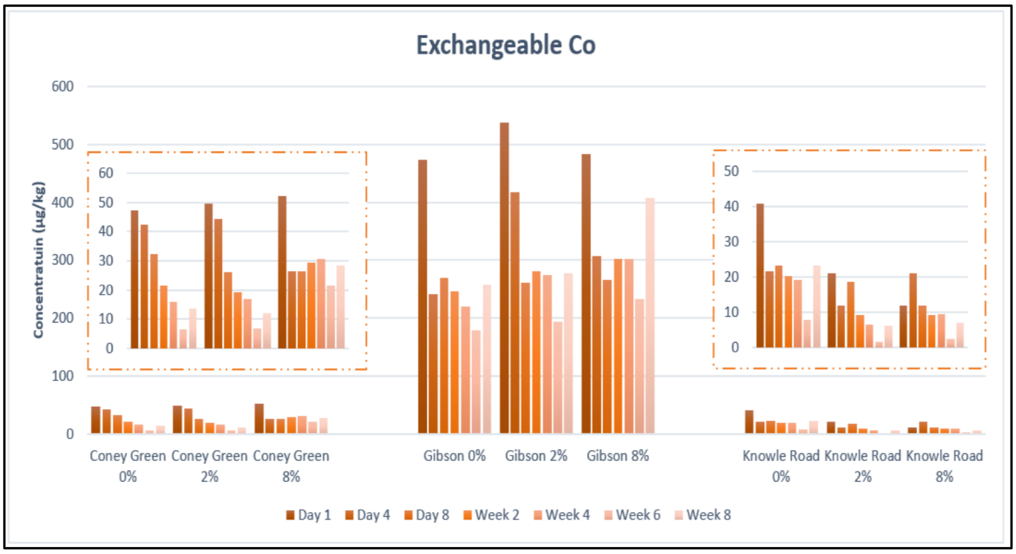
Ni and Cu. There was a significant variation in $CaCl_2$-extractable Ni and Cu for three soils with increasing quantity of crude oil amendments may be due to the competition between OM in soils and oil ligands **Figures 5.4-(B) and 5.4-C**). The measured $CaCl_2$-extractable Ni and Cu in three soils showed a significant variation with increasing crude oil treatments and incubation times. This is attributed to the varying in organic ligands competition and stability with increasing oil and aging time. The higher extractability of Ni and Cu probably attributed to high dissolved concentrations of organic matter, which can strongly complex with the metals (Iwegbue et al., 2007).

Zn. The $CaCl_2$-extractable Zn is the highest and exhibited a significant decrease in Coney Green and Knowle Road soils with increasing of crude oil amendments compared with that for control with average range from 1030.4-950 µg/kg and 1790-590 µg/kg respectively **Figure 5.4-(D)**. This is may be attributed to the formation of stable organic complexes with increasing of oil ligands. In Gibson soil the extracted Zn varied with increasing of crude oil treatments possibly due to the varying in stability of ligands with adding oil.

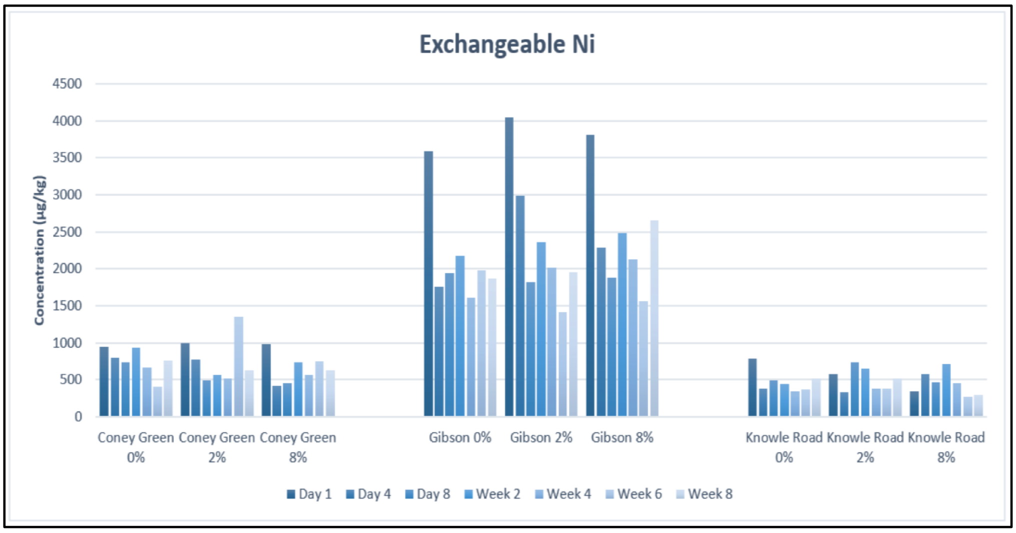
The $CaCl_2$-extractable Zn in three soils with and with no oil exhibited a general decrease due to the increase of organic ligands stability with incubation time.

Cd and Pb. As shown in **Figures 5.6-(E)** and **5.6-(F)** the $CaCl_2$-extractable both metals were low and not significantly different with increasing oil amendments and incubation period, which was consistent with C_{DGT} and water-soluble Cd and Pb in soil solutions in **Figures 5.2-(E), 5.2-(F), 5.3-(E)** and **5.3-(F)**. This is could be attributed to the low content of both metals in soils.

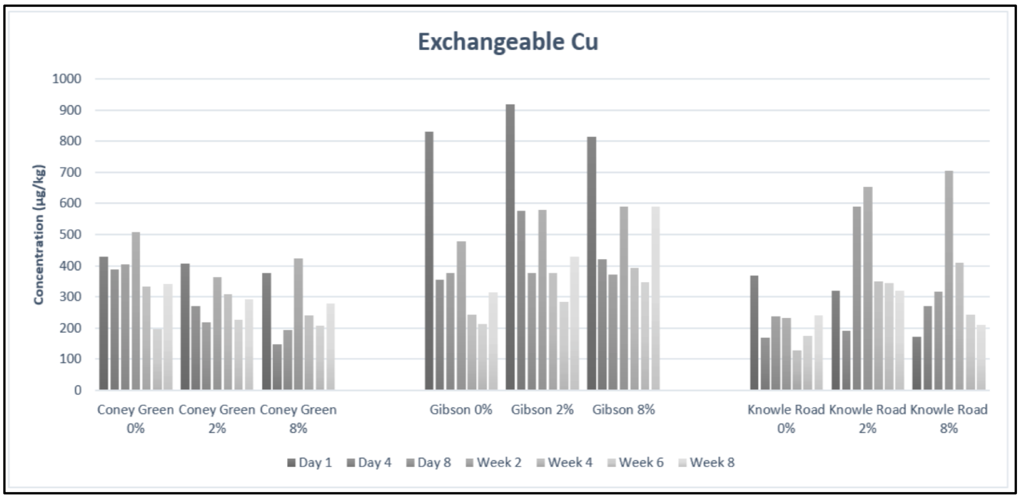
(A)



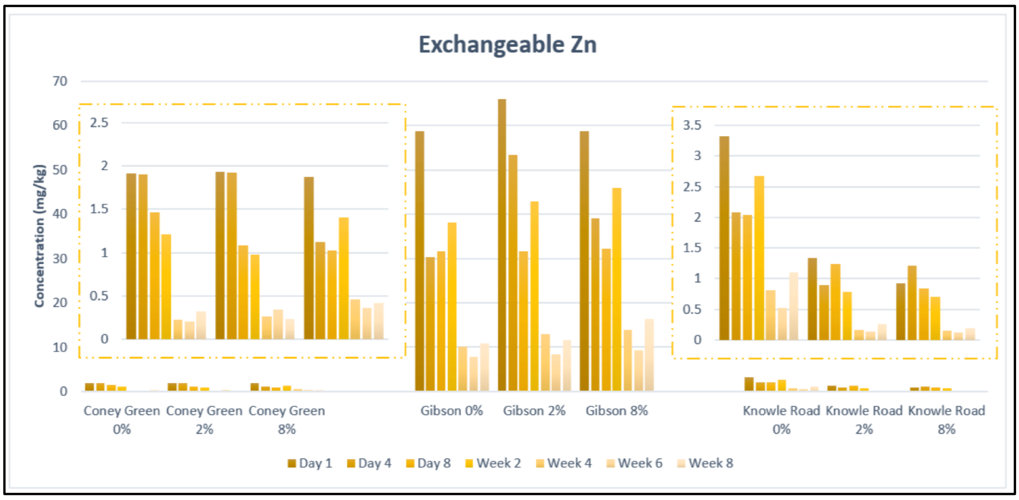
(B)



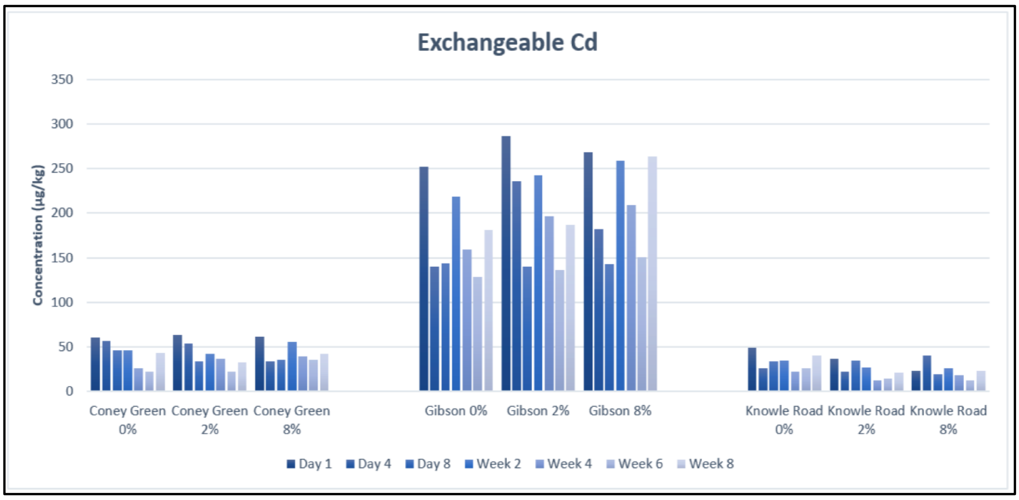
(C)


Exchangeable Cu
Concentration (µg/kg)
1000
900
800
700
600
500
400
300
200
100
0
Coney Green 0%
Coney Green 2%
Coney Green 8%
Gibson 0%
Gibson 2%
Gibson 8%
Knowle Road 0%
Knowle Road 2%
Knowle Road 8%
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8

(D)


Exchangeable Zn
Concentration (mg/kg)
70
60
50
40
30
20
10
0
2.5
2
1.5
1
0.5
0
3.5
3
2.5
2
1.5
1
0.5
0
Coney Green 0%
Coney Green 2%
Coney Green 8%
Gibson 0%
Gibson 2%
Gibson 8%
Knowle Road 0%
Knowle Road 2%
Knowle Road 8%
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8

(E)


Exchangeable Cd
Concentration (µg/kg)
350
300
250
200
150
100
50
0
Coney Green 0%
Coney Green 2%
Coney Green 8%
Gibson 0%
Gibson 2%
Gibson 8%
Knowle Road 0%
Knowle Road 2%
Knowle Road 8%
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8

(F)

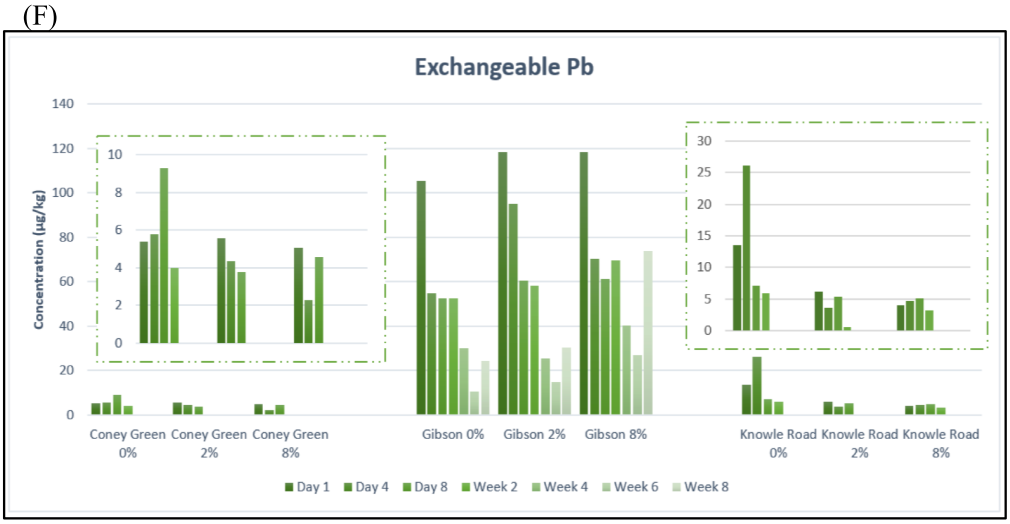


Figure 5.4-(A-F). Determinations of trace metals concentrations in extracted in $CaCl_2$ species of Co, Ni, Cu, Zn, Cd and Pb in three soils with without crude oil during aging time.

5.3.5. Effect of oil and aging on K_d

As discussed above in **section 5.2.10**, the DIFS model quantifies the dependence of (R) on trace metals species re-supply from solid phase into soil solutions coupled to diffusional supply to the interface and through the diffusion layer to the binding layer (Lehto et al., 2008). The DIFS was applied to model the obtained (R) values (**Tables 5.3-5.5**) in order to determine K_d values (plotted in **Figure 5.5**) and T_C (**Table 5.6**).

The distribution coefficient (K_d) values were estimated by measuring the concentrations of each trace metals species released in soil solutions and extractants in 0.01 M $CaCl_2$. To contribute to C_{DGT}-labile species, the trace metals in the labile solid phase pool must dissociate during time of deployment (Ernstberger et al., 2002). The distribution coefficient, K_d, expresses the ratios between the concentrations of labile trace metals species in the solid phase and its concentration in soil solutions using the following **equation (5.7)** (Lehto et al., 2008).

$$K_d = \frac{C_{\text{solid phase}}}{C_{\text{soil solution}}} \qquad (5.7)$$

The resupply kinetics of studied trace metals species in three selected soils discussed by (K_d) **Figure 5.7**

High K_d values suggest that the metal species has been retained by the solid phase through sorption reactions, whereas low K_d values show that high concentration of metal species are occur in soil solution.

Co. It can be seen that the K_d values of Co in Coney Green soil showed a general decrease with increasing of crude oil amendments compared with that for control with average range from 50 at (no oil) to 42.7 at (2% oil-amended soil) to 32 at (8% oil oil-amended soil). The crude oil amendments seemed to reduce the available solid phase pool of Co for Coney Green soil. For Gibson soil, K_d of Co values showed no significant different at (2% oil-amended soil) and decreased by nearly 22.4% at (8% oil-amended soil) compared to that for control may be due to the release of more Co concentration in solution or because of competition in reducing the sorption of metal by oil ligands (Antoniadis et al., 2007). The K_d of Co in Knowle Road soil decreased from 55 at (no oil) to 29 (2% oil-amended soil) the increased to 48 (8% oil-amended soil) probably due to the increase of solid phase capacity in soil to retain Co with increasing of oil ligands.

The (K_d) values in Coney Green soil with and with no oil were gradually decreased during incubation time, indicating an increase of Co species load in soil solutions and a decrease in the solid phase Co species pool with aging period. This is also possibly when sorption sites become saturated a lower metal complexations with organic ligands in solid phase, which inducing a rapid reduce of labile metal in the solid phase, and thus the K_d may become lower (Zhang et al., 1998; Dabrin et al., 2012). For Knowle Road, the K_d values of Co showed no significant difference in unamended soil during incubation time but decreased to nearly by 79.7% at (2% oil-amended soil) and increased with a greater variation at (8% oil-amended soil). This is possibly attributed to the varying in competition between the capacity of soil solid phase and oil ligands in solution to retain metal. For Gibson soil with and with no oil the K_d values exhibited a considerable variation with incubation time may be due to the varying in the capacity of solid phase sites for adsorbing metal during aging time (Antoniadis et al., 2007).

Ni. The K_d values of Ni were generally decreased with adding of crude oil amendments in three soils. For Coney Green the K_d decreased from 38 at (soil with no oil) to 30 at (2% oil-amended soil) to 20 at (8% oil-amended soil). Ni K_d values for Gibson soil were slowly decreased from 62 at (soil with no oil) to 59 at (2% oil-amended soil) to 51 at (8% oil-amended soil). The K_d values for Knowle Road soil slightly decreased to nearly by 26% with increasing of oil treatments compared to that for control (unamended soil). This is probably attributed to the release of Ni species from solid phase and crude oil to soil solution. On the other hands, in the presence of oil ligands the enrichment of the Ni on the solid phase could be decreases, and the K_d values are also reduced (Rocha et al., 1997).

The K_d values in three soils with and with no oil exhibited a general decrease with a slight variation during aging. This is probably Ni ions form more stable anionic complexes from crude oil and have noticeable reduction in K_d values with incubation time.

Cu. The K_d values of the Cu in Coney Green soil were decreased slowly from 25 at (soil with no oil) to 20 at (2% oil-amended soil) to 14 at (8% oil-amended soil). Also in Gibson and Knowle Road soils, the K_d values were low with average range from 12-14 and exhibited no significance different with increasing of crude oil amendments. This is probably attributed to the increase of stable Cu-ligands with oil increase. High organic content introduced by more quantity of crude oil could modify the availability of Cu from the solid phase. Thus, the proportion of labile Cu species in the solid phase probably reduced, and therefore the K_d values decrease (Zhang et al., 1998).

A gradual decrease of K_d values with incubation period can be observed for three selected soils with and with no oil, possible due to the strongest tendency of Cu to be associated with the solid phase with increasing incubation time (Refaey et al., 2014).

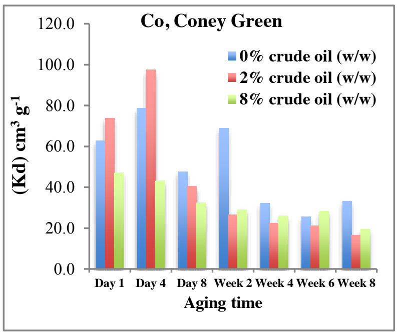
Zn. For Zn, the K_d values of Zn in three studied soils with and with no oil were similar irrespective of treatment and showed substantial variations. This reflects the variation in Zn may present as the free (hydrated) zinc ion or as dissolved complexes and compounds with similar extent of stability of in solid phase with incubation time. On the other hand, the increase of crude oil treatments could modify binding sites and changing the rate constants of Zn resupply to lower values (Zhang et al., 1998). The higher values of K_d suggest a high Zn species retention by the solid phase through sorption reactions and low concentration available in the soil solution (Mench et al., 2000).

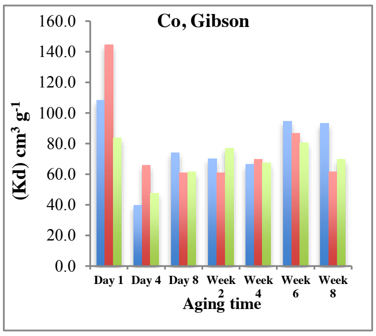
Cd. The K_d values of Cd in three studied soils exhibited greater variations with increasing of crude oil due to varying in competition of metal for soil sorption sites. On the other hand, could be attributed to the varying in stability of organic ligands with increasing oil treatments (Antoniadis et al., 2007).

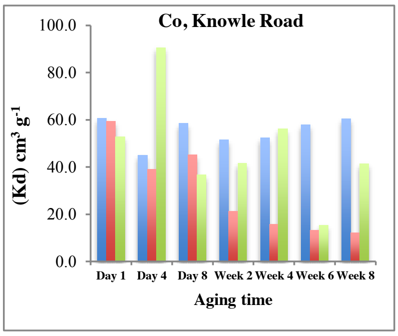
The K_d values in Coney Green soil with no oil and with 8% crude oil (w/w) amendments showed a gradual decrease during incubation time. This is maybe at unamended oil soil; Cd sorption appeared to be strongly influenced by more stable organic matter with incubation time. However, at 8% oil-amended soil organic ligands may be modified the availability of Cd species from the solid phase. Therefore, the proportion of labile Cd species in the solid phase can be reduced, and lowering the K_d values with incubation time (Zhang et al., 1998; Antoniadis et al., 2007). The measured Kd values at 2% oil amended soil increased quickly for the first couple of days and then the rate of increase in K_d slowed but continued to rise through the rest of incubation period. This suggests that at lower level of oil amendment, Cd probably strongly associated with organic ligands, which decreases it amount in soil solution (Antoniadis et al., 2007).

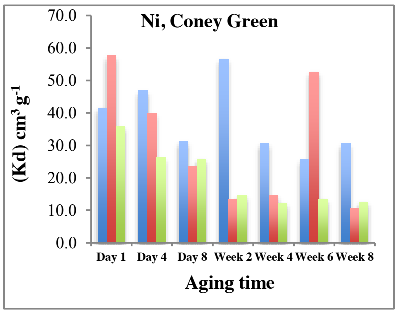
For Gibson soil, the K_d values at unamended and 2% oil amended soils significantly decreased and then the rate of decrease in K_d values continued with no considerable difference during the rest of the aging time. At 8% crude oil contamination the K_d values dramatically increased and showed no significant difference with incubation time, this is probably due to the depletion of labile Cd species with increasing of crude oil amendment (Carrillo-Gonzalez et al., 2006).

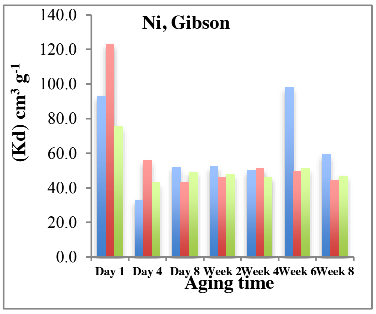
For Knowle Road with no oil, the K_d was high and significantly decreased continually during the rest of incubation time with no substantial difference. This indicating a strong Cd species retention that may be attributed to strong association to organic matter (Silveira et al., 2003). However, the K_d values at 2% and 8% oil amended-soils exhibited a general increase with no significant difference during incubation. This is attributed to the strong association of Cd species to oil ligands and adsorbed in the solid phase to a higher extent, thus is less likely to move throughout the soil solution due to low lability and mobility (Silveira et al., 2003).

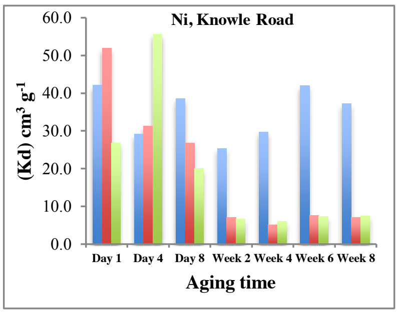

Co, Coney Green
0% crude oil (w/w)
2% crude oil (w/w)
8% crude oil (w/w)
(Kd) cm³ g⁻¹
120.0
100.0
80.0
60.0
40.0
20.0
0.0
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8
Aging time

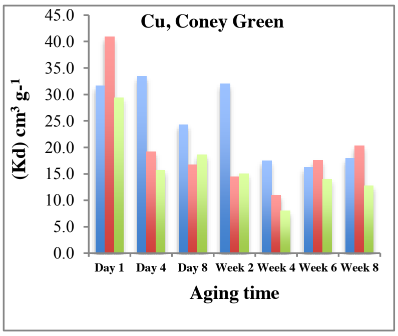

Co, Gibson
(Kd) cm³ g⁻¹
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8
Aging time

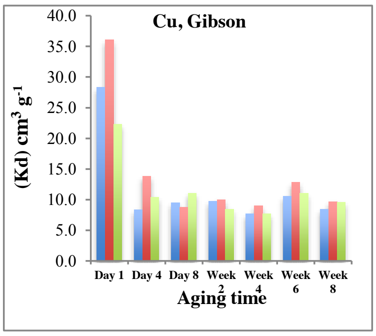

Co, Knowle Road
(Kd) cm³ g⁻¹
100.0
80.0
60.0
40.0
20.0
0.0
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8
Aging time

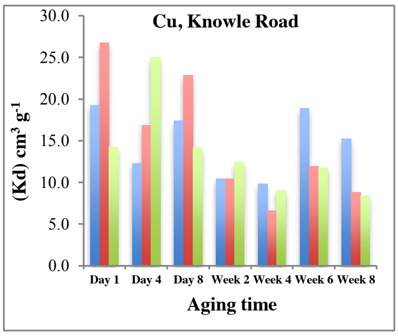

Ni, Coney Green
(Kd) cm³ g⁻¹
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8
Aging time

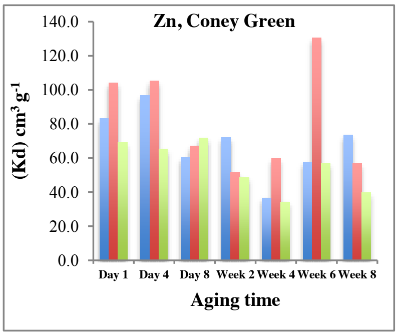

Ni, Gibson
(Kd) cm³ g⁻¹
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8
Aging time

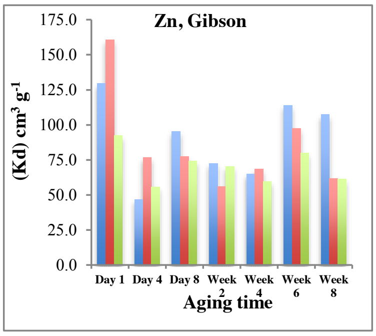

Ni, Knowle Road
(Kd) cm³ g⁻¹
60.0
50.0
40.0
30.0
20.0
10.0
0.0
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8
Aging time

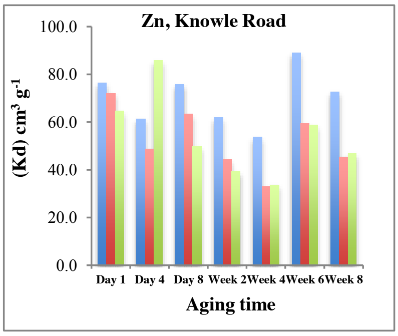

Cu, Coney Green
(Kd) cm³ g-¹
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8
Aging time


Cu, Gibson
(Kd) cm³ g⁻¹
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8
Aging time


Cu, Knowle Road
(Kd) cm³ g⁻¹
30.0
25.0
20.0
15.0
10.0
5.0
0.0
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8
Aging time


Zn, Coney Green
(Kd) cm³ g⁻¹
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8
Aging time


Zn, Gibson
(Kd) cm³ g⁻¹
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8
Aging time


Zn, Knowle Road
(Kd) cm³ g⁻¹
100.0
80.0
60.0
40.0
20.0
0.0
Day 1
Day 4
Day 8
Week 2
Week 4
Week 6
Week 8
Aging time

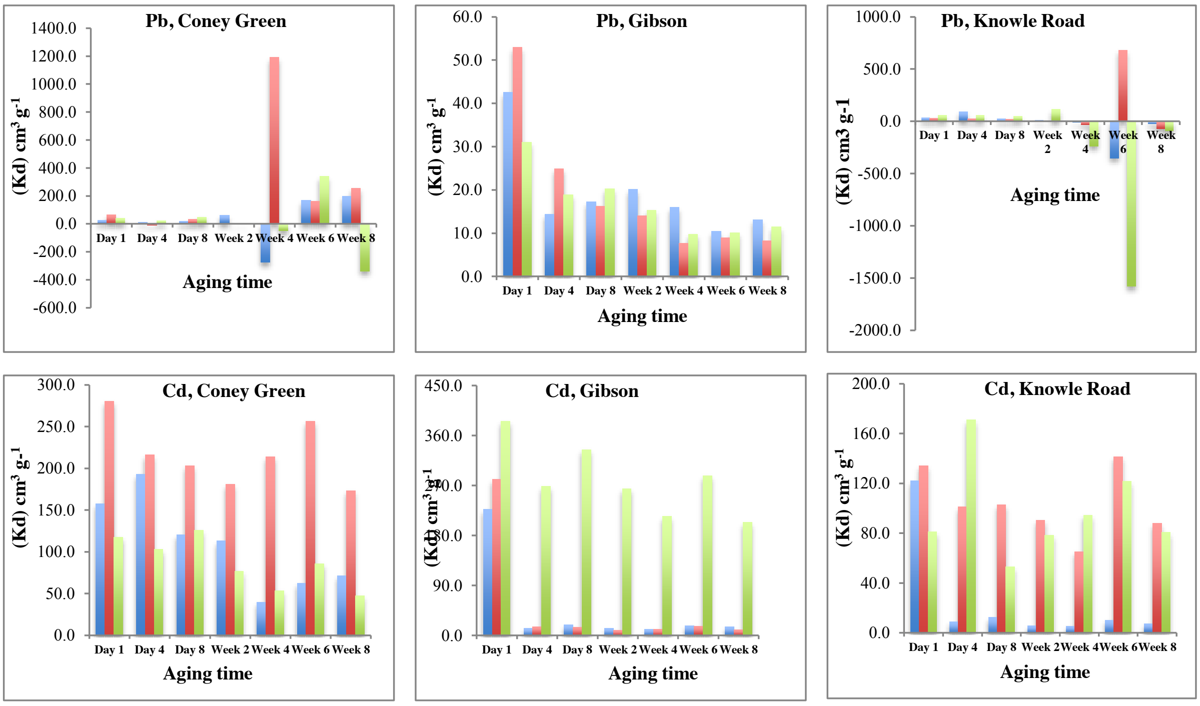


Figure 5.5. The Kd values for Co, Ni, Cu, Zn, Cd and Pb on Coney Green, Gibson and Knowle Road soils treated with varying levels of crude oil 0%, 2% and 8% w/w during incubation time.

Pb. The K_d values of Pb in three studied showed significant differences with increasing of crude oil due to varying in stability of organic ligands with increasing oil treatments (Antoniadis et al., 2007).

The K_d values in Coney Green and Knowle Road soils very low during the incubation time and not possible to calculate K_d values at weeks (4, 6 and 8) incubation time due to below-detection-limit concentrations of Pb species, which indicates low Pb content in soils.

For Gibson soils with and with no oil, the K_d values of Pb were gradually decreased with incubation time may be due to the increasing soil solution concentration with aging time. On the other hand, OM in soil and oil ligands may alter the availability of Pb from the solid phase. Thus the proportion of labile metal in the solid phase could be decreased, and therefore the K_d will be reduced (Zhang et al., 1998; Antoniadis et al., 2007).

5.3.6. DIFS calculations and interpretations for Tc

Tc represents the response time of the systems to perturbation of trace metals species from solid phase to soil solutions. The kinetic parameter T_C values of studied metals were determined for day (1) and week (8) in three selected soils with and with no oil in order to investigate the effect of crude oil and aging time on T_C.

For **Co**, it can be seen from the **Table 5.6** that the Tc values in three studied soils at day (1) and week (8) incubation time with increasing of crude oil amendments were very low and ranged between 0.12s and 0.40s, which indicates a very fast soil re-supply of Co species from the solid phase to solution solutions (Lehto et al., 2006; Lehto et al., 2008). This is simply reflecting Co depletion of the solid phase.

For Gibson soil, the T_C values at day (1) were gradually increased with increasing of oil amendments, which indicated that Co dissociation rate from the solid phase decreased with increasing of crude oil contamination, which was consistent with decrease in in water-soluble Co species in soil solutions **Figure 5.3** and C_{DGT}-labile species of Co **Figure 5.2**. At week (8), the T_C values slowly decreased at 2% w/w crude oil treatment then significantly increased with increasing of crude oil treatment to 8% w/w. This is possibly at 2% w/w oil amendment, the Co species will released from crude oil to water soluble species in soil solution and improve buffering from oil on the solid phase. However, with increasing of oil amendment to 8% w/w, T_C increased due to the increase of organic ligands supply from oil addition, which is limiting the kinetics of Co dissociation on the supply of Co species into soil solution (Lehto et al., 2006).

For Knowle Road soil at day (1), the Tc values were very low and not significantly different with increasing of crude oil contamination ranged between 0.28s and 0.5s **Table 5.6**. This reflects a rapid supply from the solid phase ensures that the Co species in soil solution are well buffered and a larger mass accumulated in the DGT device. At week (8), the Tc values in the amended soil with 2% and 8% w/w of crude oil were ~ 97% lower than those determined in untreated soil, which suggested that the supply of Co species from solid phase is limited kinetically in crude oil contaminated soil. This decreases the concentration of Co species in soil solutions.

For **Cu**, the T_C values were very low in three selected soils with and with no oil at day (1) and week (8) incubation time, which indicated that very fast resupply from solid phase to soil solution, which was consistent with increase in water-soluble Cu **Figure 5.3** and C_{DGT}-labile species **Figure 5.2.** On the other hand, the total dissolved concentrations of Cu species may include small colloidal forms and kinetically labile complexes released from oil. Even if most of the Cu species are strongly associate to the solid phase and not available in the labile pool, it is not necessary that the K_d values based on the labile species will be low (Harper et al., 1998; Lehto et al., 2006).

Table 5.6. The obtained the response time (Tc) from DIFS model using (R) values of Co, Ni, Cu, Zn, Cd and Pb for three studied soils with and amended with varying levels of crude oil (% w/w) in day (1) and week (8) during incubation time.

		Coney Green soil				
Day1	Co	Ni	Cu	Zn	Cd	Pb
0% (w/w)	0.3	0.23	0.15	0.14	4647	9990
2% (w/w)	0.4	0.44	0.30	0.52	1354	4688
8% (w/w)	0.31	2.21	0.44	0.03	1249	1752
Week 8						
0% (w/w)	0.13	223.0	0.73	0.3	23	BDL
2% (w/w)	0.27	0.14	0.35	0.45	67.41	BDL
8% (w/w)	0.4	0.23	0.41	0.24	237	BDL
Day1		**Gibson soil**				
0% (w/w)	6.21	0.29	1.07	102.4	648	1071
2% (w/w)	15.4	13.0	0.18	147.2	998	7934
8% (w/w)	180.00	193.10	0.43	840.4	985	5165
Week 8						
0% (w/w)	107.90	26.00	0.29	0.41	15.66	6.86
2% (w/w)	81.05	40.82	0.76	0.32	14.21	2.61
8% (w/w)	491.70	651.20	1.02	4.07	983.0	0.14
Day1		**Knowle Road soil**				
0% (w/w)	0.28	0.26	0.43	0.29	295	9999
2% (w/w)	0.5	0.4	0.12	0.13	999	778.6
8% (w/w)	0.4	1.55	1.49	0.27	236	18.54
Week 8						
0% (w/w)	968.00	163.70	2.12	17.58	43.5	BDL
2% (w/w)	14.81	23	0.57	45.48	32	BDL
8% (w/w)	24.50	31	0.61	23.16	1.98	BDL

For **Ni**, the Tc values at day (1) in Coney Green and Knowle Road soils with and with no oil were very low, which indicated a rapid supply from the solid phase into soils or could be released from crude oil into soil solution to ensure that the Ni species in solutions were well buffered, and more amounts of Ni species can be captured by the DGT sampler. At week (8), the Tc for Coney Green and Knowle Road soils with no oil were higher than 2% and 8% w/w oil-amended soils **Table 5.6**. For

Gibson soils, the T_C values gradually increased with increasing crude oil contamination at day (1) and week (8) incubation period, indicating a decrease in the resupply of Ni species from solid phase to soil solutions with incubation time and increasing crude oil concentrations, in which case the soil solutions become gradually depleted as Ni mass continuously taken up by the DGT sampler with aging **Figure 5.3-(B)** and **Table 5.5** (Harper et al., 1998; Lehto et al., 2006). The raise in T_C values in Gibson soil with increasing of crude oil amendments at day (1) and week (8) suggested that Ni species sorption degree from the solid phase decrease with incubation time, which was consistent with decrease in (R) values of Ni (**Table 5.3)** and C_{DGT}-labile Ni species **Figure 5.3-(B)**.

For **Zn**, it can be noted that T_C values in three soils with and with no oil were very low, which indicated that a rapid resupply from the solid phase to soil solution within the deployment time may be due to high content in soils and oil.

For **Cd** and **Pb**, the T_C values in Coney Green soil at day (1) with and with no oil decreased with increasing crude oil contamination, which represent a slower resupply of both metals from the solid phase to solutions. This implies that the dissociation of both metals from solid phase is limited kinetically due to the low content of metals in soil, which was consistent with low C_{DGT}-labile species of Cd and Pb species in soil solutions **Figures 5.2 (E** and **F)** and **Figure 5.3 (E** and **F)**. However the results for both metals were inconsistent with determined (R) ratios in **Tables 5.3-5.5**, this is likely to have resulted from a competition between organic ligands for sorption or complexation sites on solid phase and soil solutions (Yang et al., 2013). At week (8), the Tc values of Cd exhibited a gradual increase with increasing oil treatment; probably oil ligands induced a reduction of resupply from the solid phase to soil solution within the incubation time. However, the T_C values of Pb in the same soil were not determined because Pb concentrations in soils solutions and $CaCl_2$ extract were at below the detection limit (BDL) **Figures 5.3** and **5.4**. This is possibly due to Pb species tightly bound to solid phase and not available in the labile pool or attributed to the low Pb content in the soil (Harper et al., 1998).

For Gibson soil, at day (1), the Tc values for both metals were higher in treated soils with oil, which suggested faster resupply of both metals from solid phase in unamended soil. At week (8), it appears that the kinetics of dissociation of both metals from solid phase to solutions is fast, except of Cd, which exhibited a stronger kinetics limitation at 8% oil-amended soil. This my imply that the oil ligands can form chelates with Cd species tightly bound to solid phase, which is consistent with decrease in (R) ratios of Cd labile species in **Table 5.4** (Lin et al., 2015). The Tc values of Cd in Knowle Road soil with oil at day (1) were higher than those at week (8), probably due to the form of fast dissociating complexes with oil ligands during incubation time (Lehto et al., 2006; Degryse et al., 2009). For Pb, at day (1) there was a significant decrease in Tc values with increasing oil amendment overall ($p<0.05$), Tc decreases from 3 hours to 18.54s and not detected at week (8) incubation time **Table 5.6**. This is because K_d values of Pb could not be estimated due to the concentrations of Pb species in soil solutions and $CaCl_2$ extracts were below detection limits. This is maybe Pb species were tightly bound to solid phase with incubation time and increasing oil ligands, thus unavailable for release to the soil solution and extractants calcium chloride ($CaCl_2$), which is significantly reduce Pb lability and mobility in the soil solution (Sauvé et al., 1998).

5.3.7. Dissociation rate (K_{-1})

The dissociation rates k_{-1} in **Figure 5.6** were calculated from Tc, Pc, and K_d using **equation (5.6)**. The obtained values of k_{-1} have been showed for three selected soils Coney Green, Gibson and Knowle Road soils at day (1) and week (8) amended by varying ratios of crude oil; (0, 2, 8 %w/w). In general, the highest values of T_C produce minimum values of k_{-1}. The dissociation rate K_{-1} represents the inverse of Tc, therefore embraces the capacity of the labile trace metals on the solid phase to dissociate and release into soil solution (Zhang et al., 2006). For three soils K_{-1} values were substantially variables with crude oil treatment.

Cobalt (Co). For Co, in Coney Green and Knowle Road soils, K_{-1} values with increasing crude oil treatments exhibited similar trends at day (1) and week (8). The values were increased at 2% w/w crude oil treatment then decreased with increasing crude oil treatments. For Gibson soils, the K_{-1} decreased gradually with increasing crude oil amendment and incubation time. The pattern of k_{-1} values for three soils with and with no oil at day (1) and week (8) showed no significant differences and ranged between (1.8×10^{-3} s^{-1} and 2.3 s^{-1}). This indicates that the slight differences in obtained Tc values above are may be as a result of the increased concentration of Co species supplied by crude oil amendments rather than kinetic effects. The trend changes with crude oil amendments in three soils at day (1) and week (8) incubation, which could be an evident for the influence of crude oil contamination on the Kinetics of Co exchange.

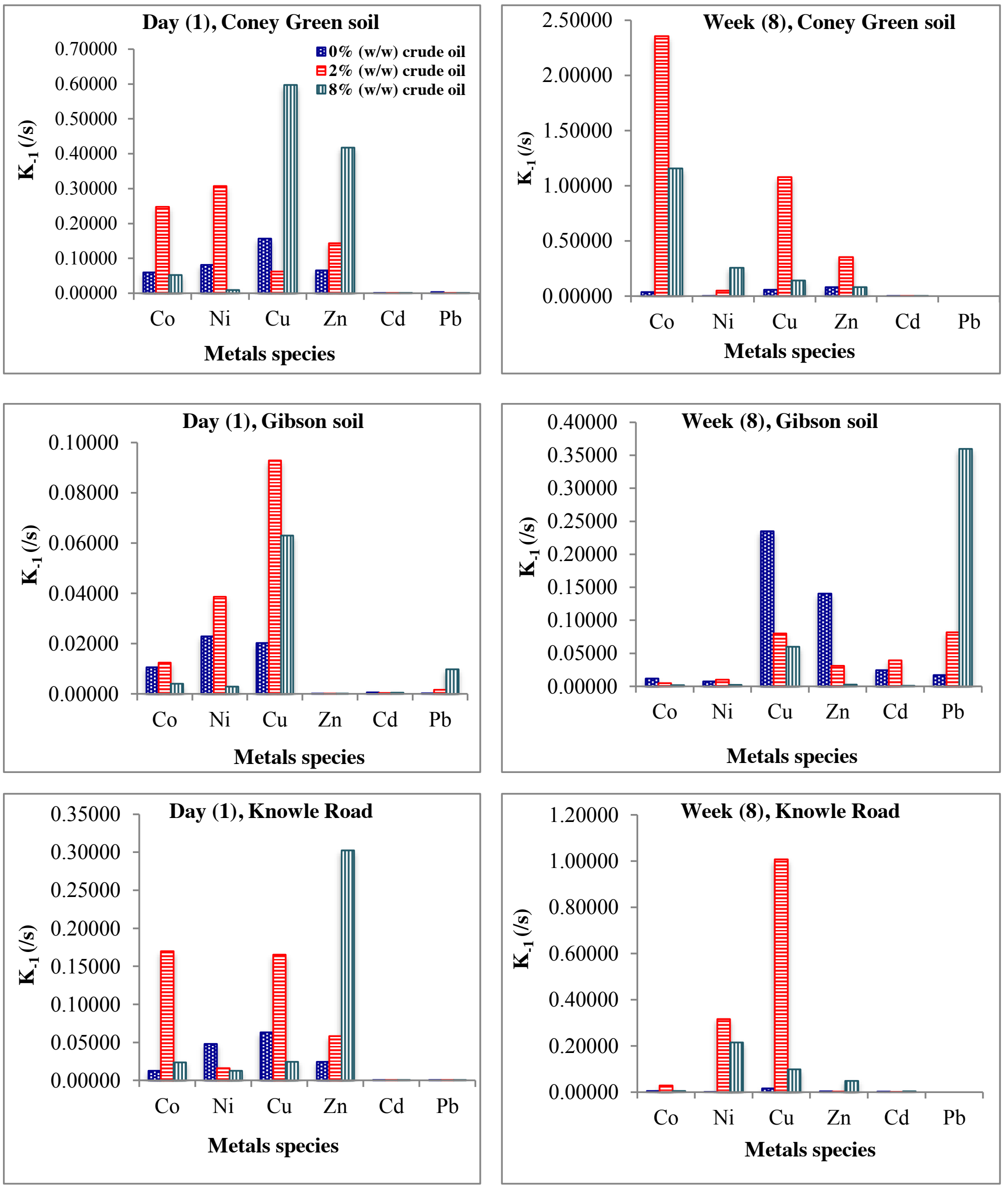


Figure 5.6. Dissociation rate, K_{-1} estimated for Co, Ni, Cu, Zn, Cd and Pb using DIFS at day (1) and week (8) of three studied soils impacted with different concentrations of crude oil, (0, 2, 8 % w/w).

Nickel (Ni). For Ni, the estimated K_{-1} values show an inverse relationship when compared to the Tc values in the **Table 5.6**. For Cony Green soil, during incubation time, the slow decrease in Ni species desorption rate (k_{-1}) from solid to solution phase in soil with no oil from (8.15×10^{-2} s^{-1} to 1.13×10^{-4} s^{-1}) was consistent with decrease in Ni C_{DGT} and water-soluble Ni, **Figure 5.2** and **Figure 5.3**, indicating that labile Ni was changed to non-labile. The K_{-1} values for 8% v/w oil amended–soil were increased from 9.7×10^{-3} s^{-1} at day (1) to 0.26 s^{-1} at week (8), which was consistent with the increase of C_{DGT}-labile Ni species in soils 8% v/w oil-amended soil during aging. The K_{-1} values for 2% v/w oil-amended soil showed a general decrease as shown in **Figure 5.6**, but inconsistent with the increase of C_{DGT}-labile factions of Ni and the increase of Ni total dissolved concentrations in soil solutions. This suggests that the increase of Ni C_{DGT} labile species at 2% w/w oil treatment as described above are may be attributed to the increase of spiked Ni concentration or Ni release from oil rather than kinetic effects (Lehto et al., 2006; Zhang et al., 2006).

For Gibson soil, at day (1) and week (8) there was a slight decrease in K_{-1} values for soil with and with no oil with incubation time and inversely related to Tc values in **Table 5.6**, which is consistent with decrease of Ni labile species in C_{DGT} and in soils solution.

For Knowle Road soil, the K_{-1} values of Ni at day (1) were gradually decreased with increasing crude oil contamination from (0.048 s^{-1} to 0.012 s^{-1}). At week (8), the K_{-1} values were increased at 2% w/w oil treatment from (1.3×10^{-3} s^{-1} to 0.3 s^{-1}) then decreased slightly to 0.2 s^{-1}. This is consistent with the measured concentrations of Ni in C_{DGT} and soil solutions.

Copper (Cu). The K_{-1} values of Cu for three soils with and with no oil exhibited substantial variations at day (1) and week (8) as shown in **Figure 5.6**. It is likely that the differences to Tc values following treatment again because of the increased concentration of Cu or oil ligands instead of kinetic influences. This is also consistent with obtained concentrations of Cu in C_{DGT} and soils solutions.

Zinc (Zn). The K_{-1} values of Zn for Coney Green soil at day (1) were increased gradually with increasing crude oil. At week (8) the values of K_{-1} were increased at 2% w/w oil treatment from (0.07 s^{-1} to 0.352 s^{-1}) then decreased to 0.08 s^{-1} with increasing of oil treatment. These values are inconsistent with the decreases of Zn labile species in C_{DGT} probably due to the competition between organic ligands in soils with those from oil amendments rather than kinetic influences.

For Gibson soil at the K_{-1} values day (1) very low and decreased gradually from 4.7 x 10^{-5} s^{-1} to 8.0 x 10^{-6} s^{-1}. At week (8) the K_{-1} values are larger than those in day (1) and decreased from (0.14 s^{-1} to 2.5 x 10^{-3} s^{-1}). The K_{-1} values at week (8) inconsistent with increases of Zn concentrations in DGT and in soil solutions with increasing crude oil amendment, probably due to the release of Zn species from crude oil or sorbed to the weakly sites in soils. For Knowle Road soil, the K_{-1} values were increased gradually with increasing oil amendment and incubation time at day (1) and week (8), which is consistent with decreases of Zn concentrations in DGT and soils solutions. The K_{-1} values of three soils with and with no oil amendment were inversely related to Tc values. The reductions in availability of added Zn with incubation time probably attributed to the conversion of Zn species into more stable FeOx–Zn or Zn-ligands (Ma and Uren, 2006).

Cadmium (Cd). The K_{-1} values at day (1) and week (8) for three soils with and with no oil treatment were very low, ranged from 1.07 x 10^{-6} s^{-1} to 3.9 x 10^{-2} s^{-1}. These results were constent with the measured cocmntrations of Cd in DGT and soil solutions. The values showed inverese relatioship with T_C values in three soils.

Lead (Pb). For Coney Green and Knowle Road soils with and with no oil, the K_{-1} values of Pb at day (1) were very low, 1.58 x 10^{-5} s^{-1} to 3.2 x 10^{-3} s^{-1}. At week (8) the

K_{-1} values were not determined because K_d values were below dection limit (BDL) as discussed above in **section 5.3.5**.

For Gibson soils, the K_{-1} values of Pb at day (1) and week (8) were gradually increased with increasing crude oil treatment. During incubation time, the K_{-1} values consistent with decrease in Pb C_{DGT} and water-soluble Pb, indicating that labile Pb was changed to more stable Pb-ligands and not labile.

From above it can be obsereved that the trend changes for K_{-1} values of studied metals in three selected soils were influenced by crude oil amendemnets and aging time. It is expected that because the duration of the experiment is only (8) weeks, there was insufficient time for treatments to significantly influence kinetic parameters.

From the above discussion, a comparison of two different rates (2% and 8%) v/w of applied crude oil often showed no significant changes for Coney Green and Knowle Road soils on the concentration of Cd and Pb in soil solutions and DGT. Thus, it is necessary to mention that the applied concentrations (1% and 2% v/w) were insufficient in some cases for such enormously contaminated soils, where intensive competition and strong ligand formation during sorption of studied metals was recorded.

5.4. Conclusion

The present work showed the effect of crude oil and aging on the trace metals availability in soils of different properties. Both factors were found to significantly influence the measured metal concentrations of DGT-labile, extractable by $CaCl_2$ and soil solutions. It can be indicated that the measurement of studied metals species by DGT applied to soil solution for a described time corresponds to a small species of the total metal. In this study low proportion of the total Cd and Pb present in the soil solutions of the three studies soils with and without oil. Increases of crude oil treatments in soils promoted the formation of non-labile species of Cu and Pb and limited the availability of both metals. The time scales of the kinetic exchanges obtained from DGT measurements and DIFS modelling was reflected by the range of determined Tc values: from seconds to 3 hours. The study showed that Co, Cu, Ni and Zn are supplied rapidly from the solid phase to soil solutions that the DGT measurements do not affected by supply kinetics. The distribution coefficients (K_d), is an index studied metal's potential mobility. The greater the K_d values of metal mean the stronger of its sorption onto the soil surfaces, and therefore the lower its solubility in soil solution. The gradual decrease of Cu K_d values in three studied soils with and without oil application during incubation time may be attributed to the strongest tendency of Cu to be associated with the solid phase with increasing incubation time. The K_d values of Ni were decreased with increasing of crude oil amendments in three soils may be due to the release of Ni species from solid phase and crude oil to soil solution.

The dissociation rate constant (k_{-1}) from the solid phase, which indicated dynamic process in soils, decreased with aging time. The trend changes for k_{-1} values of studied metals in three selected soils were influenced by crude oil amendemnets and aging time. The work has demonstrated that DGT technique is robust and reliable tool that can be used to assess the effect of crude oil ligands on the concentrations of available trace metals species in soils. Furthermore, two different applied ratios (2% and 8% v/w) often had no significance effect on Cd and Pb labile metals concentrations in studied soils. Therefore, it is necessary to point out that future work need to be conducted on crude oil contaminated soils using higher concentrations and different type of crude oil to assess the effect of oil ligands on metals speciation in soils.

Chapter 6 – Assessing Water Quality and soil quality in Oman Using Developed Dynamic Speciation Technique DGT

6.1. Introduction

The present study represents an important part of research in this thesis in regard to applying the DGT technique to the contamination of metals and crude oil in the aquatic environment of Oman. There has been a rapid increase recently in the economic activities along the coast of the Sea of Oman. Industries and oil refineries around the commercial ports have great impact on marine systems and groundwaters because of the discharge of chemical contaminants into the surrounding area. Some research has been conducted to assess the level of trace metals and their impact on the marine systems around Al Fahal and Sohar ports (Al-Shuely et al., 2009; Al-Husaini et al., 2014)**.** These studies indicated that the trace metals of considerable concern were Cu, Zn, Cd, Pb, Cr and V, due to their increased levels in seawaters around industrial regions, oil spills during shipping, terminal transfers, or discharge point of refineries (Al-Shuely et al., 2009; Baawain, 2011; Al-Husaini et al., 2014). However, no study has been done to measure the speciation of metals and to assess the effect crude oil ligands on the availability of metals in marine systems and surrounding areas. Moreover, so far very little data on trace metals concentrations and speciation have been published for the Sohar Industrial Region (SIR) and Al Fahal port in the Sultanate of Oman. Bazzi (2014) measured the total concentrations of heavy metals Cu, Zn, Pb, Cd, Cr, Ni, fe and Mn in coastal waters along the Oman Sea and they were ranged between 3.37 to 5.74, 18.01 to 22.62, 4.24 to 4.52, 0.15 to 0.19, 20.16 to 21.46, 16.42 to 17.14, 15.43 to 24.76 μg/L and 7.06 to 8.67 μg/L, respectively. The highest values of heavy metals were observed during summer and the lowest during winter due to high levels of industrial and domestic discharges (Bazzi, 2014). Study by Al-Rashdi and Sulaiman (2013) assessed the presence of heavy metals Fe, Al, Ni, Zn, Cr, Co, Cu, Pb in farm soils and alfalfa around Sohar Industrial Region, (SIR). The heavy metals content in the soils were high but within the permissible limits of the USEPA standards (Al-Rashdi and Sulaiman, 2013). Al-Shuely et al. (2009) investigated environmental status of coastal sediments, with respect to heavy metals content around (SIR). The study found that Cr, Ni and Mn were high at some sites.

Therefore, it is important to introduce the dynamic speciation technique as a new robust tool for the assessment of labile metals in Sohar and Rusail industrial regions, and Al Fahal port, to understand and to prevent metal contaminations in that area. Firstly, because most regions in Sultanate of Oman heavily upon the groundwaters and seawater as a source of irrigation and fresh water through desalination (de Mora et al., 2004). Furthermore, to determine the contribution of oil refineries and industrial areas to the trace metals loads in marine and groundwaters. Moreover, the simultaneous determination of labile concentrations of arsenic (As), molybdate (Mo), antimonite (Sb), vanadate (V), selenium (Se), and tungstate (W) in these areas, also need to be determined to assess the contribution of oil contamination on oxyanions trace metals availability in dominant anthropogenic activities, and alterations in the organic and inorganic ligands concentrations.

The determination of trace metal concentrations and chemical form (speciation) is challenging in the Sea of Oman around Sohar Industrial Region (SIR) and Al Fahal port due to their complex chemistry, oil ligands matrix, high salinity, and frequent occurrence at low concentrations. According to data obtained by Al-Shuely et al. (2009) using HNO_3 acid extraction, to investigate the environmental status of coastal sediments, with respect to heavy metals content around (SIR), can appear the high total content of As, Ni, Mn and Cr attributed to industrial effluents from (SIR) (Al-Shuely et al., 2009). However, there is no information about the background concentrations of trace metals fractionation in the Sea of Oman; in particular, no published data for the economic ports.

The concentration of metals species in natural waters is influenced by dynamic interchanges rather than existing in a regular equilibrium situation. Therefore, collecting a volume of water samples will not represent the real situation as it affect the balanced physical and chemical processes that govern the distribution of trace metals (Gimpel et al., 2003). For *in situ* measurements, without transferring water samples to the laboratory, a reliable and robust technique is highly sought after. Few techniques are available that can be applied easily in the field apart from DGT.

The DGT is a simple, reliable, and robust dynamic technique that can be deployed in situ in groundwater, seawater, rivers, sediments and soils (Zhang and Davison, 1995; Zhang and Davison, 2000).

The aim of this study is to apply DGT technique in Oman environments and to assess the water quality and the soil quality in selected areas. Measure the labile concentrations of Cu, Ni, Co, Zn, Pb, Cd, Al, Fe, Mn, Cr, As, Sb, Se, W, Mo and V by deploying DGT with Chelex as binding layer and DGT with ferrihydrite as binding layer. Simultaneous deploy DGT with different membranes, OP-DGT, (1000 MWCO)-DGT, (Nafion112)-DGT for further speciation measurements. It is crucial to obtain more complete speciation information and to understand fully the geochemical cycling and bioavailability of trace metals in the Sea of Oman. The DBLs thicknesses were determined in seawater locations and in groundwaters (6 wells) by deploying DGT devices containing four varying hydrogel thicknesses.

Deploy DGT in soils near SIR, and in sediments in Al Fahal port near the discharge point to assess the available metal concentrations and their resupply from soild phase to solution. The DIFS model was used for soils to estimate Tc (response time) and k_{-1} (dissociation rate). The information provided in the study will contribute to generating frameworks, standards, and regulations that will assist in the development of criteria for protecting the Omani environment.

6.2. Experimental and Field Deployments

6.2.1. Description of the study area

Two economic ports: Al Fahal port and the Rusayl Industrial Estate located in the Muscat region, and SIR and Sohar ports in the Al Batinah in the Sultanate of Oman, were chosen for this study. They occupy an important location on the Coast of the Sea of Oman. Al Fahal port is located in the Muscat region at about 23°39′N., 58°32′E., and Sohar port in Al Batinah region is sited at about 24°23′N., 56° 45′E (L.L.C., 2010; NATIONAL GEOSPATIAL-INTELLIGENCE AGENCY Springfield, 2014). Mina Al Fahal is a significant harbour located in Muscat. It comprises three Single Buoy Mooring (SBM) Systems named SBM1, SBM2, and SBM3, which are located at separate sites throughout the harbour, see **Figure 6.1** (Badawy et al., 1992; Al-Husaini et al., 2014).

The industrial and port areas were selected for their crude oil activities. Moreover, as Muscat port (Mina Qaboos) is to be converted into a tourism area, all shipping activities were transferred by the end of August 2014 to Sohar port, which led to an increase in trade and anthropogenic activities in the Sohar Industrial Region (SIR) (Potter, 2014). Approximately 90% of the Sohar port catchment is industrialised, and developments include refineries, petrochemical industries, heavy industries, iron and aluminum works, commercial and marine shipping facilities (Costenla, 2014).

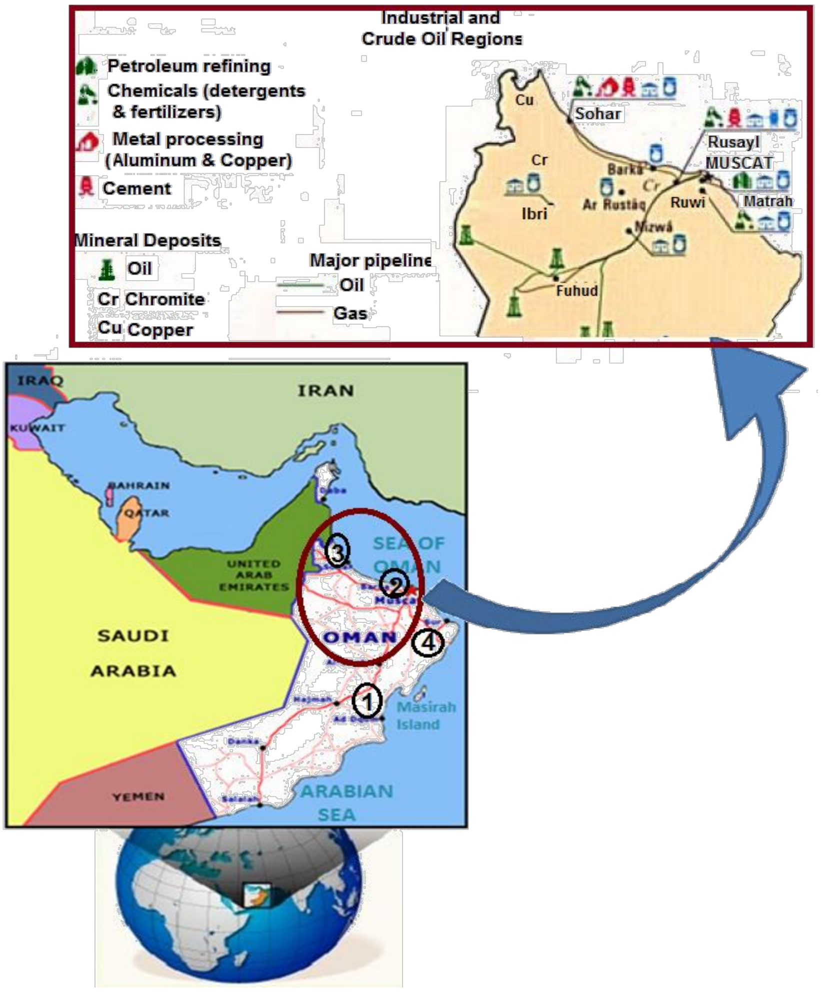


Figure 6.1. Schematic map showing locations of sampling areas in economic regions in Muscat and Sohar in the Sultanate of Oman (Baawain, 2011; S. A. Al Maashri 2011).

Moreover, most of the world's heavily trafficked tanker routes surround this port, which contributes to the trace metals contamination in marine waters through exporting and importing crude oil activities. The seawater is completely distributed by huge waves, especially in the summer session. This condition could result in the redistribution of crude oil constituents, including inorganic and organic species through water-soluble fraction (WSF) in the coastal environment. As a result, the elevated inorganic and organic discharges will put strong pressure on marine waters and coastal areas. Thus, it is necessary to ascertain to what extent those inputs can impact the water quality around the economic ports. The sampling areas included seawaters, groundwaters, soils, and sediments at both areas. The sampling site for wells is at 300-500 meters from each port area and indusrial region. A number of sediments and coastal soils were collected to evaluate the effect of anthropogenic sources on the environment quality around the economic ports.

6.2.2. Chemicals and Materials

All types of DGT devices (OP-DGT, (1000 MWCO)-DGT, (Nafion112)-DGT and FH-DGT), containing varying diffusive gel thicknesses (0.014 (filter membrane), 0.039 cm, 0.08 cm, 0.196 cm) were prepared as described in **Chapters 3** and **4**. Chemicals and materials needed for field work also include Milli-Q water (high purity water, Milli-Q water system, provided by SQU, Sultanate of Oman), HNO_3 (BDH ARISTAR® ULTRA, high purity acid for quantitative trace metals analysis), fish cage for protecting DGT devices in seawater, clean cool box with ice to protect samples and DGT devices, acid washed syringes, cellulose nitrate filters (0.45 μm porosity), acid washed 1 L bottles for collecting water samples and cylinder measurement. A thermometer, a pH and conductivity meter, were provided by the Food and Water Laboratories Center (FWLC) in Muscat, Sultanate of Oman. All bottles, DGT samplers, filters, filtration devices and containers for trace metal analysis were carefully acid washed in 10% (v/v) HNO_3 (ARISTAR grade, Merck) for 24 hours and rinsed thoroughly with Milli.Q water before use, and were protected during transport with clean polyethylene plastic bags. All handling was performed with plastic gloves.

6.2.3. Field deployments and sample collections

The DGT devices were deployed in December 2014 and January 2015 in sites located in Muscat (Al Fahal port and Rusayl Industrial Estate) and Sohar (SIR and Kadafan).

6.2.3.1. Deployment in seawater

The DGT deployments were carried out at Al Fahal port in Muscat and Sohar port (SIR). Four types of DGT samplers (OP-DGT, (1000 MWCO)-DGT, (Nafion112)-DGT and FH-DGT) were deployed in triplicates at two locations 300 meters from each other at each site. Twelve DGT samplers containing varying hydrogel thicknesses (0.014 cm (only filter membrane), 0.039 cm, 0.08 cm, 0.196 cm) for estimating DBL thicknesses were deployed at both sites at each location. The DGT devices were deployed for 5 days at ≈ 1–1.5 m beneath the seawater surface by being fastened to the outside of large fish net cages **Figure 6.2**.

The DGT units were fastened using a clean fishing rope attached inside the cage, and had a weight of 30 kg at the end of the rope attached below the cage. Floats and a 5 kg floating buoy on the surface were used for flagging, also a light was fastened to it. The parameters including pH, conductivity, temperature, and salinity were measured daily at all locations in Muscat and Sohar using a conductivity/pH meter, thermometer, and thermosalinometer.

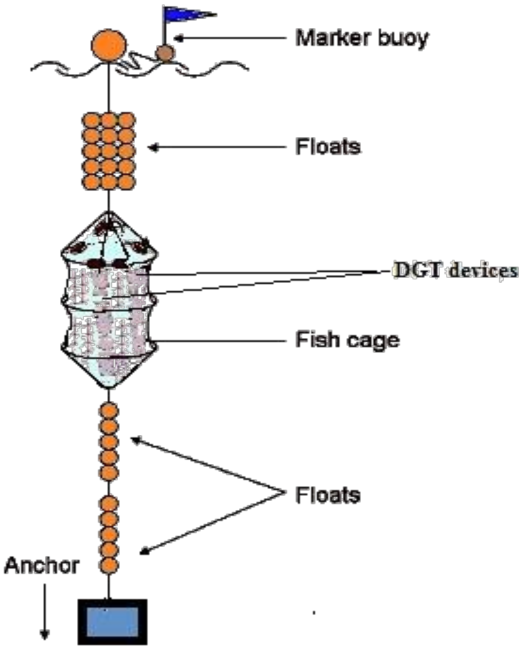


Figure 6.2. Modified figure, the DGT set-up and anchoring in fish cage for seawater deployment (Harman et al., 2010)

The seawater samples were collected daily by immersing a capped 1 L bottles about 20 cm under the seawater surface using PVC talc free gloves. The bottles were opened beneath the water's surface and allowed to fill with seawater then re-capped properly before being removed from under the water (Musselman, 2012). The grab samples then passed through a syringe filtration apparatus (0.45 µm) and were immediately acidified using HNO_3 (BDH ARISTAR® ULTRA). Unfiltered samples for total metals measurements were also acidified. All collected samples were protected in clean plastic bags and stored inside a cool box in the dark with ice at < 4 °C, then kept in the fridge for the analysis stage (Panther et al., 2012). After the allocated deployment time, the DGT devices were removed and washed with Milli.Q water and stored individually in labeled, clean plastic bags, and protected in a big clean plastic bag in a cool box in ice at < 4°C, and then transferred to the fridge and kept until further laboratory treatments.

6.2.3.2. Deployment in groundwaters

The assessment of groundwaters quality in the present work was carried out by selecting six open wells near industrial areas and economic ports, three open wells at each site, representing localities around the industrial areas in Muscat and Sohar regions. The wells were located at 300 – 500 meters from industrial areas and about 150 meters from each other. The investigation was achieved by deploying in triplicates the same set of the above DGT devices at each open well water. The DBL thicknesses at each well water were determined using DGT devices containing different thicknesses of diffusion layer following procedures in Warnken et al. (2006). The DGT devices were fastened by fishing rope (Polypropylene rope) and attached to a float and weight, and deployed 50 cm below the water surface for 5 days. A rope was used to attach a weight to a clean acid washed 1 L bottle (**Figure 6.3**). The bottle was carefully uncapped to avoid the entry of dust or any contamination. The weighted bottle was lowered into the well and immersed under the water surface without touching the bottom or sides of the well, or moving the sediment (Bartram and Ballance, 1996).

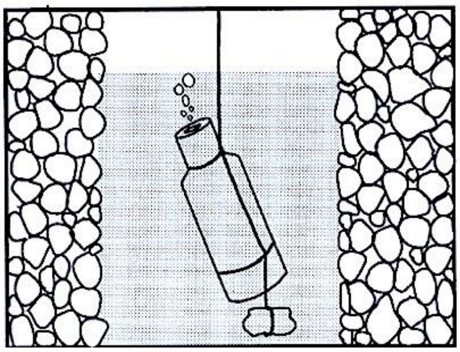


Figure 6.3. Collecting well water samples by lowering a weighted bottle into an open well (Bartram and Ballance, 1996)

Temperature, salinity, conductivity (EC), and pH parameters for each open well were measured daily during DGT deployments for each site. Unfiltered well waters for total metals measurements and 0.45 µm filtered grab water samples were collected daily in an acid cleaned 1 L bottles during DGTs deployments. The grab samples were immediately acidified to 2% HNO_3 after passing through an acid washed syringe filtration apparatus as described above. The blank values of metals at each deployment location was obtained by analysing the Chelex-100 resin gel in 4 or 5 blank DGT devices (not deployed in water samples), which are prepared in the same way.

Samples analysis. After returning to the laboratory, the DGT devices were opened, and all binding layers carefully removed using clean tweezers. They were then transferred to the clean 1.5 centrifuge tubes and 1 ml of 1 M HNO_3 was added to each tube for elution and left for 24 hours prior to ICP-MS analysis. For the ICP-MS analysis, an aliquot of 0.1 ml was taken from each tube and diluted 10 times. The groundwater~~s~~ samples were diluted 10 times; however, seawaters samples were diluted 50 times for IC-PMS analysis to minimise the effect of chloride and Na suppress in the seawater due to high ionic strength, as referenced in **Chapters 3** and **4**.

6.2.3.3. Collection of sediments and DGT deployments.

Marine sediments from nine locations at two sites were collected around discharge points of the Mina Al Fahal oil refinery. Surface water was collected from the same locations. The collected samples were kept at about < 4°C and transported immediately to the laboratory for deployment. All sediments were homogenised and distributed carefully into nine clean containers to obtain a 2-2.5 cm layers of subsamples. The collected surface water samples were poured carefully on to all sediments in containers to make a 5 cm overlying layer of seawater. The sediments were left for 4 days to equilibrate at 23±0.25°C in the laboratory. The overlying seawater in all selected sediments in containers was slowly and carefully removed to preserve the natural state of the sediment water interface (SWI) as much as feasible (Gao et al., 2012). Two versions of DGT devices (OP-DGT and FH-DGT) were immersed 1 cm deep into prepared sediments (Roulier et al., 2010; Gao et al., 2012). The DGT units were deployed for 5 days, and the average temperature measured was 21±0.5°C. After 5 days, the DGT devices were removed from the sediments and washed using Milli.Q water to remove sediment particles. After the devices being opened, the Chelex-100 gel and the ferrihydrite gel were transferred to 1.5 centrifuge tubes and eluted with a 1 ml of 1M HNO_3 solution for 24 hours. The pore waters were extracted by centrifuging sediments at 3000 rpm for 15 minutes, then 1 ml for each sediment passed through a Acrodisc 0.45 µm, syringe filter (Whatman), and acidified with 10 µL of 7 M HNO_3 (Nitric Acid, BDH ARISTAR® ULTRA) (Gao et al., 2012).

6.2.3.4. Collection of soils and DGT deployment.

The contribution of an oil refinery and industrial region in Sohar on trace metals loads was studied in coastal soils near (SIR). Fifteen soils were collected in January 2015 from two sites around SIR to assess the environmental status of its coastal soils with respect to trace metals fractionation south and north of SIR, as shown in **Figure 6.4**. Two versions of DGT samples, OP-DGT and FH-DGT, were used as described above in the experimental section. Sandy coastal soils were collected from fifteen locations about 400 meters the distances between each other, from the top of 40 cm of each location around Sohar port and industrial area, and brought to the laboratory. They were air dried and sieved to 2-mm, and stored in plastic containers before use. The soils' maximum water holding capacity (MWHC) was determined in the laboratory, as described in **Chapter 5**.

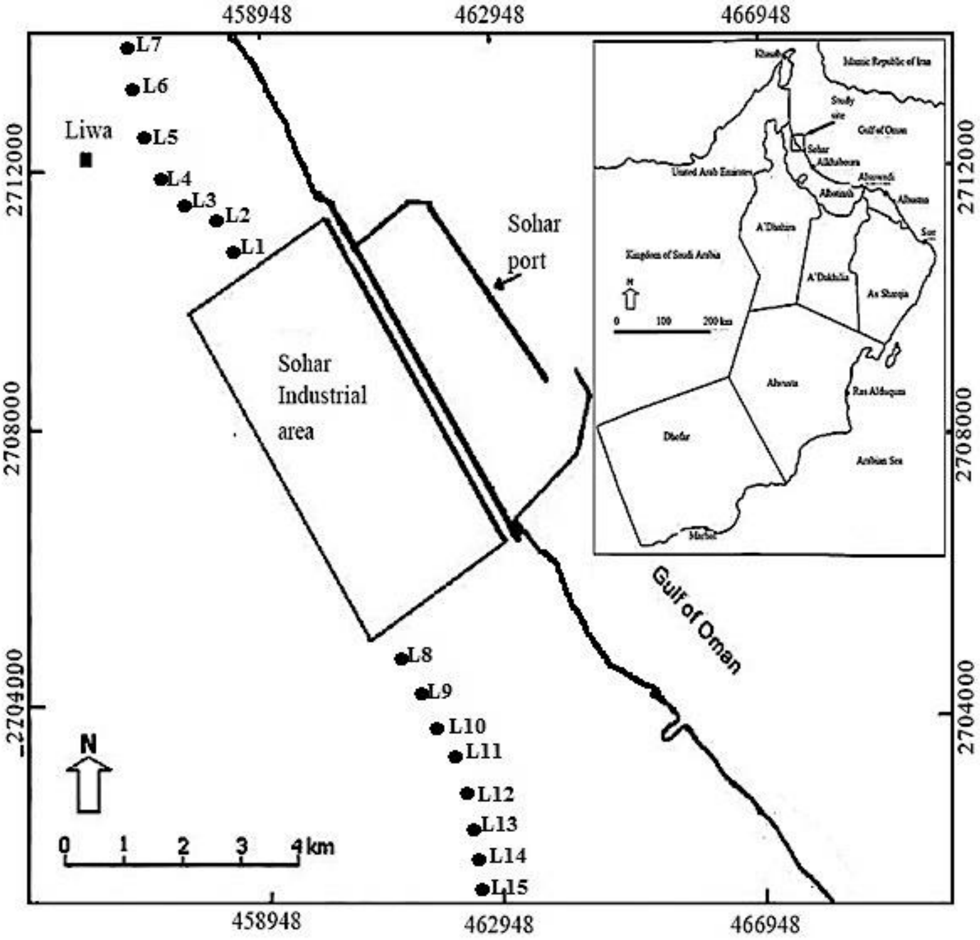


Figure 6.4. Modified map of soils sampling locations in (SIR) (Al-Shuely et al., 2009).

Soil samples were prepared for DGT deployments using 200 g of each soil sample and appropriate amounts of Milli.Q waters were added to bring samples soils to 40%-60% (MWHC); They were left for 1 day before further water added to reach about 80% of MWHC. The soils were equilibrated for further 24 hours before DGT deployment. The temperature was maintained at 22±2°C, and two OP-DGT and FH-DGT versions were deployed for 16 hours (Zhang et al., 1998; Liang et al., 2014). The

DGT devices were removed from soils and washed by rinsing with Milli.Q water and eluted as described above. All samples were diluted 10 times for ICP-MS analysis.

6.3.3.5. Properties of soils

Organic carbon content (%OC)

Traditional method of loss on ignition (LOI) was performed to obtain the organic carbon content. 10 g of dried soil sample was placed in a clean porcelain crucible and baked at 450 ºC for 16 hours in a furnace. Then the sample was re-weighed immediately after cool down to room temperature. The percentage of organic matter was calculated using the following **equation (6.1)**:

$$\%\mathrm{OC} = \frac{loss\ in\ weight}{intial\ weight} \times 100 \qquad (6.1)$$

Soil pH

The pH of all soils was measured in a suspension of soil and calcium chloride ($CaCl_2$) solution, as described in **Chapter 5**. Solution mixture of 25 ml Milli.Q water and 2 ml of 0.125 M $CaCl_2$ was added to 10 g of dried soil in a 50 ml polyethylene beaker. They were mixed and stirred vigorously using a glass rod and left for 30 minutes to stand. The pH of the solution was determined by pH meter, taking care to avoid contacting the electrode with the settled soil particles.

Total metals content

All collected soil samples were acid digested by pressurised microwave for metals extraction in soils. The soil digestion was followed by procedure in SW846-3051 method (CEM, 1991). Approximately 0.5 g of each soil sample was weighted into acid washed Teflon microwave vessels followed by adding 10 ml 69%

concentrated nitric acid (HNO_3). Two acid blanks of the same matrix were also included in the experiment. The containers were sealed and placed in the microwave for heating for 10 minutes. They were then carefully removed from the microwave and left to stand for 2 hours. The digestion vessels were opened, and diluted five times by solubilizing 2 ml of the digests in 10 ml of Milli.Q water, and then filtered with 0.45µm qualitative cellulose filters. The filtrates were diluted 10 times for ICP-MS analysis.

6.3.3.6. Calculation of kinetic parameters using DIFS

The metal concentrations in soil solution were measured after DGT deployments to estimate the ratio of C_{DGT} to C_{soln} using the following **equation (6.2)**:

$$R = \frac{C_{DGT}}{C_{soln}} \tag{6.2}$$

Kinetic parameters, response time (Tc) and rate constant of dissociation (k_{-1}), as mentioned in **Chapter 5,** were estimated from measurements of (R) values and K_d using DIFS model.

6.4. Results and Discussion

6.4.1. Metal concentrations and speciation in seawater

Water samples from studied locations (seawaters and groundwaters) were collected daily at the DGT deployment sites and the salinity, pH, conductivity, and temperature were measured and presented in **Table 6.1**.

Table 6.1. Parameters for ten sampling locations in Muscat and Sohar regions.

Parameters	Muscat					Sohar				
Site	**Seawater-L1**	**Seawater-L2**	**Well-1**	**Well-2**	**Well-3**	**Seawater-L1**	**Seawater-L2**	**Well-1**	**Well-2**	**Well-3**
Salinity	36.7	36.4	4.5	5	1.8	36.6	36.68	10.5	17	10
Conductivity (μS/cm)	50000	49500	8150	8879	3310	51000	49700	18500	28350	18355
Temperature (C)	23	22	28	26	27	23	24	29	27	30
pH	8.2	8.3	6.52	7.3	6.8	8.083	8.1	7.8	7.3	6.7

6.4.1.1. Measurements of DBL

The DGT devices containing varying thicknesses of diffusive gel (0.014 cm (only filter membrane), 0.039 cm, 0.08 cm, 0.196 cm) were deployed in triplicates for five days in two locations in seawater in Al Fahal port and (SIR) to determine the thicknesses of the diffusive boundary layer (DBL, δ) using **equation (6.3)** (Warnken et al., 2006).

$$\delta = \frac{I}{S}\left(\frac{D_w}{D_{gel}}\right) \tag{6.3}$$

The plots of inversed mass accumulated by DGT devices 1/mass (ng^{-1}) versus Δg (cm) of metals Cd, Cu, Ni and Co showed a good linearity of regressions with R^2 values ranging between 0.9940 – 0.9987 despite low mass accumulated (**Figure 6.5**).

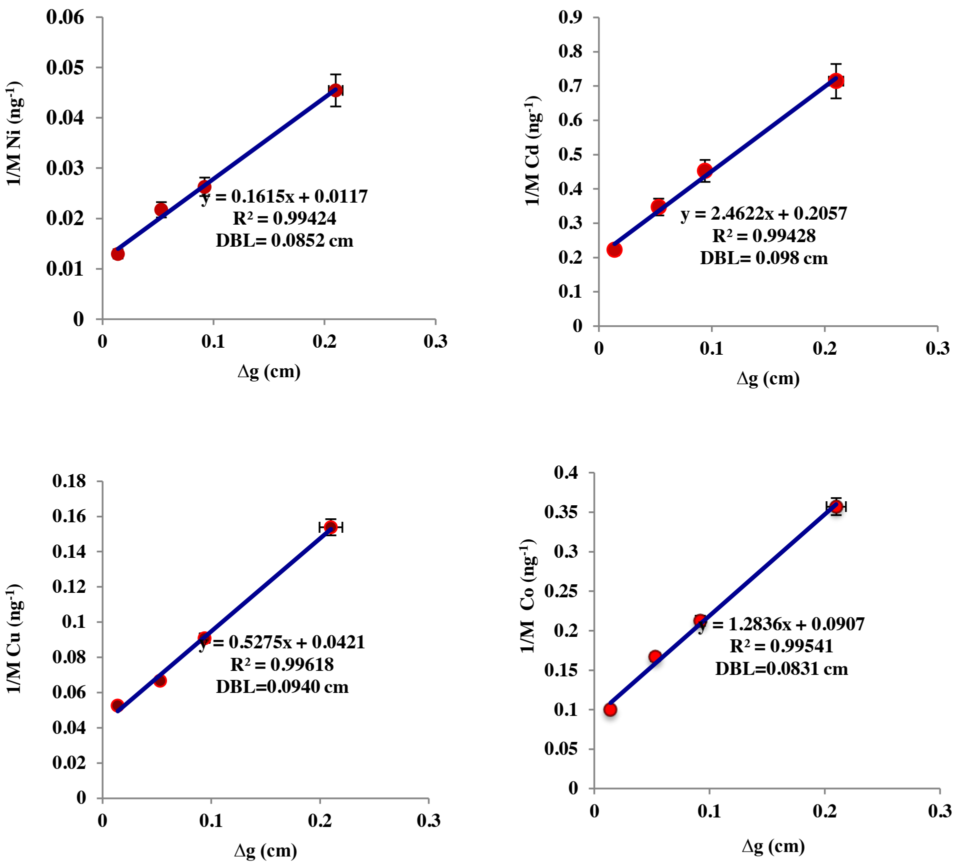


Figure 6.5. Plots of 1/mass Ni, Cd, Cu and Co (ng^{-1}) accumulated in DGT devices versus diffusion layer thicknesses (Δg, cm) at two locations in the Sohar Industrial Region.

Plots for the Sohar Industrial Region (SIR) are presented in **Figure 6.6**. The obtained values of DBLs thicknesses, 0.098 ± 0.00495 cm in Al Fahal port, and 0.086 ± 0.00571 cm in SIR, agree well with the measured thicknesses of DBLs in the study by Turner et al. (2014). The flow rate in the ports is very low, as reflected by the estimated large DBLs at both sites, they were also larger than the diffusion layer thickness, Δg, in the used DGT devices, thus cannot be ignored (Uher et al., 2013). If the DBL was ignored in the calculation C_{DGT} would have been underestimated by 39%-47% at both sites. The concentrations of labile metals at all locations were obtained from **equation (6.4)** using A = 3.80 cm^2 and the estimated DBL (Warnken et al., 2006), as described in **Chapter 3**.

$$C_{DGT} = \frac{M(\Delta g + \delta)}{DAt} \tag{6.4}$$

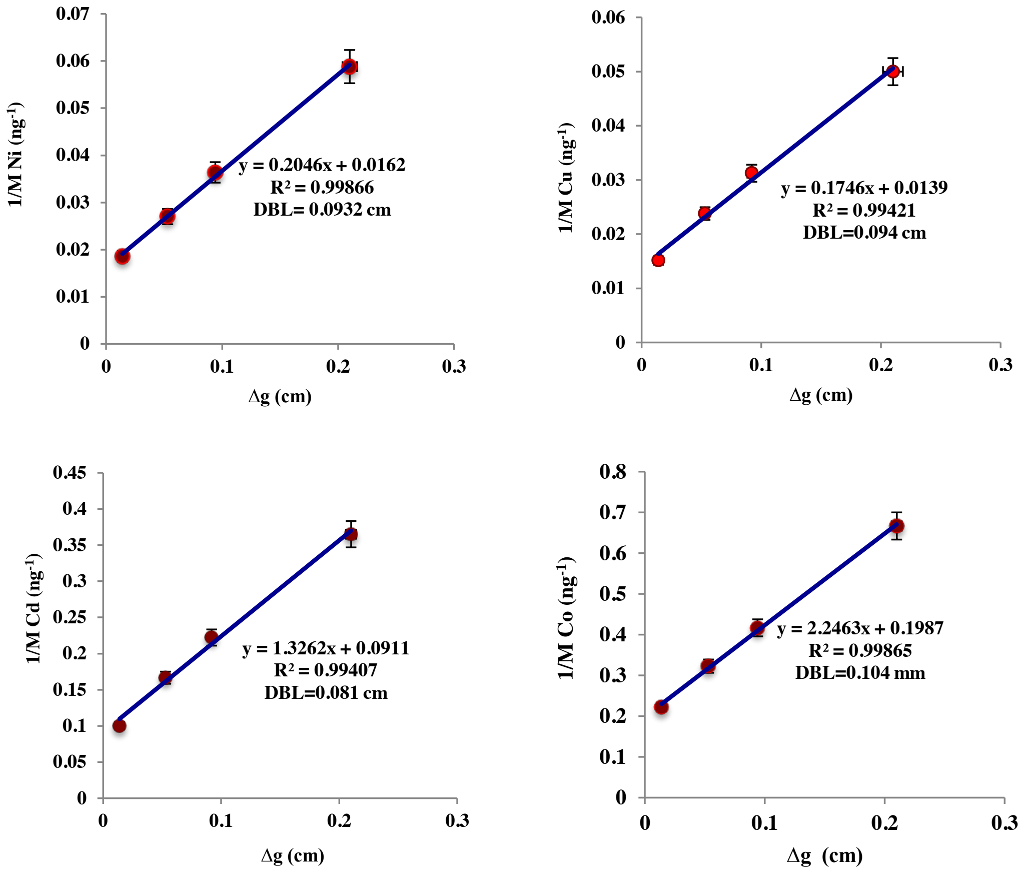


Figure 6.6. Plots of 1/mass Ni, Cd, Cu and Co (ng^{-1}) accumulated in DGT devices versus diffusion layer thicknesses (Δg, cm) at two locations in Sohar Industrial Region.

6.4.1.2. Speciation of cation metals

The metals speciation in Oman Sea at Al Fahal and (SIR) ports were assessed by deploying in triplicates three versions of DGT samplers, OP-DGT, (1000 MWCO-dialysis)-DGT and (Nafion112)-DGT in the same seawater locations at the same time. The measured labile species of all trace metals studied in both ports locations (1 and 2) except (Zn in L_2-AlFahal) and (L_1 and L_2 in SIR) were much lower and did not agree with the 0.45 μm filtered measurements obtained from grab samples ($C_{Sol\ (0.45\mu m)}$), as shown in **Figure 6.7** and **Table 6.2.** This is attributed to the influence of crude oil activities in the ports regions releasing high concentrations of Zn into the seawaters.

For **Al** and **Fe**, the measured concentrations of labile species in OP-DGT at both selected locations in (SIR) are 7.5±0.42 μg/L - 10±1.07 μg/L and 19.5± 0.67 μg/L - 26 ±1.31 μg/L, and Al Fahal port are 7±1.27 - 9±1.04 μg/L, respectively. The percentages of measured labile metal by OP-DGT- account in locations of AlFahal port for 4%-5% Al and 9%-13% Fe, whereas 2%-6.5% Al and 10.4%-20% Fe for (SIR) locations, respectively as illustrated in **Figure 6.7**. This reflects the presence of strong complexing ligands from refinery industries bound with both metals and unable to dissociate fast within the time scale to be taken up by the resin (Mengistu et al., 2012). More than 97% of Al and 94% of Fe were non-labile fractions in 1000 MWCO-dialysis and Nafion112 at all the selected seawaters locations in Al Fahal and (SIR) ports. This indicated that the dissolved both metals fractions were dominated by negatively charged organic ligands and large molecular weight (>1000 MWCO) ligands, which are excluded by the membranes (Panther, Bennett et al. 2012, Liu, Lead et al. 2013). At (SIR) the obtained concentrations of labile trace metals of Al and Fe by OP-DGT samplers at both locations are slightly higher than the locations studied at the Al Fahal port site, which is consistent with the presence of industrial discharges around the main economic activities in Sohar port (**Figure 6.7**). The obtained Fe labile species in SIR locations were slightly higher than those measured in Al Fahal port locations reflecting the presence of more aromatic organic complexes and colloids near SBM3 oil refinery area at selected locations in Al Fahal port (Al-Husaini et al., 2014).

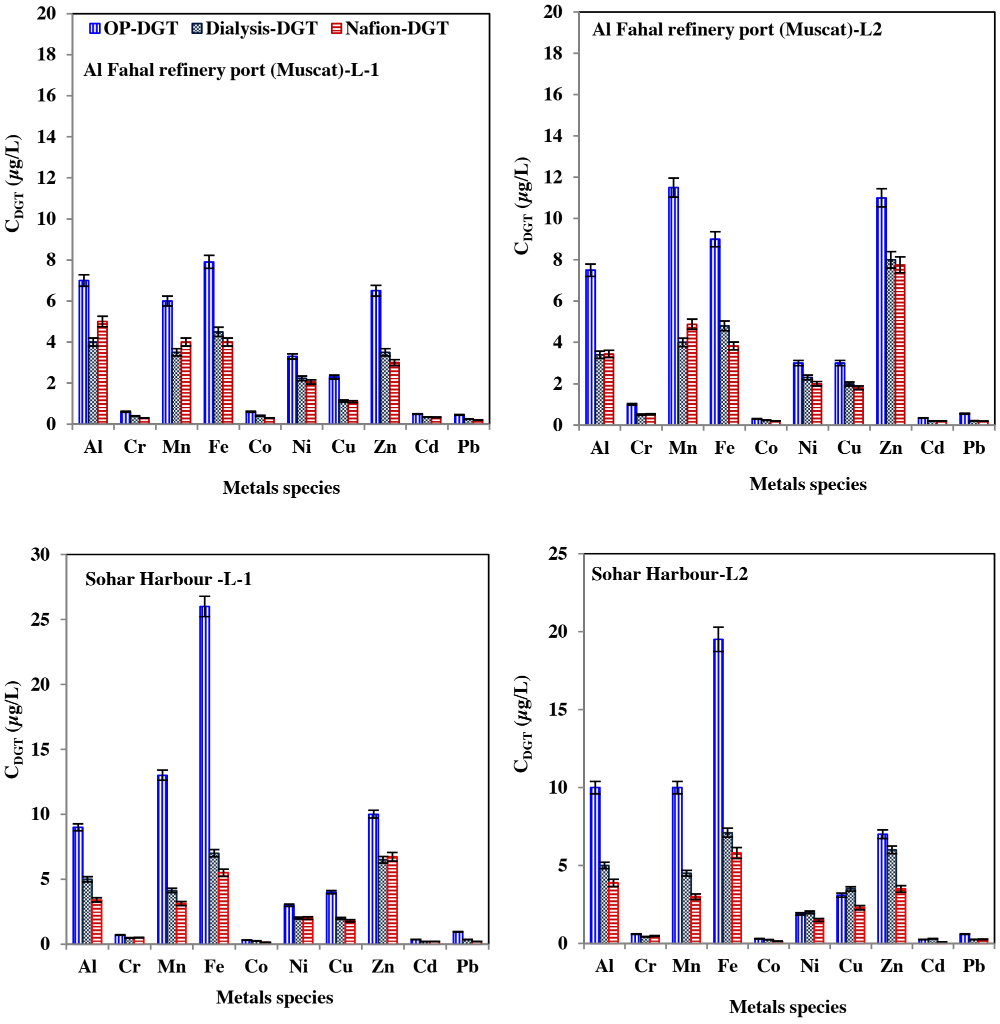


Figure 6.7. Measured labile metal concentrations by OP-DGT, (1000 MWCO-dialysis)-DGT and (Nafion112)-DGT at four locations of seawaters in the Al Fahal port and SIR.

For **Cr**, **Co**, **Ni**, **Cu**, **Cd**, and **Pb,** it can be noticed that the measured C_{DGT}-labile fractions of Cr, Co, Ni, Cu, Cd, and Pb using all DGT versions were in general low with no significant difference at all selected seawater locations near refineries and industrial activities **Figure 6.7.** This suggests that the labile fractions in both locations were complexed strongly with ligands that are less dynamic and unable to dissociate fast enough (non-labile) to be measured by the DGT sampler. On the other hand, most concentrations of these trace metals are probably present in the forms of colloids and complexes ligands in seawater in a similar range of sizes (Ingri et al., 2004). The percentages of measured these metals by OP-DGT in Al Fahal port were, 7%-9% Cr, 7%-15% Co, 12%-16% Cu, 9%-11% Cd, 10%-12% Ni and 55%-68% Pb and 6%-7% Cr, 6%-8% Co, 18%-19% Cu, 8%-13% Cd, 10%-28% Ni and 77%-82% Pb in (SIR) **Figure 6.8**.

The percentages of labile Cr, Co, Ni, Cu, Cd species in (1000 MWCO-dialysis)-DGT and (Nafion112)-DGT were very low comparing to those measured in OP-DGT, ranging between 4.6% and 11% at all locations in selected seawaters sites as shown **Figure 6.8**. The concentrations of labile species of these metals in (Nafion112)-DGT samplers were very low and close to those values obtained in (1000 MWCO-dialysis)-DGT devices; this indicates that most these metals complexes are large (> 1000MWCO) and most of them are negatively charged excluded by Nafion112 membrane (Blom et al., 2003; Sahu et al., 2009; Ramkumar, 2012).

The percentages of labile Pb species in (1000 MWCO-dialysis)-DGT and (Nafion112)-DGT at all studied seawater's locations were not significantly different; except at location-2 in (SIR), where they were 34% and 41% respectively as shown in **Figure 6.8**. This implies that Pb-complexes in location-2 in (SIR) are of small sizes and positively charged; therefore, they diffused through Nafion112 and dialysis membrane in DGT devices to be retained in resin gel. The Nafion112-DGT measured higher percentages of Pb labile species than (1000MWCO-dialysis)-DGT in L1-AlFahal probably due to small-sized nonlabile Pb-complexes crossing the Nafion112 membrane barrier. The Pb complexes must be neutral or positively-charged in order to pass the Nafion112 membrane (Lam et al., 1997).

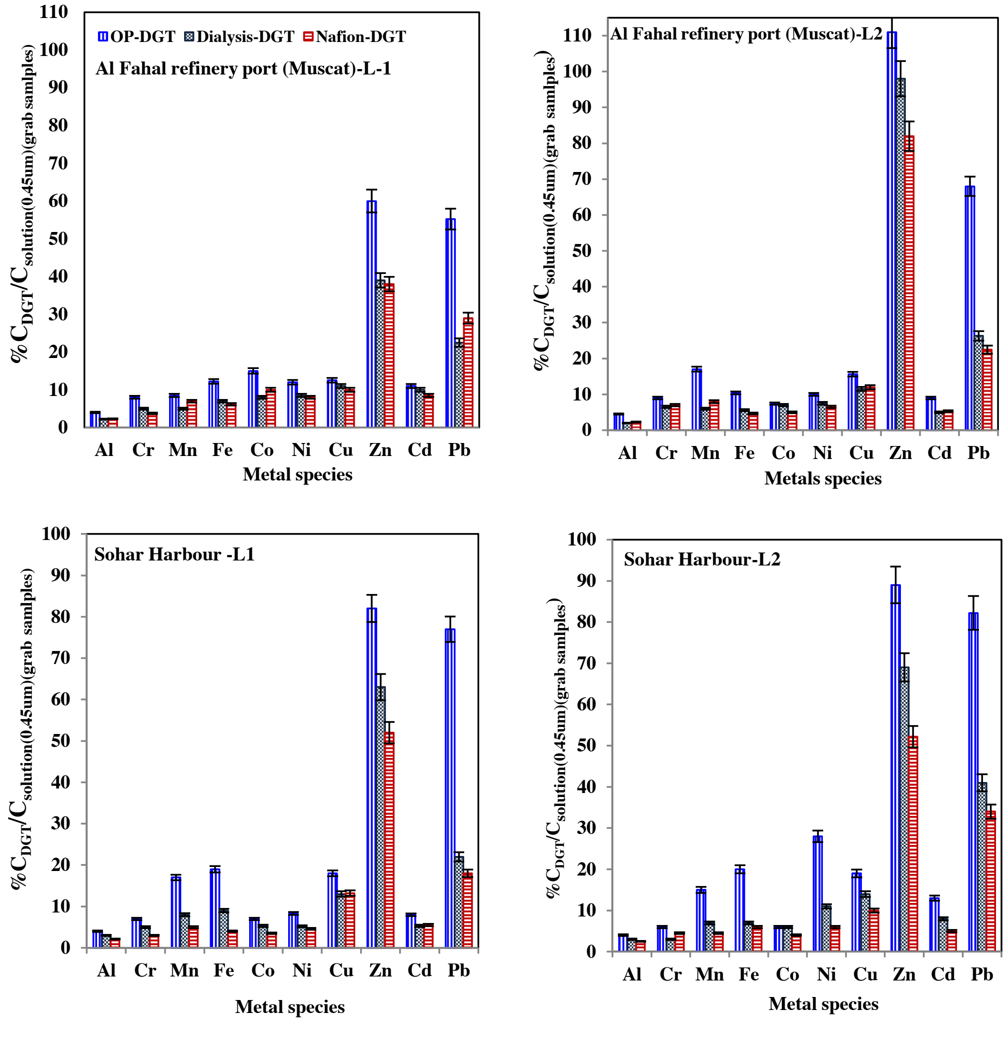


Figure 6.8. The ratios of DGT labile metal species in 0.45 μm filtered grab samples from four selected locations in Al Fahal port and Sohar Industrial Region (SIR).

For **Zn**, the measured OP-C_{DGT}-labile fractions of Zn in the selected AlFahal-location-2 and both locations in (SIR) is very close to total metal concentration in the filtered grab samples ($C_{Sol\ (0.45\ \mu m\ filtered)}$) with the $\%C_{DGT}$ ranged between 82% and 111%. The agreement between C_{DGT}-labile fractions of Zn and total fractions in the filtered grab samples is attributed to the Zn release from oil and small ligands (size < 5 nm), which were more predominant in the DGT-labile species of Zn in locations-2 near to the most heavily trafficked oil tanker routes. Only 60% of Zn labile fractions measured in L-1 of Al Fahal port, which reflecting the presence of large organic ligands size (> 5nm) in the location maybe attributed to the oil organic ligands discharged into the ballast water from the tankers anchoring near location of Al Fhal port (Al-Husaini et al., 2014). The percentages of labile Zn species in (1000 MWCO-dialysis)-DGT and (Nafion112)-DGT at location-2 of Al Fahal port were 98% and 82% respectively, which are also very close to the total metal content in the 0.45 µm filtered grab samples at location-2 of Al Fahal port, and in comparison to other selected seawater areas. This consistency could reflect the presence of total labile content as free and organic or inorganic complexes of smaller molecular mass (< 1000 MWCO), and is positively charged compared to the other selected locations; it can be measured by both DGT devices only in location-2.

For **Mn**, the Mn species in natural waters exist generally as simple inorganic fractions due to its weak tendency to associate with organic ligands (Gimpel, Zhang et al. 2003). The measured C_{DGT}-labile species of Mn in the four locations were similar to those obtained by Kersanach et al. (2009) in impacted marine waters with fertiliser, oil and petrochemical industry activities. About 15-20% of total Mn exist in the particulates and colloids (size > 0.45 µm), see **Table 6.2**. The measured concentrations of Mn labile fractions in (1000 MWCO-dialysis)-DGT were low and ≈48% of measured Mn species in OP-DGT at the four locations, ranging from 3.5±0.30 µg/L to 5±0.11 µg/L with no significant differences in percentages ranging between 5%-8%

Figures 6.7 and **6.8**. This is attributed to the presence of high amounts of particulate species and large ligands tend to form strong organic metallic fractions. The measured Mn species in (Nafion112)-DGT were lower than (1000MWCO dialysis)-DGT at both locations of (SIR) probably due to the presence of higher proportions of the large negatively charged organic complexes near oil refineries, which are eliminated by the Nafion barrier (Blom et al., 2003).

Filtration normally conducted on samples to for metals content analysis. The difference is usually made between a water sample to be analysed for total metal content (unfiltered) and a sample to be analysed for total dissolved metals content in grab samples (filtered samples). Typically, a dissolved metals analysis of a water sample can be achieved by removing the particulates with a filter membrane, followed by analysing the filtered water for metals. The most common filters used for this purpose have a 0.45 µm pore size (Saar, 1997). From **Table 6.2** it can be seen that the total metals content (unfiltered) at four selected locations in Oman Sea are slightly higher than total dissolved metals (filtered) in seawaters. Similar findings obtained for all four studied sites. Al is the highest at all locations, which is probably attributed to the crude oil activities in the area. Pb is the lowest maybe due to the presence of oil ligands (size >0.45µm) in selected locations able to form large and stable Pb-complexes. Although a comparison of time-integrated DGT-labile data with 0.45 mm-filtered data from grab samples is uncertain, it may assist in validating DGT data. For the targeted trace metals at all locations in Al Fahal port and (SIR), filtered samples $C_{sol\ (0.45\ \mu m)}$ ranged from 33.3% - 92.1% of the total trace metals measurement $C_{sol\ (unfiltered)}$ as shown in **Table 6.2.**

Table 6.2. The total metals concentrations in 0.45 mm- filtered grab samples and unfiltered samples measurements (µg L^{-1}) ratios of ($Csol_{(0.45\ \mu m\ filtered\ grab)}$/ $C_{sol(unfiltered)}$) of all targeted metals in four sites of Sea of Oman.

Locations	Metals	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
AlFahal port. L1	$C_{sol(0.45\mu m)}$	175.0	8.0	61.0	65.0	4.0	27.0	11.0	8.0	3.6	0.7
	$C_{sol(UF)}$	190.0	11.0	75.	80.0	5.0	36.0	15.0	13.0	6.0	1.1
	$\%C_{sol(0.45\mu m)}$	92.1	72.7	81.	81.3	80.0	75.0	73.3	61.5	60.7	62.6
AlFahal port. L2	$C_{sol(0.45\mu m)}$	170.0	8.0	64.0	82.0	4.0	31.5	16.0	9.0	4.0	0.8
	$C_{sol(UF)}$	190.0	11.3	80.0	120.0	5.0	40.0	21.0	12.0	6.0	1.0
	$\%C_{sol(0.45\mu m)}$	89.5	70.8	80.0	68.3	80.0	78.8	76.2	75.0	66.7	80.0
(SIR). L1	$C_{sol(0.45\mu m)}$	173.0	10.0	75.0	106.0	4.5	36.0	21.0	11.5	4.0	0.9
	$C_{sol(UF)}$	197.0	13.0	86.	155.	6.0	45.0	27.0	17.0	5.7	1.1
	$\%C_{sol(0.45\mu m)}$	87.8	76.9	87.2	68.4	75.0	80.0	77.8	67.6	70.2	79.1
(SIR). L2	$C_{sol(0.45\mu m)}$	172.0	10.0	67.0	103.0	4.8	38.0	24.0	11.0	4.6	0.7
	$C_{sol(UF)}$	198.0	16.0	78.0	151.0	7.0	47.	31.0	14.0	7.0	2.0
	$\%C_{sol(0.45\mu m)}$	86.9	62.5	85.9	68.2	68.6	81.09	77.4	78.6	65.7	32.5

6.4.1.3. Concentrations of oxyanion metals

Ferrihydrite $Fe(OH)_3$)-DGT has proved to be useful for oxyanions determination in aquatic systems (Luo et al., 2010; Österlund et al., 2010; Price et al., 2013). In this study, FH-DGT was used for the simultaneous measurements of V, As, Mo; Se, Sb, and W in Oman Sea at same selected above sites. The DGT concentrations were calculated using **equation (6.3)**. The diffusion coefficients (D) for vanadate, arsenate, molybdate, antimonate, selenium, and tungstate were recalculated using values obtained by Luo et al. (2010) and Panther et al. (2013), and by using the equation in Zhang and Davison (1995), as described in **Chapter 4**. This equation gives diffusion coefficients of every analytes at any given temperature D_T, at which deployment was achieved Scally et al. (2003). For high ionic strength deployments in seawater (≈ 0.7 mol/L NaCl in seawater), a value of 0.9×D was applied for all the calculations for analytes (Panther et al., 2013). As illustrated in **Figures 6.9** and **6.10,** there is a significant difference between total contents in 0.45 µm filtered grab samples and determined FH-DGT labile oxyanions fractions for V, As, Mo, Se, Sb, and W in the four selected locations.

For **vanadium (V)**, it is generally used as a fingerprinting of the source of crude oil contamination in aquatic systems present in V-ligands forms in crude oil contaminated marine systems (Al-Husaini et al., 2014). The measured total concentrations of V content in both unfiltered and 0.45 µm filtered grab samples in the four locations were found to be much higher than the concentrations obtained in Al Fahal port near SBM in (2010) by Al-Husain, which indicates that it is a result of oil contamination caused by oil the refinery and passing tanker traffic, see **Table 6.2.** The measured concentrations of labile fractions of V in the FH-DGT sampler was very low at the four locations when compared to the total content in the 0.45 µm filtered grab samples, which ranged from 5.5 ± 0.74 µg/L to 8 ± 1.04 µg/L; around 4%-5% of the total dissolved concentration. This is attributed to the contribution of high levels of large ligands and colloids in grab samples bound strongly with V, which are small enough to pass through the 0.45 µm pore size in filters, but too large (size > 5 nm) to cross through diffusive layer.

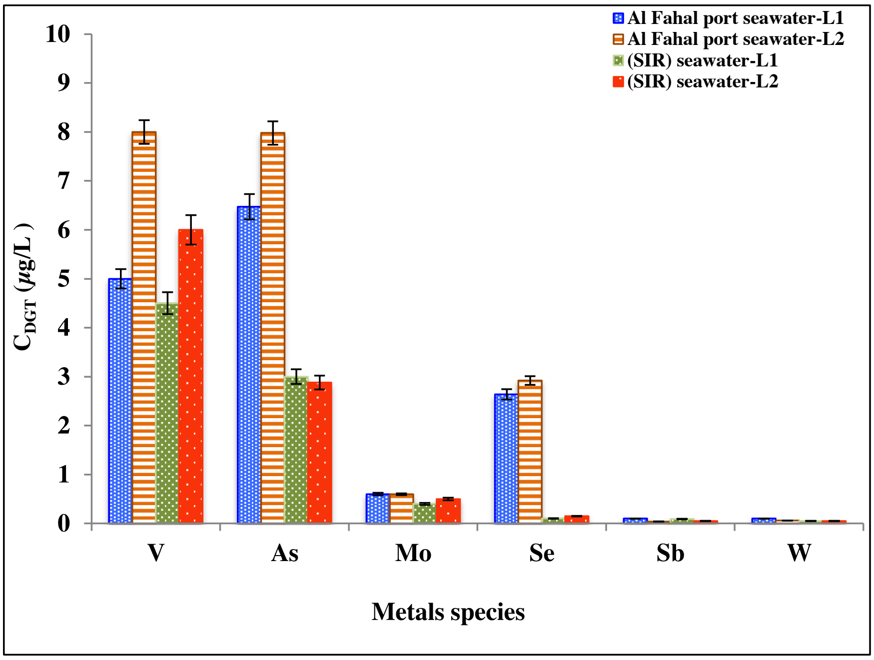


Figure 6.9. Ferrihydrite DGT concentrations of labile V, As, Mo, Se, Sb and W in four locations of seawater in Al Fahal port and SIR.

For As, the measured concentrations of As labile species in four locations were ranged between 2.88±0.33 µg/L to 7.98±1.65 µg/L, which exceeded the natural background in seawater 1.5 µg/L (Smedley and Kinniburgh, 2002) due to oil industries contaminations and discharged treated ballast waters from tankers, especially in Al Fahal port around SBM systems. The results showed that the percentages of FH-DGT labile As fractions in filtered grab samples were 20% and 21.8% in (SIR), and around 61.4% and 75.52% in Al Fahal port (**Figure 6.10**). This could reflect the presence of higher levels of hydroxides of Fe, Al, and Mn at the SIR site than other locations in Al Fahal adsorbing as species. On the other hand, it is probably that there was a proportion of As fractions that could be adsorbed to colloidal oxy(hydr)oxides Fe^{3+} that was not accumulated by the FH-DGT devices (Dixit and Hering, 2003; Panther et al., 2008).

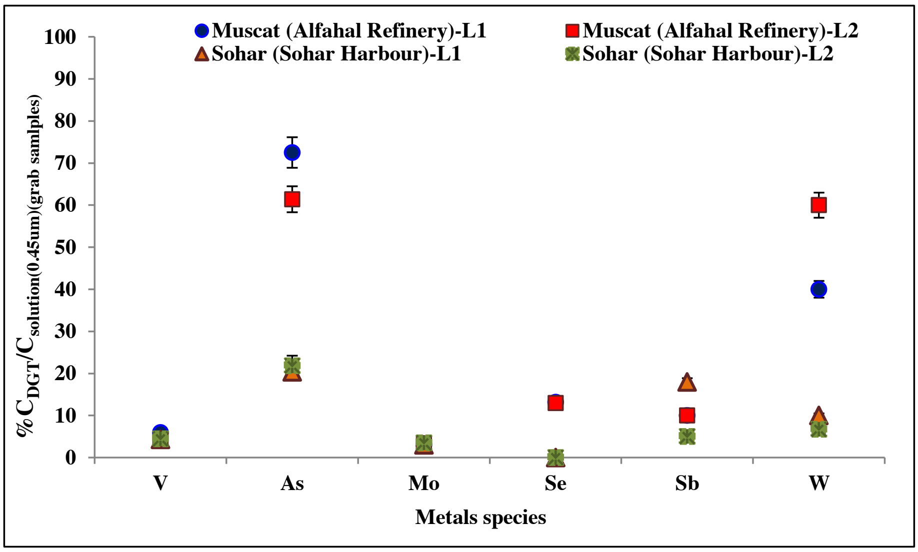


Figure 6.10. The percentage of DGT labile V, As, Mo; Se, Sb and W 0.45 μm filtered grab samples from four selected locations in Al Fahal port and Sohar Industrial Region (SIR).

The FH-DGT concentrations of labile Mo species in all locations were very low, ranging between 0.37±0.08 μg/L and 0.6±0.23 μg/L with percentages of 3%-3.5% of total concentration in grab samples. This reflects that Mo is present in colloidal and organic ligands forms (size > 5 nm) in natural waters, and can pass through 0.45 μm filtration in grab samples; but unable to cross the diffusive gel to binding layer. This is also probably because of weaker binding of these anions to (FH) resin at high pH in seawater; observed for molybdate measurements at all locations (Österlund et al., 2010; Vasyukova et al., 2010).

For **Se**, the measured FH-DGT concentrations of labile Se at the Al Fahal site were higher than those obtained in (SIR), ranging between 2.6 ± 0.04 μg/L to 3.0 ± 0.10 μg/L and 0.1 ± 0.012 μg/L and 0.14 ± 0.013 μg/L respectively. This probably attributed to the presence of high levels of Fe, Al, and Mn dissolved organic complexes some of them present in the form of colloidal particles of hydrous metallic oxides can bound strongly to Se species. This is consistent with findings obtained in seawater by Price et al. (2013). Vasyukova et al. (2010) also found similar observations in seawater for other oxyanions.

For **Sb** and **W**, the FH-DGT labile concentrations of both oxyanions were very low at the four locations, and ranged between 0.01 ± 0.007 µg/L and 0.09 ± 0.002 µg/L respectively. This is may be attributed to the weaker binding of Sb and W anions to Ferrihydrite at a high pH in seawater. On the other hand, that aromatic organic ligands and organo-mineral colloids, Al, Mn, and Fe^{3+} oxyhydroxides, act as the main carriers of these anions at all selected locations (Österlund et al., 2010; Vasyukova et al., 2010).

Table 6.3 highlights that the levels and overall mean concentrations of oxyanion metals As, Mo, Se and V, are high in all collected 0.45 µm filtered grab and unfiltered samples at all locations. This is possibly attributed to the illegal discharges of oil and wastes by passing tankers at all locations throughout the neighborhoods of refineries and those conducting industrial activities. Vanadium (V) is oil related metals, and mainly occur in metal complexes forms in crude oil, normally considered as an indicator of oil ligands pollution (Al-Husaini et al., 2014). W is the lowest in all selected locations of Oman Sea due to its very low occurrence in seawater. For Mo, molybdenum in marine systems are mostly present as MoO_4^{2-} fractions and its concentration is unaffected by 0.45 µm filtration in grab samples, which is very close to the total content in unfiltered samples at the four selected locations, as shown in **Table 6.3**.

Table 6.3. The total oxyanion metals concentrations in 0.45 mm- filtered grab samples and unfiltered samples measurements (μg L^{-1}) ratios of ($Csol_{(0.45\ \mu m\ filtered\ grab)}$/ $C_{sol(unfiltered)}$) of all targeted metals in four sites from the Sea of Oman.

Locations	Metals	V	As	Mo	Se	Sb	W
AlFahal port. L1	$C_{sol(0.45\mu m)}$	110.0	11.3	17.0	20.0	0.4	0.2
	$C_{sol(UF)}$	125.0	14.0	20.0	24.0	0.6	0.4
	$\%C_{sol(0.45\mu m)}$	88.0	80.7	85.0	83.3	65.6	42.9
AlFahal port. L2	$C_{sol(0.45\mu m)}$	105.0	13.0	17.0	21.0	0.5	0.1
	$C_{sol(UF)}$	125.0	16.0	22.0	27.0	0.7	0.3
	$\%C_{sol(0.45\mu m)}$	84.0	81.3	77.3	77.8	64.3	33.3
(SIR). L1	$C_{sol(0.45\mu m)}$	129.0	14.0	15.0	12.0	0.4	0.2
	$C_{sol(UF)}$	140.0	17.0	19.0	23.0	0.8	0.4
	$\%C_{sol(0.45\mu m)}$	92.1	82.4	78.9	52.2	50.6	52.6
(SIR). L2	$C_{sol(0.45\mu m)}$	113.0	13.0	15.0	11.0	0.4	0.2
	$C_{sol(UF)}$	152.0	18.0	18.2	16.0	1.0	0.4
	$\%C_{sol(0.45\mu m)}$	74.3	72.2	82.4	68.8	44.3	42.9

Consequently, it can be observed that according to DGT findings in Al Fahal port and SIR, the high extent of anthropogenic activities in these two economic regions has been identified as showing evidence of contributing most to trace metals loads in marine systems. The distribution of the various groups and forms of labile trace metals species indicates the presence of the different contamination sources in the studied sites. In fact, both sites characterised by the presence of refinery and industrial activities may represent point sources of primary trace metals contamination, which are extensively present in crude oil or used in industries such as aluminum, iron, and copper mining. All obtained concentrations for V, Ni, Zn, Mn, Al, and Fe in 0.45 μm filtered grab samples in all locations were high, which confirms that all port sites have been impacted by oil spills and/or oil transportation and industrial discharges taking place in both selected locations. Significantly low DGT-labile of fractions were measured compared to the concentrations in 0.45 μm filtered grab samples at all DGT types. This reflects the presence of high concentrations of large aromatic ligands and colloids, including oxide-hydroxides, in the studied areas where oil refineries, tankers, and industries influence the trace metals speciation.

6.4.2. Metal concentrations and speciation in groundwaters

Following seawater quality assessment around two main economic ports, groundwaters quality around Rusyal Industrial Estate (RIE) in Muscat, and (SIR) were also assessed by deploying the same set of the above DGT versions at the same time in six open wells. Water temperature, EC, salinity, and pH of all selected six wells were measured daily during the deployment period using the average values of the obtained values, **Table 6.1**.

6.4.2.1. DBL measurements

Diffusive boundary layer (DBL) was determined at each deployment open well waters to investigate if the DBL thickness affected by very low flow rates in the studied six well waters. To measure the thickness of the DBL in open well waters, DGT devices were deployed at each well's waters around RIE in Muscat and in Khadafan near (SIR) in Sohar for 5 days as described above. The inverse of mass of metal retained by DGT unites (1/M) were plotted versus diffusion layers (Δg), as shown in **Figure 6.11.** A good linearity of regressions (R^2) 0.9935-0.99837, despite the low mass of some targeted trace metals such as Cd (0.01±0.0015 μg/L – 0.14±0.012 μg/L) in Well-1 in Khadafan near SIR, and Pb (0.83±0.013 μg/L – 2.6±0.017 μg/L) in Well-3 in RIE, were accumulated by DGT units in all open wells of the studied locations, probably due to the presence of large ligands and colloids bound strongly to trace metals unfilterable through 0.45 μm pore size. The determined thicknesses of DBL of trace metals in the selected open wells using the **equation (6.3)**, were larger than those obtained in the laboratory (see **Chapter 3)** and in seawater in this study as shown above and were variable for the other metals (Warnken et al., 2006). In comparison with the obtained DBLs thicknesses in seawaters, 0.098 ± 0.00495 cm in Al Fahal port, and 0.086 ± 0.00571 in SIR, as the mean of estimated DBLs of trace metals are ≈11% lower than DBLs in open wells (Turner et al., 2014). This attributed to the very low flow rate and presence of large ligands of high stability as described above in **section 6.4.1.1**. The dissociation of a metal-ligand is kinetically limited: the accumulated mass by DGT is decreased and 1/mass will be higher (Warnken et al., 2007). The DBL in this situation cannot be ignored because it is high and will affect the calculation of the concentrations of labile trace metals fractions (C_{DGT}) (Warnken et al., 2006; Uher et al., 2013). Similar observations were found for Co and Cu by Shiva et al. (2016).

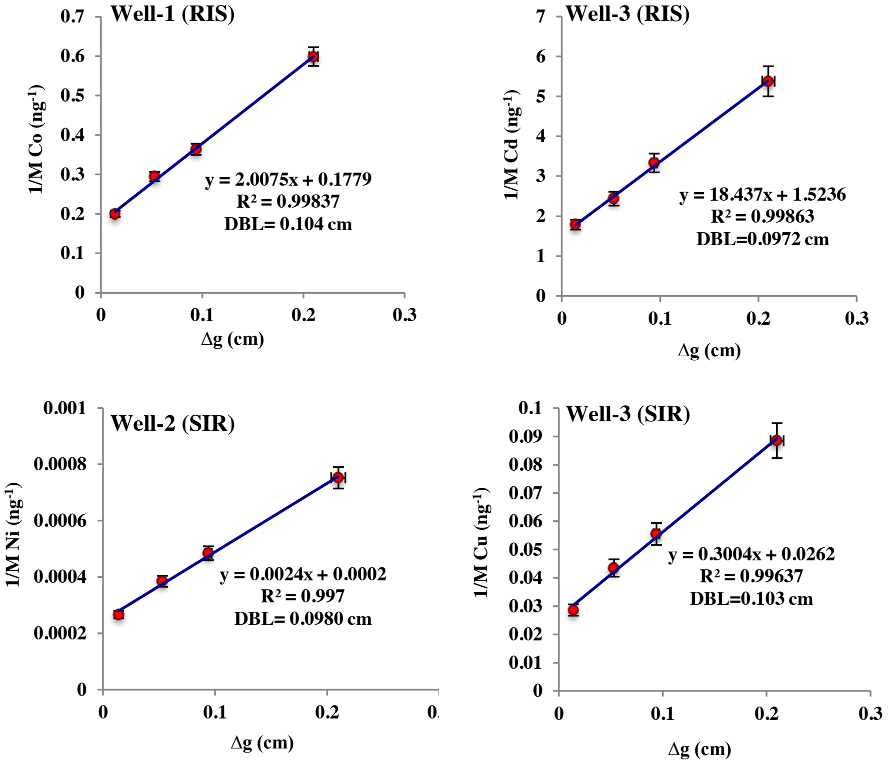
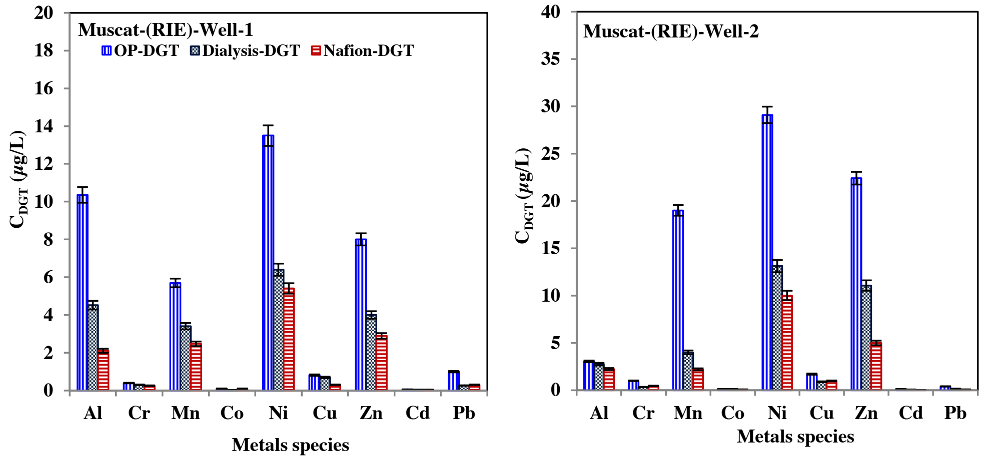


Figure 6.11. DGT results for Co, Ni, Cu and Cd in selected wells waters at RIE in Muscat and SIR in Sohar, plotted as 1/mass of versus the diffusive layer thickness (Δg, cm).

The average of the measured DBLs at the abovementioned experimental conditions 1/M (ng^{-1}) was 0.103 cm. For a comparison, if a 0.078 cm hydro gel was used in a piston probe, the obtained (DBL) in open wells comprises more than 25% of the total diffusive distance (Δg) from the overlying water to the resin, thus playing a significant effect in equation calculations. The obtained data for the DBLs are placed in **Appendix (C)**.

6.4.2.2. Speciation of cation metals

The measured concentrations of labile trace metals species by each type of DGT samplers (OP-DGT, (1000 MWCO-dialysis)-DGT and (Nafion112)-DGT) and their percentages of the total content in 0.45 μm filtered grab samples are shown in **Figures 6.12** and **6.13,** and **Table 6.4** illustrates the obtained labile metals contraptions in Well-1 near (SIR). It can clearly be observed that there is a considerable concentration difference between total content in grab samples and DGT labile fractions in all used versions for trace metals studied in all selected open well waters.



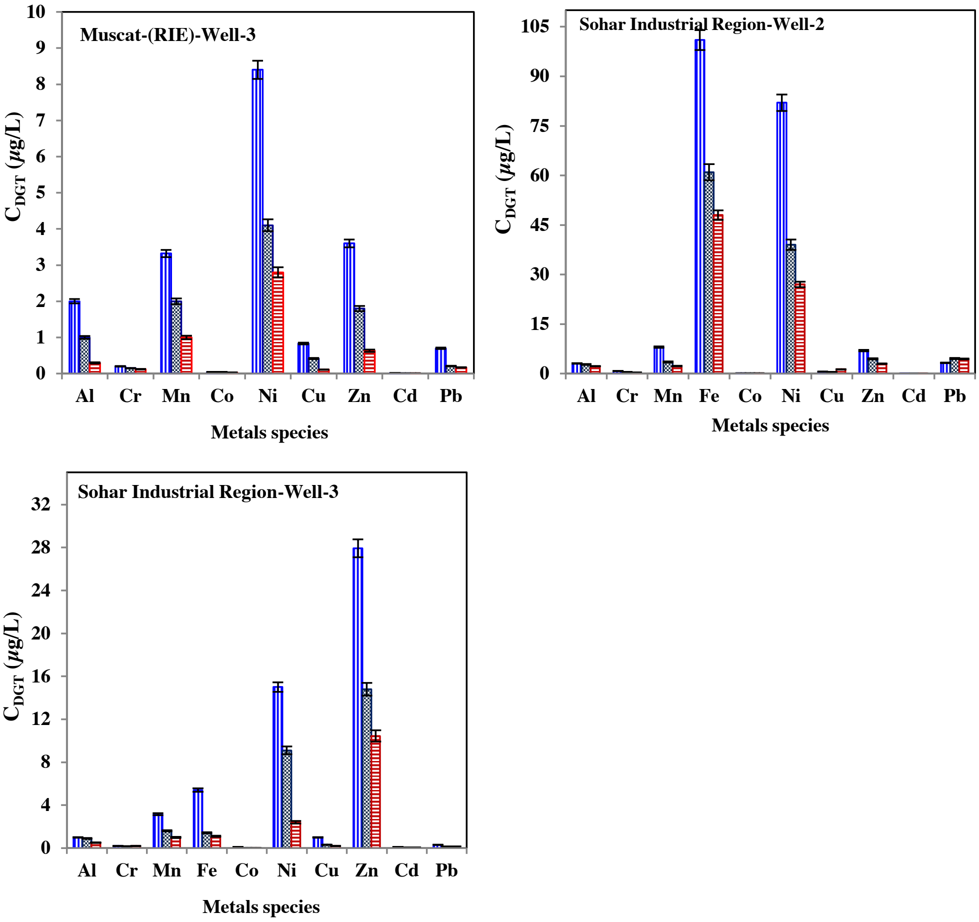


Figure 6.12. Measured trace metals fractions in five open well waters at different sites by three versions of DGT samplers.

Table 6.4. The measured concentrations of DGT labile species (µg/L) by OP-DGT, (1000 MWCO-dialysis)-DGT and (Nafion112)-DGT in open well water-(1) in SIR.

Metal	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
OP-DGT	1.4	0.6	760	2628	1.72	10.23	0.11	37.0	0.03	0.038
Dialysis-DGT	1.25	0.22	523	1451	1.79	5.21	0.1	14.2	0.01	0.029
Nafion-DGT	0.38	0.24	493	493	1.35	5.27	0.1	13.5	0.01	0.035

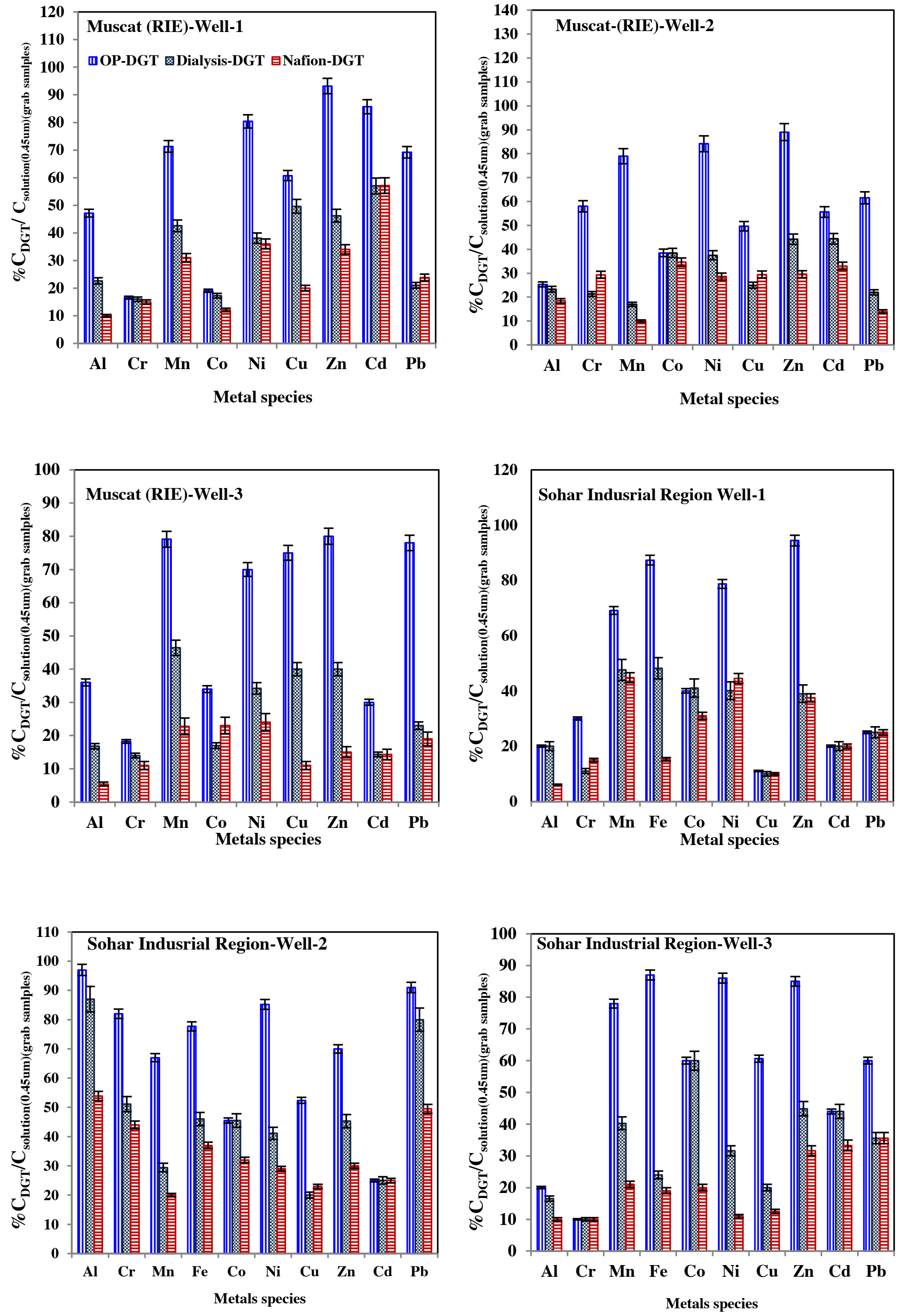


Figure 6.13. The percentages of C_{DGT}-labile metal species in studied wells of the total content in 0.45-µm filterable grab samples.

For **Al**, the measured concentrations of Al labile fractions OP-DGT were low in all selected wells ranged between 1.0±0.046 µg/L and 10.36±0.93 µg/L. The measured percentages of Al fractions obtained by OP- DGT in (RIE)'s wells (1,2 and 3) were 25.3%%, 47.1% and 36% of the total dissolved content in grab samples, respectively. Whereas in (SIR)'s wells (1,2 and 3) were 20%, 16.5% and 97%, respectively of the total content as shown in **Figures 6.12** and **6.13.** This is probably due to the complexation of Al by large ligands and colloids in wells waters that can cross the pore size 0.45 µm in filterable grab samples but find it difficult to diffuse through the hydrogel. On the other hand, humic substances in wells waters favored the formation of highly stable complexes that would slow the diffusion of Al species to the resin layer, and are typically released from industrial and agricultural (pesticides and fertilizers) practices near development sites and farms (Panther et al., 2012; Malassa et al., 2013). The higher ratio in (SIR)-well 2 could be attributed to a species of Al associated to DOMs and colloids, which are small enough to pass through a 5 nm pore size in the diffusive gel. The (1000 MWCO-dialysis)-DGT labile concentrations closely followed those values measured by OP-DGT for Well-2 in RIE, and Wells-1, -2 and -3 in SIR, with the smallest proportion of Al labile species (16.5% - 23.3%) and a large percentage (89%) of the total content in grab samples for Well-2 at (SIR), see **Figure 6.12**. The big differences between (1000 MWCO-dialysis)-DGT and OP-DGT measurements reflect the presence of large complexes of molecular mass (> 1000 MWCO) in these open wells waters; they cannot diffuse through dialysis. In (RIE)'s wells-(1) and (3), the measured labile Al by (1000 MWCO-dialysis)-DGT were significantly lower than OP-DGT, with percentages 22.6% and 16.8%, probably due to Al associated to DOMs and colloids, which are too large to diffuse through dialysis (> 1000 MWCO).

The (Nafion112)-DGT concentrations of Al labile species in all selected open wells waters were lower than those estimated by both above versions ranged from 5% - 53%. The differences are statistically substantial at all sites, applying a paired t-test at ($p < 0.05$). This indicates that Al species bound to large natural organic ligands and colloids in all studied open wells were excluded by the Nafion112 membrane.

For **Cr**, the measured concentrations of Cr labile species in all DGT versions were very low and not significantly different at all selected open wells; ranging between 0.12±0.045 μg/L and 0.74±0.095 μg/L. This is attributed to the presence of small organic ligands in all studied open wells (< 1000 MWCO), and they should be neutral and positively charged in order to cross through the Nafion112 membrane (Lam et al., 1997). On the other hand, the results showed that the discrimination of Cr in groundwaters depends on the nature of water and their sources. For example, around 44%, 51.1%, and 82% of Cr labile Cr fractions were detected by OP-DGT and (1000 MWCO-dialysis)-DGT devices in Well-2 in Khadafan near SIR. However, less than 18.2% of the total content in filterable grab samples were detected on the same versions of labile Cr species in Well-3 in Muscat near RIE, and Well-3 in Khadafan in SIR, which reflects the variations of metal speciation in studied open wells waters (Ernstberger et al., 2002; Liu et al., 2013).

For the trace metals **Co**, **Cu**, **Cd** and **Pb**, all DGT versions captured very low concentrations of labile in these metals, and they are similar in all selected open wells. This implies that the proportions of ligands, particulates, and colloids associated with these metals were in a similar range, and were neutral or positively charged to pass through the Nafion112 membrane (Sigg et al., 2000; Blom et al., 2003). This is consistent with measured total content of these metals in both filtered and unfiltered grab samples, see **Figure 6.12** and **Table 6.4**. Similar results were found by Taghipour et al. (2012) in irrigation wells. Based on the measured low concentrations by DGT versions in six open well~~s~~ waters at both sites, the studied open wells can be considered uncontaminated by these metals.

For **Zn**, the relative concentrations of labile Zn fractions in the studied open wells that are able to diffuse through (Nafion112)-DGT were 2.3-5.7 fold lower than those measured by OP-DGT, whereas in (1000 MWCO-dialysis)-DGT they were 1.2-2.87 fold lower. It is possible that fractions of Zn were associated with large natural ligands, such as DOM, near industrial and agricultural (fertilisers and pesticides) activities and thus were eliminated by the Nafion112 membrane, or were unable to dissociate fast enough to be retained by the binding layer (Blom et al., 2003; Guéguen et al., 2011). The observed high concentrations in Zn in (RIE)'s well-2 and (SIR)'s well-1 and well-3 may be attributed to the industrial effluents, agricultural practices (fertilizers and pesticides) and oil refineries activities (Gonçalves Jr et al., 2014).

For **Ni**, the obtained concentration of labile Ni species by OP-DGT in Well-2 at Khadafan near (SIR) was 3 times higher than those found in Well-2 near (RIE), and about 7 times higher than those in Wells-1 and -3 in Muscat near RIE, and Wells-(1) and (3) in Khadafan around (SIR); they ranged between 8.4 µg/L and 82 µg/L, as shown in **Figures 6.12** and **6.13**. The percentages of labile Ni fractions in OP-DGT devices ranged between 70% to 86% in all selected open wells, which can be attributed to the fast dissociation of Ni-DOC complexes of higher Ni-DOC ratios, or due to the presence of small ligands (size < 5 nm) that can diffuse through the hydrogel to the resin. This originates from industrial and refinery activities where the potential source contaminants inputs include treated effluents from the refinery that are released into the groundwater streams. The mixing of freshwaters with industrial and municipal effluents around anthropogenic activities, is one of the big problems facing managing and regulations of freshwater quality, as mentioned above (Chakraborty et al., 2006). Around 30%-40.1% of the total Ni content in filterable grab samples were (1000MWCO-dialysis)-DGT labile Ni^{2+} fractions in 6 open wells. This indicates that Ni probably associated with organic ligands of molecular mass (>1000 MWCO) and excluded from DGT measurements (Gimpel et al., 2003; Österlund et al., 2012). The smallest proportion of Ni labile species (11%-29%) were measured by (Nafion112)-DGT in all selected open wells except in Well-1 near (SIR) where it slightly exceeded those in (1000 MWCO-dialysis)-DGT (44.5% of the total concentration in the filterable grab sample).

For **Mn**, the measured concentrations of labile Mn fractions were low in the studied open wells waters, except for Well-1in Khadafan near SIR by three DGT versions. The higher levels of Mn is probably associated with the low amount of dissolved oxygen in Well-1 in Khadafan which enhanced the reduction process of MnO_2 to Mn and Mn^{2+} (Liu et al., 2013). The ratios of DGT labile free Mn ions, inorganic fractions, and small labile organic complexes in the above DGT devices are in the range of 67%-79% in OP-DGT, 17%-47.6% in (1000 MWCO-dialysis)-DGT, and 10%-44% in Nafion112. The measured low percentages of labile Mn inorganic species by (1000 MWCO-dialysis)-DGT and (Nafion112)-DGT, reflects the presence of large particulates and colloids of molecular weight >1000 MWCO bound strongly to Mn. For Zn, the relative concentrations of labile Zn fractions in the studied open wells that are able to diffuse through (Nafion112)-DGT were 2.3-5.7 fold lower than those measured by OP-DGT, whereas in (1000 MWCO-dialysis)-DGT they were 1.2-2.87 fold lower. It is possible that fractions of Zn were associated with large natural ligands, such as DOM, near industrial and agricultural (fertilisers and pesticides) activities and thus were eliminated by the Nafion112 membrane, or were unable to dissociate fast enough to be retained by the binding layer (Blom et al., 2003; Guéguen et al., 2011).

For **Fe**, there were substantial differences in the measured concentrations of labile Fe fractions at all selected open well waters using three DGT versions (**Figure 6.12** and **Table 6.4**), which indicates the complex chemistry of iron. Iron (II) is in an unstable oxidation state in freshwater, it can be oxidized immediately to the very stable oxidation state Fe (III) as it is exposed to oxygen, and could exist at an appreciable concentration in water (Liu et al., 2013). Thus, the measured Fe labile fractions by DGT samplers in open well groundwaters were expected to present as small sized and be relatively mobile. In Muscat, the measured Fe labile species in all selected open wells around RIE were below detection limit BDL. This is possibly linked to high dissolved oxygen in all studied open well waters, which is likely enhancing the oxidation process of FeO to Fe_2O_3. On the other hand, various organic ligands, colloidal Fe particles, too large to be filtered through a 0.45 µm pore size due to very slow diffusion (Gimpel et al., 2003; Liu et al., 2013). In Khadafan, the relative Fe labile concentration in Wells-1 and -2 were much higher than those in Well-3 and (RIE)'s wells. The percentages of (Nafion112)-DGT-labile Fe species in (SIR) well, 1, 2 and 3 were 15.3%, 37% and 19% of the total content in 0.45 µm filterable grab samples, which reflects the presence of Fe in large colloids/particulates, nagatively and natural ligands excluded by the Nafion112 membrane **Figure 6.13** (Hill and Aplin, 2001). Similar observations were found by Gimpel et al. (2003). The high concentrations in Well-1 (SIR) were above the permissible level of the Omani standard of 20 µg/L, which attributed to the industrial activities near sampling regions (S. A. Al Maashri 2011). Further studies should be conducted to investigate trace metals levels, and to assess the contribution of industrial regions and economic ports on the trace metals loads and speciation in groundwater and marine systems in other locations in the Sultanate of Oman.

Table 6.5 shows the average of total trace metals concentrations from unfiltered grab samples and 0.45 μm filtered grab samples. The data obtained in grab samples can be used to evaluate the suitability of DGT samplers in assessing the quality of aquatic systems. The concentrations obtained in 0.45 μm filtered grab samples are higher than C_{DGT}, which indicates that the obtained measured concentrations in all used DGT versions in the above discussion, represent the labile fractions of either free metals ions or weak metal-DOM, which are bioavailable in the samples. This is attributed to the presence of large metals-ligands and colloids in the studied area that can pass through pore size in 0.45 m filters, but are too large to cross the hydrogels and the membranes used in DGT devices (Gimpel et al., 2003; Mengistu et al., 2012; Panther et al., 2012). It can be observed that the targeted trace metals in all selected wells waters were low, except Al, Mn, Fe, Ni and Zn which were higher in others selected open well waters, as shown in **Table 6.5.** This suggests that there is a continuous input of more trace metals from oil refineries and industrial regions.

Table 6.5. Comparison of targeted trace metals concentrations (µg/L) in 0.45µm filtered and unfiltered collected waters from well samples at selected wells in RIE and SIR regions.

Locations	Metals	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Well-1(RIE)	Csol(0.45 µm)	30	2	8	BDL	0.58	16.8	1.35	8	0.07	1.3
	Csol(UF)	36	8	12.5	BDL	0.75	23	1.7	9.7	0.09	1.65
	%Csol(0.45µm)	83	25	64	BDL	77	73	79	82	78	79
Well-2(RIE)	Csol(0.45 µm)	12	1.5	24	BDL	0.26	35	3.25	25	0.085	0.65
	Csol(UF)	20	3.2	32	BDL	0.32	44	4.1	32	0.1	1.3
	%Csol(0.45µm)	60	46.87	75	BDL	0.1	79.5	79.3	78.1	85.0	50.0
Well-3(RIE)	Csol(0.45 µm)	5.6	1.1	4.2	BDL	0.2	12	1.1	4.5	4	0.9
	Csol(UF)	11	1.8	6	DDL	6	16	1.85	10	5.7	1.1
	%Csol(0.45µm)	50.9	61.1	70.0	DDL	3.3	75.0	59.5	45.0	70.2	81.8
Well-1 (SIR)	Csol(0.45 µm)	7	2	1100	3012	4.4	13	1.1	36	0.05	0.12
	Csol(UF)	9	3.4	1310	3240	5	30	1.3	54	0.083	0.23
	%Csol(0.45µm)	77.8	58.8	84.0	93.0	88.0	43.3	84.6	66.7	60.2	52.2
Well-2 (SIR)	Csol(0.45 µm)	39	0.9	12	130	0.22	96	2.5	10.4	0.04	5
	Csol(UF)	45	1.26	16	141	0.56	115	3	15	0.062	8
	%Csol(0.45µm)	86.7	71.4	75.0	92.2	39.3	83.5	83.3	69.3	64.5	62.5
Well-3 (SIR)	Csol(0.45 µm)	5.02	2.02	4	6.2	0.05	22.5	1.6	33	0.09	0.45
	Csol(UF)	7	3	6	8	0.13	27	2	45	0.14	0.7
	%Csol(0.45µm)	71.7	67.3	66.7	77.5	38.5	83.3	80.0	73.3	64.3	64.3

6.4.2.3. Concentrations of oxyanion metals

FH-DGT devices in triplicates were deployed at the same studied open wells waters at the same sampling times as for the above cation metal measurements by DGT. The labile concentrations of V, As, Mo, Se, Sb, and W (C_{DGT}, µg/L) were calculated using **equation (6.3)**, and diffusion coefficients obtained by Luo et al. (2010) and Österlund et al. (2010). The obtained DBLs values in the above section were included in the calculations. The results are presented in **Figure 6.14**. The results showed substantial differences at all studied open wells, with percentages ranging between 8% and 95% of all studied oxyanions in filterable grab samples, see **Figure 6.15**.

For **vanadium (V)**, V species normally enters aquatic systems due to oil sands, industrial activities, and mine wastes. The FH-DGT concentrations of labile V species in all studied wells, except Well-3 near (SIR), exceeded the typical background concentration in groundwater of (1 < µg/L), with ratios ranging from 31% to 93.7% of the total concentration in the filterable grab samples (Dušek, 2002; Li et al., 2014). This is likely to originate from higher anthropogenic inputs near industrial regions. Additionally, the lower level of FH-DGT labile V fractions attributed to the presence of a high amount of particulates and large ligands bound to V species (size > 5 nm).

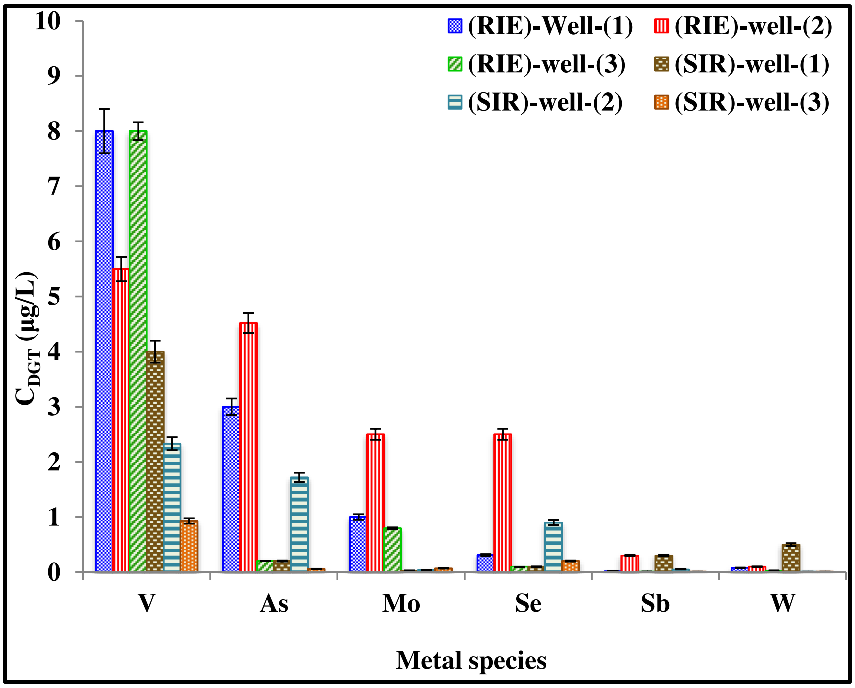


Figure 6.14. The measured concentrations of FH-DGT labile V, As, Mo, Se, Sb and W species in the selected six open Wells waters in Muscat near RIE and Sohar in Khadafan near SIR, in the Sultanate of Oman, in January 2015.

For **As**, **Mo**, **Se**, **Sb** and **W**, the FH-DGT labile species of these metals were very low, and lower than their background concentrations in groundwater in most countries:

<10 µg /L, < 10 µg /L, <10 µg /L, <5 µg /L and <1 µg /L respectively (Weiner, 2010; Li et al., 2014). Based on the obtained results, the studied open wells at both sites can be considered uncontaminated by the above oxyanions. The percentages of all targeted oxyanions labile fractions in the three studied wells in Khadafan near (SIR) ranged between 8% and 86%, which reflects the presence of iron and large organic colloidal particles that are too large to pass through the diffusive gel (Vasyukova et al., 2010); similar to the observations by Österlund et al. (2010) in river waters.

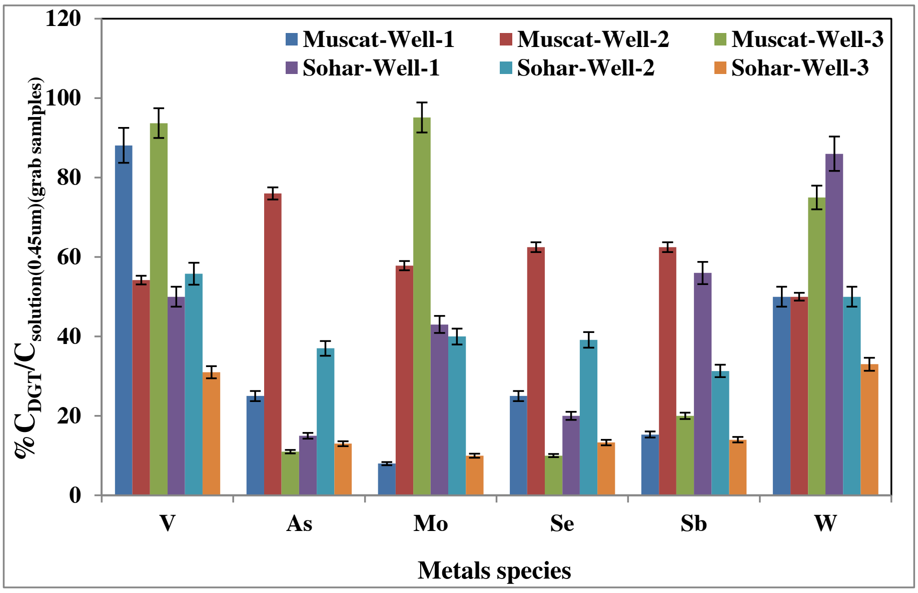


Figure 6.15. The percentages of FH-DGT labile V, As, Mo, Se, Sb and W fraction to 0.45 µm filterable grab samples in all studied six open well waters in Muscat near (RIE) and Sohar in Khadafan near (SIR), in the Sultanate of Oman, in January 2015.

It can be observed that the targeted oxyanions metals in all selected wells were low as shown in **Table 6.6**. The filtered are lower than unfiltered which is consistent with all findings. The W is the lowest because it is naturally occurring at very low level (Thorgersen et al., 2015).

Table 6.6. Comparison of targeted oxyanions metals concentrations (µg/L) in 0.45 µm filtered and unfiltered collected waters from well samples at selected wells in RIE and SIR regions.

Locations	Metals	V	As	Mo	Se	Sb	W
Well-1(RIE)	**Csol(0.45μm)**	9	12	4	4.5	0.13	0.02
	Csol(UF)	12	16.5	5.6	6	0.196	0.035
	%Csol(0.45μm)	75	73	71	75	66	57
Well-2(RIE)	**Csol(0.45μm)**	9.6	6	5	3.8	0.08	0.09
	Csol(UF)	11	8	7	5	0.1	0.12
	%Csol(0.45μm)	87.3	75.0	71.4	76.0	80.0	75.0
Well-3(RIE)	**Csol(0.45μm)**	8	2.1	0.82	1	0.05	0.041
	Csol(UF)	9	3	1.3	1.6	0.091	0.082
	%Csol(0.45μm)	88.9	70.0	63.1	62.5	54.9	50.0
Well-1 (SIR)	**Csol(0.45μm)**	8	2	0.07	0.5	0.52	0.7
	Csol(UF)	13	2.9	0.1	0.7	0.8	0.9
	%Csol(0.45μm)	61.5	69.0	70.0	71.4	65.0	77.8
Well-2 (SIR)	**Csol(0.45μm)**	4	4.7	0.09	2.3	0.16	0.04
	Csol(UF)	5	6	0.13	4	0.23	0.06
	%Csol(0.45μm)	80.0	78.3	69.2	57.5	69.6	66.7
Well-3 (SIR)	**Csol(0.45μm)**	3	0.9	0.7	1.3	0.07	0.031
	Csol(UF)	4	1.6	1.24	2	0.13	0.062
	%Csol(0.45μm)	75.0	56.3	56.5	65.0	53.8	50.0

6.4.3. Assessing labile metals and their resupply in sediments of Al Fahal port

Two versions of DGT samplers, OP-DGT and FH-DGT, were deployed in triplicates in sediments collected from two sites of beach near to a discharge point at Al Fahal port after high tides. Each site was divided into three locations perpendicular to the beach, and 300 m from each other. The results obtained after the deployment confirmed the possibility of these passive samplers being used to assess the effect of effluents discharged on trace metals fractionation, as shown in **Table 6.7** and **Figure 6.16**.

From the data, it can be seen that most of the total concentrations of the trace metals that were considered for the present work (Fe, Ni, Cu, V, As, Se and Mo) were high in 0.45 µm filterable pore waters at all selected locations, and did not vary significantly. This is probably attributed to the high inputs originating from antifouling paints, discharges from the refinery, and oil spill.

Table 6.7. Measured concentrations total content of all studied trace metals in 0.45 filtered pore waters and labile studied trace metals fractions by OP-DGT and FH-DGT (µg/L) for oxyanions near discharge point of refinery in Al Fahal port, Muscat, Sultanate of Oman.

Metals	Al Fahal sediments site (A) at 200 m distance from the discharge point.						Al Fahal sediments site (B) at 400 m distance from the discharge point.					
	A-L1		A-L2		A-L3		B-L1		B-L2		B-L3	
	C_{ICP-MS} pore water (µg/L)	C_{DGT} (µg/L)	C_{ICP-MS} pore water (µg/L)	C_{DGT} (µg/L)	C_{ICP-MS} pore water (µg/L)	C_{DGT} (µg/L)	C_{ICP-MS} pore water (µg/L)	C_{DGT} (µg/L)	C_{ICP-MS} pore water (µg/L)	C_{DGT} (µg/L)	C_{ICP-MS} pore water (µg/L)	C_{DGT} (µg/L)
Al	9.00	0.67	3.50	0.40	4.25	0.27	5.00	0.23	7.00	0.30	10.00	0.35
Cr	6.00	0.20	4.70	0.20	3.00	0.04	3.00	0.10	7.00	0.06	6.00	0.04
Mn	0.90	0.60	0.72	0.48	0.92	0.50	0.70	0.47	1.50	0.65	1.10	1.00
Fe	50.00	14.70	56.00	17.00	64.00	17.00	73.00	24.50	100.0	22.00	78.00	20.50
Co	0.30	0.01	0.38	0.01	0.40	0.02	0.36	0.01	0.40	0.02	0.45	0.02
Ni	4.00	0.31	6.00	0.30	5.00	0.20	11.00	0.02	11.00	0.30	13.00	0.30
Cu	5.00	0.20	7.50	0.25	8.00	0.16	10.00	0.15	8.00	0.13	11.00	0.14
Zn	9.00	1.90	6.50	2.00	5.00	1.40	5.00	1.30	5.00	1.30	7.00	2.17
Cd	0.09	0.01	0.08	0.01	0.07	0.02	0.10	0.03	0.10	0.02	0.10	0.03
Pb	0.05	0.03	0.08	0.02	0.09	0.03	0.20	0.04	0.40	0.04	0.17	0.06
V	70.00	0.70	68.00	0.75	65.00	0.67	62.00	0.90	67.00	1.00	80.00	0.71
As	13.80	1.00	12.00	0.40	13.00	0.31	11.00	0.46	11.00	0.48	12.00	0.45
Se	21.00	4.00	22.00	0.30	12.00	0.39	9.00	0.20	7.00	0.12	6.00	0.12
Mo	20.00	0.53	12.00	0.40	10.00	0.43	12.00	0.70	10.00	0.40	14.00	0.43
Sb	1.30	0.02	0.56	0.02	0.30	0.03	0.39	0.02	0.31	0.03	0.45	0.02
W	0.40	0.01	0.37	0.03	0.31	0.03	0.20	0.04	0.25	0.19	0.25	0.03

This is consistent with observations made by Al-Husaini et al. (2014) for Cu and V in Al Fahal port. Vanadium (V) and Nickel (Ni) are generally considered as a fingerprint of oil contamination present in organometallic complexes in crude oil (Duyck et al., 2007).

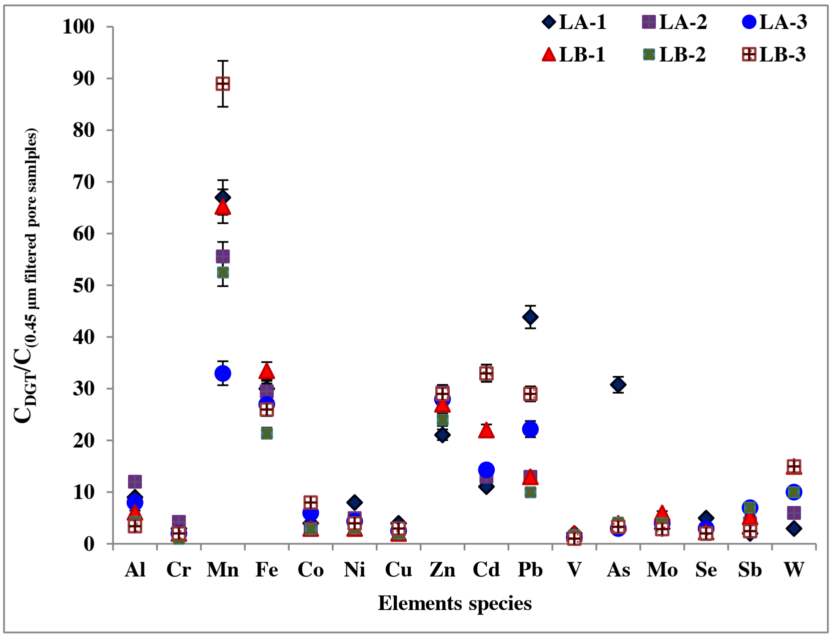


Figure 6.16. Percentages of labile trace metals fractions using OP-DGT and FH-DGT in 0.45μm filterable pore waters near discharge point of a refinery in Al Fahal port, Muscat, Sultanate of Oman.

The C_{DGT}-labile fractions of Fe, Ni, Cu, and V increased towards location LB-3 as the distance increased away from the discharge point. Lacerda et al. (2013) found similar observations near oil exploration activity. This could be attributed to the decrease of large and strong organic ligands (size > 5 nm) away from the discharged effluents, and water discharges from an oil production refinery. On the other hand, they could be associated with organic ligands that can dissociate fast and cross the diffusive gel to the resin. The ratios of concentrations of DGT-labile fractions of Al, Cr, Co; Ni, Cu, Zn, Cd, and Pb showed slow resupply from solid phase in sediments at all selected locations, and varied slightly with ranging from 0.01-0.44 (**Figure 6.16**). This suggests that all species associated with strong DOM in the areas studied, and colloidal Fe oxy/hydroxides (size > 5 nm), are able to pass through the 0.45µm filters sample, but they are too large to cross through the hydrogel to be trapped in the resin. In many coastal and harbour environments, Mn and Fe can be measured at high concentrations. It can be observed that Cu and Cr measured at very low percentages, which indicates that both metals fractions associate more strongly to many different chelating agents and large aromatic DOM, than other divalent species in all studied locations, due to intensive oil transportation refinery industry activities.

For **Mn**, it binds more weakly with ligands compared to other metals, in accordance with the Chelex-100 information in the manual from Bio-Rad. The percentages of C_{DGT}-labile Mn fractions were higher and ranged between 0.33 and 0.89, which reflects that Mn is present as free ions with fast diffusing species through the hydrogel in DGT, or bound weakly to ligands that can dissociate fast. Often Mn^{2+} can be displaced by Fe^{2+} in sediments containing high levels of Fe, and measured at very low concentrations (Tankéré-Muller et al., 2012). As Fe is not stable, it can be oxidized to the more stable Fe, which is complexed strongly with carboxylic acid functional groups in Chelx-100. The ratio of C_{DGT}-labile of Fe labile species ranged from 0.22 to 0.334 in all studied sites, which indicates that Fe species associated with aromatic organic ligands/colloids and sulfides released from the refinery and discharged water ballast from transport tankers (Gao et al., 2009; Al-Husaini et al., 2014). Similar results were found by Ahumada et al. (2011) for the above trace metals in sediments.

The FH-DGT concentrations of labile V, As, Se, and Mo fractions were very low and not significantly different at all studied locations; they were consistently higher than the concentrations in pore waters ($p<0.001$) with percentages (0.01-0.3) as shown in **Table 6.7** This is most probably attributed to the weaker binding of these anions to FH at high pH ≈ 8.17, or it could be associated with Fe oxyhydroxides and organic colloids around the refinery industry (Österlund et al., 2010; Vasyukova et al., 2010).

Considering the above, it can be said that the fractionations of the studied trace metals were strongly influenced by sulfide, carbonate, aromatic organic matter, colloids, and other ligands, in the sediments at all selected locations in Al Fahal port near a discharge point of the refinery. Based on the obtained findings, it can be observed that certain locations in Al Fahal economic port suffer from a slight increase in some metals, such as V, Fe, Ni, and Cu. This is consistent with a previous study by Al-Husaini et al. (2014); furthermore, similar observations were found by Al-Shuely et al. (2009).

6.4.4. Assessing labile metals, pool size and their kinetic properties in soils

6.4.4.1. Soil pH, Organic Matter and Total Metal Concentrations

The chemical properties of collected soils (%OC, pH and total extractable metals concentrations) obtained according to the methods described in **section 6.3.3.5**, are presented in **Table 6.8**. The %OC levels were varied and ranged between 11% and 19% with significant differences between Locations (1, 12, 13, 14 and 15), ($p<0.05$) for all the selected locations, which shows the variation degree of organic matter contamination along the coast near SIR. All collected soils samples contained medium organic matter levels, except in location-1 near to (SIR) which exhibited a high percent of OM; this reflects the presence of more intense oil and industrial contamination.

Table 6.8. General properties of soils collected from the study area near Sohar Industrial Region, Sultanate of Oman.

Location	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L12	L13	L14	L15
%OC	19	15	15.7	14.7	14.6	15.7	14.9	14	14.4	15	14.3	11	12	12	11
pH (CaCl2)	9.6	9.2	8.6	8.6	8.1	8.06	8.2	7.43	8.7	8.1	8.6	8.4	8	8.4	8.7
Metals	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)	Total(mg/Kg)
Al	6867.0	6409.0	6211.0	6180.0	5547.0	6590.0	3976.0	5624.0	6122.0	5068.0	4290.0	4716.0	4690.0	6369.0	6191.0
Cr	243.7	229.8	207.5	228.4	164.8	261.8	154.0	154.0	194.0	196.0	152.0	176.0	155.0	220.0	151.0
Mn	407.5	442.8	536.3	463.0	385.9	483.3	337.1	404.1	479.6	385.5	387.9	430.6	438.3	438.3	417.4
Fe	10670.0	11910.0	12270.0	12310.0	9823.0	12530.0	10820.0	11270.0	12210.0	10560.0	9936.0	893.5	13340.0	11460.0	10630.0
Co	18.1	21.9	23.7	23.8	16.1	22.9	17.5	19.8	400.3	18.3	16.6	19.5	23.5	20.9	18.0
Ni	758.9	871.3	957.2	928.3	684.8	919.9	707.1	802.3	753.9	883.2	694.4	789.7	921.0	883.2	746.6
Cu	13.0	9.6	11.4	10.9	9.1	11.6	7.4	9.0	11.6	10.4	8.8	11.1	9.9	10.6	12.3
Zn	94.9	144.9	24.6	135.2	96.1	124.8	136.1	64.7	28.3	87.9	132.5	71.7	83.0	76.1	67.7
Cd	0.0340	0.0300	0.0400	0.0340	0.0450	0.0340	0.0190	0.0260	0.0290	0.0310	0.0320	0.0270	0.0190	0.0240	0.0240
Pb	1.464	1.355	1.510	1.489	1.260	1.657	1.005	1.193	1.434	1.330	1.271	1.197	1.167	1.564	1.276
V	6.486	8.000	7.000	7.400	6.036	8.331	7.488	7.040	6.584	6.425	5.876	7.445	10.570	6.506	7.267
As	6.842	4.994	5.292	4.457	5.774	5.112	3.845	4.792	4.813	4.583	5.029	4.508	4.762	3.414	3.448
Se	0.055	0.143	0.118	0.062	0.007	0.018	0.008	0.002	0.002	0.001	0.001	0.013	0.002	LD	0.001
Mo	0.463	0.206	0.206	0.453	0.415	0.246	0.195	0.163	0.252	0.891	0.205	0.229	0.202	0.295	0.165
Sb	2.532	2.063	0.081	2.080	1.947	2.339	1.773	1.631	1.730	1.556	1.780	1.741	1.693	1.935	2.071
W	0.160	0.125	0.186	0.093	0.081	0.081	0.062	0.061	0.058	0.049	0.060	0.091	0.043	0.044	0.036

The **pH** soils were measured following the method described in **section 6.3.3.5**. At all studied locations, there was no substantial difference in the obtained values of the soils' pH: they ranged from 7.43-9.6. At locations-1 and -2, pH values exceeded 9 (highly alkaline), which indicates presence of high levels of bicarbonate, carbonate, aluminum (Al), and iron (Fe) fractions due to the influence of various human activities related to the refinery and heavy industries in (SIR) (Leytem and Mikkelsen, 2005; Dursun and Mikailsoy, 2015).

Total concentrations of studied trace metals were determined according to the method described in **section 6.3.3.5.** The background levels of trace metals in soils are important: Soil background concentrations of heavy metals are essential standards for assessing the quality of soils in the environment (Chen et al., 2004). There is a lack of database on background concentrations in Oman soils, and there is limited information on local measurements. Various international studies have reported background concentrations of trace metals in soils, as shown in **Table 6.9** (Boulding, 1996; Chen et al., 2004; Su and Yang, 2008; Alloway, 2010; Alfaro et al., 2015).

Table 6.9. Natural background levels (mg/kg) of studied metals in soils from other countries in the literature.

Metals (mg/kg)	Cuba	China	Ireland	USA	Beijing	The average
Cd	1.2	0.07	0.2	1.6	0.119	0.64
Pb	34.6	24	20	16	57.5	30.42
Zn	90.7	67	72	48	57.5	67.04
Cu	83.7	20.0	19.15	17	18.7	31.71
Ni	294.2	23	12.45	13	24.6	73.45
Cr	463.2	54	37	37	29.8	124.20
V	127.1	77	47.5	58	ND	77.40
Sb	6.9	1.1	ND	ND	ND	4.00
Co	31.4	11	8.4	16.5	ND	16.83
Mo	0.5	1.2	0.3	ND	ND	0.67
As	10.8	9.2	3.2	17.8	7.09	9.62
Al (g/kg)		49.9				49.90
Fe (g/kg)		19.1				19.10
W			0.7-2.7			0.7-2.7
Se		0.1-2				0.1-2
Mn		0.5-500				0.5-500

The average of the measured total content of studied trace metals in soil samples at all selected locations was within the international standard for soils, except for Co and Ni in all analysed samples which exceeded the alert levels, as illustrated in **Tables 6.8** and **6.9**. The high concentrations of Ni and Co in the soils around commercial areas is no doubt associated with the important influence of refinery and industrial activities. Similar observations showing exceeding concentrations of Ni were reported by Baawain et al. (2014).

6.4.4.2. Labile metals, soil solution and solid phase extraction

DGT-measured concentrations.

The data for the concentrations of studied metals measured by DGT are shown in **Tables 6.10** and **6.11**. It can be seen that all studied metals were detected by DGT in almost all selected soils along coastal area around (SIR). Results showed a significant variation of measured metal concentrations by both the DGT and soil solutions methods in all selected soils probably attributed to the variation of industrial effluents and crude oil spills. The highest DGT concentration of Al, Fe and Mn at (L6, L7, L8, L9, L10, L11, L12 and L14) soils ranged from (12-22 µg/L), (14-63 µg/L) and (9-17µg/L) respectively. The values indicate that, among the metal Fe was present in high concentration; however, it was in the range of background level (Aslam et al., 2013). Whereas, Cr, Co, Ni, Cu, Zn, Pb and Cu were present relatively in low DGT concentrations at average range between 0.02 µg/L and 2.1 µg/L in all selected soils samples. This is probably attributed to the stable colloids and large aromatic ligands that hinder metals resupply from the solid phase. Additionally, it may be possible to increase the time deployment of DGT from 16 hours to 24 hours, which would allow for more dissociation of labile organic fractions and stable colloidal ligands through the diffusive layer (Conesa, Schulin et al. 2010).

The FH-DGT concentrations of labile V, As, Se, Mo, Sb, and W fractions were very low and follow a similar trend in all collected soils, with average range between 0.02±0.0026 µg/L to 2.13± 0.12 µg/L. Based on the C_{DGT} of studied trace metals in the selected soils around (SIR), the coastal soils can be considered uncontaminated and safe.

Soil solutions concentrations

The concentrations of studied trace metals in the soil solutions (post-DGT deployment) are shown in **Tables 6.10** and **6.11**. Similarly, here also a significant variation among the metals concentrations was observed and the highest concentrations were detected by both the DGT and porewater methods in the locations soils (L6, L7, L8, L9, L10, L11, L12 and L14). The general distribution of Cr, Mn, Co, Ni and Zn and Sb concentrations in soil solutions is similar to that of the measured concentrations in DGT **Tables 6.10** and **6.11**. The reasonable correlation for most studied metals at most locations indicates that DGT sampler is a suitable dynamic technique for assessing soil solutions metals concentrations trends in coastal sandy soils impacted with industrial and crude oil activities. Interestingly, the concentrations of Al in soil solutions at locations (L2, L12 and l3) was higher than 6 times higher than C_{DGT}-labile Al fractions, which reflects the poorer accumulate of Al by the Chelex resin (Panther et al., 2012). The highest soil solutions concentrations of Fe were measured in the locations soils (L9, L10 and L11), 119, 129 and 133 µg/kg respectively, however low ratios of Fe were detected by DGT in these selected soils samples, indicating lower lability of Fe fractions in locations. The total dissolved concentrations of Cd, Pb, V, As, Se, Mo, Sb, and W in all selected soils were generally low, which was consistent with its lower total content.

R values = ($C_{DGT}/C_{solution}$)

The R values of metals in all collected soils presented in **Tables 6.10** and **6.11**. The R ratios for Cr, Mn, Co, Ni and Zn ranged between (0.30-0.80), (0.5-1.08) and (0.39-0.84), (0.50-0.86) and (0.35-0.82) respectively, representing an intermediate capacity for metal resupply from the solid phase. Also, it appears that Mn and Ni are resupplied more easily than Cu from the soil solid phase. Whereas the R values of Al, Fe, Cu, Cd and Pb ranged between 0.14 and 0.80, generally indicating an intermediate capacity for metal resupply from the solid phase.

The obtained R values of V, As, Se, Mo, Sb, and W species in collected soils ranged from 0.04 to 0.70 at all locations, as shown in the **Tables 6.10** and **6.11**, which indicates poor buffering of metals concentrations from solid phase resupply. This is attributed to the presence of non-labile metal-ligands and colloids dissociating very slow providing poor resupply to the solution (Zhang et al., 1998; Senila et al., 2012).

The R values for all metals except Mn generally did not show such good agreement between C_{DGT} and $C_{solution}$ for all selected soils. This appears that metals in the soils generally are appreciably complexed by organic ligands and diffuse slowly through the gel, and DGT will measure only a proportion of the metal in solution (Zhang et al., 2006).

$CaCl_2$ extraction (solid phase)

The averages of extractable targeted metal contents obtained by 0.01M $CaCl_2$ extractions are presented in **Tables 6.10** and **6.11**. Compared to the metal contents in the **Table 6.8**, the average concentrations of the $CaCl_2$ extracted metals fractions were relatively low in all selected soils may be due to Fe and Mn oxide minerals and ligands. The concentrations of Co, Cr, Cu, Pb, Cd, V, As, Se, Mo, Sb, and W showed a considerable variation and were low at all selected locations, which is consistent with the findings in **Table 6.8**, probably due to the low content in soils. The measured total dissolved concentrations of Fe and V were high in L13 and L15 probably due to the crude oil contamination in these areas. Similarly, the obtained concentrations of Al, Mn, Fe and Ni were also low (166-277), (22-44), (210-666) and (44-85) respectively, which is inconsistent with the high total content in **Table 6.8** this may be attributed to the present of large stable oil ligands in the area.

Table 6.10. The measured C_{DGT} (μg/L), Csol, R values and extracted concentrations in $CaCl_2$ solutions (μg/kg) of targeted 10 trace metals in fifteen sandy coastal soils, around (Sohar Industrial Region), Sultanate of Oman, January 2015.

Metal			Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd
L1	C_{DGT}	μg/L	7.50	0.40	4.00	12.0	0.08	1.40	0.91	2.00	0.02
	Csol	μg/L	30.00	1.35	7.00	83.0	0.19	2.50	2.40	3.00	0.06
	R		0.25	0.30	0.57	0.14	0.43	0.56	0.38	0.67	0.33
	C.CaCl2	μg/Kg	277.50	2.44	22.20	310.80	3.33	84.36	28.86	222.00	1.22
L2	C_{DGT}	μg/L	6.00	0.44	7.10	13.0	0.13	1.30	0.60	1.31	0.03
	Csol	μg/L	42.00	1.40	10.00	32.0	0.18	2.60	2.50	3.20	0.07
	R		0.14	0.31	0.71	0.41	0.74	0.50	0.24	0.41	0.43
	C.CaCl2	μg/Kg	177.60	3.33	27.75	199.80	2.22	74.37	36.63	199.80	1.11
L3	C_{DGT}	μg/L	12.00	0.60	5.00	13.0	0.10	1.60	1.22	2.10	0.01
	Csol	μg/L	41.00	1.44	7.20	30.0	0.08	2.70	2.90	4.81	0.06
	R		0.29	0.42	0.63	0.43	1.27	0.59	0.42	0.44	0.24
	C.CaCl2	μg/Kg	155.40	5.00	25.86	388.50	1.55	73.04	38.85	238.65	1.44
L4	C_{DGT}	μg/L	9.30	0.83	13.50	10.3	0.07	1.30	0.82	1.53	0.02
	Csol	μg/L	41.00	1.10	11.00	29.0	0.09	2.00	2.18	4.35	0.07
	R		0.23	0.75	1.23	0.36	0.75	0.65	0.38	0.35	0.31
	C.CaCl2	μg/Kg	166.50	4.55	24.42	255.30	32.19	65.49	41.07	182.04	2.22
L5	C_{DGT}	μg/L	10.42	0.70	10.10	9.0	0.12	3.300	1.21	1.64	0.02
	Csol	μg/L	45.00	1.20	8.00	25.0	0.16	5.00	2.20	2.00	0.07
	R		0.23	0.58	1.26	0.33	0.75	0.66	0.55	0.82	0.34
	C.CaCl2	μg/Kg	166.50	6.33	23.31	255.30	33.30	65.49	35.52	182.04	2.22
L6	C_{DGT}	μg/L	11.83	0.50	11.60	42.0	0.20	4.50	1.30	1.10	0.02
	Csol	μg/L	41.00	1.33	11.00	98.0	0.10	7.00	3.80	5.40	0.05
	R		0.29	0.38	1.05	0.43	2.08	0.64	0.34	0.20	0.37
	C.CaCl2	μg/Kg	166.50	4.44	25.53	410.70	4.44	66.60	46.62	155.40	1.33
L7	C_{DGT}	μg/L	12.11	0.90	15.60	24.0	0.30	6.10	1.72	1.30	0.04
	Csol	μg/L	50.00	1.80	15.00	113.0	0.37	5.00	4.80	2.40	0.05
	R		0.24	0.50	1.04	0.21	0.81	1.22	0.36	0.54	0.80
	C.CaCl2	μg/Kg	157.62	3.89	33.30	210.90	21.31	56.61	37.74	166.50	1.33
L8	C_{DGT}	μg/L	13.00	1.00	16.33	52.0	0.15	5.00	0.16	2.00	0.05
	Csol	μg/L	39.00	1.60	18.00	109.0	0.06	7.00	3.11	6.00	0.07
	R		0.33	0.63	0.91	0.48	2.50	0.71	0.05	0.33	0.71
	C.CaCl2	μg/Kg	161.50	5.10	33.30	222.00	33.30	44.40	38.85	144.30	2.22
L9	C_{DGT}	μg/L	10.30	0.60	14.60	50.0	0.12	3.10	0.82	1.00	0.03
	Csol	μg/L	41.00	1.10	13.50	119.0	0.06	4.50	3.70	2.10	0.05
	R		0.25	0.55	1.08	0.42	1.97	0.69	0.22	0.48	0.60
	C.CaCl2	μg/Kg	133.20	9.99	25.53	188.70	24.42	44.40	39.96	155.40	1.11
L10	C_{DGT}	μg/L	17.20	0.70	10.00	31.0	0.08	3.00	1.50	4.50	0.01
	Csol	μg/L	57.00	1.50	11.00	129.0	0.07	5.00	4.50	12.00	0.07
	R		0.30	0.47	0.91	0.24	1.17	0.60	0.33	0.38	0.14
	C.CaCl2	μg/Kg	155.40	7.77	33.30	222.00	2.22	44.40	28.86	172.05	4.44
L11	C_{DGT}	μg/L	16.20	0.50	14.34	59.0	0.15	6.00	1.22	3.50	0.03
	Csol	μg/L	53.00	1.50	12.80	133.0	0.24	7.00	4.50	5.00	0.07
	R		0.31	0.33	1.12	0.44	0.63	0.86	0.27	0.70	0.43
	C.CaCl2	μg/Kg	188.70	7.77	44.40	222.00	19.98	55.50	33.30	166.50	4.44
L12	C_{DGT}	μg/L	9.20	0.30	9.00	17.0	0.20	3.00	2.00	1.50	0.02
	Csol	μg/L	51.00	1.40	11.00	112.0	0.30	7.00	6.00	2.00	0.08
	R		0.18	0.21	0.82	0.15	0.67	0.43	0.33	0.75	0.25
	C.CaCl2	μg/Kg	166.50	4.44	38.85	222.00	4.44	49.95	33.30	155.40	5.00
L13	C_{DGT}	μg/L	8.00	0.40	15.00	24.0	0.10	3.00	1.30	2.00	0.01
	Csol	μg/L	45.00	1.60	13.50	14.0	0.27	5.10	5.00	4.00	0.07
	R		0.22	0.25	1.11	1.71	0.37	0.59	0.26	0.50	0.15
	C.CaCl2	μg/Kg	160.95	5.55	38.85	222.00	21.09	44.40	33.30	133.20	3.33
L14	C_{DGT}	μg/L	22.00	0.60	17.00	63.0	0.43	6.00	1.50	2.00	0.03
	Csol	μg/L	51.00	1.55	16.50	111.0	0.54	5.00	6.00	3.00	0.08
	R		0.43	0.39	1.03	0.57	0.80	1.20	0.25	0.67	0.37
	C.CaCl2	μg/Kg	144.30	6.66	38.85	366.30	2.78	49.95	33.30	144.30	0.22
L15	C_{DGT}	μg/L	13.00	0.40	10.00	31.0	0.12	2.00	1.40	1.30	0.01
	Csol	μg/L	53.00	1.53	12.40	107.0	0.30	2.82	3.00	2.00	0.08
	R		0.25	0.26	0.81	0.29	0.40	0.71	0.47	0.65	0.12
	C.CaCl2	μg/Kg	133.20	11.10	44.40	666.00	21.09	44.40	33.30	133.20	0.22

Table 6.11. The measured C_{DGT} (µg/L), Csol, R values and extracted concentrations in $CaCl_2$ solutions (µg/kg) of targeted oxyanions metals in fifteen sandy coastal soils, around (Sohar Industrial Region), Sultanate of Oman, January 2015.

Metal			V	As	Se	Mo	Sb	W
L1	C_{DGT}	µg/L	1.00	0.52	0.30	1.00	0.20	0.10
	Csol	µg/L	5.30	2.80	4.00	6.00	0.30	0.56
	R		0.19	0.19	0.08	0.17	0.67	0.18
	C.CaCl2	µg/Kg	17.76	19.98	27.75	46.62	33.30	33.30
L2	C_{DGT}	µg/L	0.68	0.54	0.20	0.95	0.16	0.17
	Csol	µg/L	5.90	3.60	3.00	2.00	0.23	0.25
	R		0.12	0.15	0.07	0.48	0.70	0.68
	C.CaCl2	µg/Kg	4.63	18.87	22.20	43.29	32.19	22.20
L3	C_{DGT}	µg/L	1.10	0.60	0.20	0.89	0.15	0.06
	Csol	µg/L	7.00	4.40	3.20	3.60	0.13	0.28
	R		0.16	0.14	0.06	0.25	1.18	0.22
	C.CaCl2	µg/Kg	38.85	26.64	24.42	38.85	25.77	23.31
L4	C_{DGT}	µg/L	0.60	1.00	0.30	0.60	0.06	0.02
	Csol	µg/L	6.20	4.00	3.00	4.70	0.14	0.25
	R		0.10	0.25	0.10	0.13	0.43	0.08
	C.CaCl2	µg/Kg	16.65	25.53	22.20	34.41	24.42	21.09
L5	C_{DGT}	µg/L	0.70	0.50	0.40	0.74	0.07	0.02
	Csol	µg/L	9.00	1.70	6.00	4.00	0.24	0.25
	R		0.08	0.29	0.07	0.19	0.28	0.06
	C.CaCl2	µg/Kg	27.75	36.63	18.65	34.41	18.87	19.98
L6	C_{DGT}	µg/L	1.00	0.50	0.60	1.40	0.10	0.03
	Csol	µg/L	8.83	4.50	5.00	6.00	0.20	0.09
	R		0.11	0.11	0.12	0.23	0.50	0.33
	C.CaCl2	µg/Kg	37.74	34.41	31.08	44.40	22.20	18.87
L7	C_{DGT}	µg/L	0.78	0.44	0.40	2.10	0.11	0.04
	Csol	µg/L	7.63	2.70	6.00	6.00	0.40	0.08
	R		0.10	0.16	0.07	0.35	0.28	0.44
	C.CaCl2	µg/Kg	41.07	27.75	29.97	35.74	7.77	15.54
L8	C_{DGT}	µg/L	0.50	0.47	0.30	1.66	0.12	0.03
	Csol	µg/L	12.00	2.00	4.20	7.00	0.40	0.20
	R		0.04	0.24	0.07	0.24	0.30	0.15
	C.CaCl2	µg/Kg	25.86	37.74	22.20	66.60	22.20	13.32
L9	C_{DGT}	µg/L	0.70	0.67	0.20	0.70	0.30	0.02
	Csol	µg/L	10.00	3.80	3.00	4.50	0.57	0.08
	R		0.07	0.18	0.07	0.16	0.53	0.25
	C.CaCl2	µg/Kg	29.97	28.19	27.75	55.50	22.20	11.10
L10	C_{DGT}	µg/L	0.63	0.61	0.20	0.90	0.10	0.02
	Csol	µg/L	13.00	6.50	3.00	6.00	0.30	0.10
	R		0.05	0.09	0.07	0.15	0.33	0.20
	C.CaCl2	µg/Kg	38.85	35.52	14.43	33.30	22.20	11.10
L11	C_{DGT}	µg/L	0.70	1.00	0.20	1.00	0.07	0.04
	Csol	µg/L	8.00	4.00	4.00	4.30	0.24	0.09
	R		0.09	0.25	0.05	0.23	0.29	0.45
	C.CaCl2	µg/Kg	33.30	25.20	22.20	33.30	22.20	11.10
L12	C_{DGT}	µg/L	0.69	0.52	0.30	0.80	0.09	0.04
	Csol	µg/L	9.00	5.00	6.00	4.00	0.30	0.09
	R		0.08	0.10	0.05	0.20	0.30	0.44
	C.CaCl2	µg/Kg	25.53	32.19	22.20	33.30	16.65	8.33
L13	C_{DGT}	µg/L	0.50	0.42	0.50	1.20	0.09	0.04
	Csol	µg/L	8.00	3.00	4.80	5.00	0.25	0.10
	R		0.06	0.14	0.10	0.24	0.36	0.40
	C.CaCl2	µg/Kg	166.50	24.98	22.20	33.30	22.20	6.66
L14	C_{DGT}	µg/L	0.70	0.50	0.70	1.30	0.09	0.02
	Csol	µg/L	7.00	3.00	3.00	4.50	0.25	0.09
	R		0.10	0.17	0.23	0.29	0.36	0.23
	C.CaCl2	µg/Kg	33.30	15.54	22.20	38.85	34.41	6.11
L15	C_{DGT}	µg/L	0.70	0.60	0.20	1.50	0.03	0.03
	Csol	µg/L	9.00	4.00	2.20	5.80	0.27	0.10
	R		0.08	0.15	0.09	0.26	0.11	0.26
	C.CaCl2	µg/Kg	44.40	21.09	19.98	25.53	14.43	5.00

6.4.4.3. Assessing resupply pool size and kinetic parameters using DIFS

Whereas K_d basically controls the extent of the amount of trace metals that can be resupplied by the solid phase in soils, Tc and k_{-1} relate directly to capacity of solid phase to resupply the metals concentration into soil solutions (Chen et al., 2014).

6.4.4.3.1. The distribution coefficient, (Kd)

The distribution coefficient, K_d, expressed as the ratio between the concentrations extractable metal in the solid phase and its concentration in soil solutions using the following **equation (6.5)** (Lehto et al., 2008):

$$K_d = \frac{C_{\text{solid phase}}}{C_{\text{soil solution}}} \qquad (6.5)$$

For 15 selected soils K_d ranged from (1.8-33) ml/g for (Al, Cr, Mn, Fe, Ni and Cu) as illustrated in **Table 6.11**. The crude oil spills and industrial effluents in these locations appeared to decrease the available solid phase pool of these metals for selected soils. This is consistent with lower labile metals concentrations of (Al, Cr, Mn, Fe, Ni and Cu) in DGT and the total dissolved content in soil solutions with a significant variation in all soils. For Co, clearly the (K_d) values in soils samples of (L1, l2, L3, L10, L12 and L14) are low and ranged between (5-34) ml/g, probably due to the organic ligands introduced by crude oil spills may modify the availability of Co species from the solid phase. For soils samples from locations (L4, L5, L6, L7, L8, L9 and L13), the K_d values were high and ranged between (46-555) ml/g, which suggests that suggest that a substantial fraction of the background metal is in non-labile form.

The K_d values of Zn were low in soils at (L6, L8, L10, L11 an L13), ranged between (14-33) ml/g and high at (L1-5, L7, L9, L12, L14 and L15) ranged from (41-

91) ml/g. For the soils collected from (L10-L13), the K_d values of Cd were higher than other locations and ranged between (50-63) ml/g **Table 6.11**. The K_d values of Pb were high at (L2, L7, L8 and L11) of 266, 65, 43 and 55 ml/g respectively. The higher values of K_d indicated that a high metals fractions retention by the solid phase through sorption reactions and low concentration available in the soil solution (Mench et al., 2000).

The K_d values of oxyanion metals V, As, Se and Mo in **Table 6.12** are low at all selected locations, which suggests that the metals sorption appeared to be strongly influenced by more stable colloidal organic ligands in the all selected soils or due to their low contents in the soils. The elements Sb and W showed in general a high average values of (K_d) in the selected soils, indicating highly labile, which imply that a substantial fraction of the background metal is in non-labile form (Mench et al., 2000).

6.4.4.3.2. Response time (Tc)

Tc values were obtained using DIFS model as described in **Chapter 5**. Tc reflects the kinetics of supply, which is influenced by both the concentration in the solid phase, pool size, and the dissociation rate (Zhang et al., 2006). It can be noted that Tc values of all trace metals in selected metals were low, indicating a very fast supply of metals (**Table 6.12**). For oxyanions metals they obtained Tc values generally high in all selected soils, which indicates a reduction of resupply from the solid phase to soil solution due to low content of these metals in soils (**Table 6.13**). This is consistent with findings of total content in soils in **Table 6.8**.

6.4.4.3.3. Dissociation rate (K_{-1})

The dissociation rates k_{-1} were calculated from Tc, Pc, and K_d using **equation (5.6)** in **Chapter 5**. The maximum values of Tc produce minimum values of k_{-1} as shown in **Tables 6.12** and **6.13**. For Al in soils samples in (L1 and L2), Co in (L13), Cu in (L8 and L9), Zn in (L2, L3, l4, L6 and L9), Cd in (L1, L3, L4, L5, L10, L11, L12, L13 and L15), values of k_{-1} were approximately in the average 6.1 x 10^{-5} /s. This is consistent with the high R values in **Table 6.9**, showing that soils in the locations had poorer resupply ability from solid phases to the soil solutions. For Pb, the K_{-1} values for soils in locations (L1, L2, L4, L8, L9, L12, L15) were, 4.3 x 10^{-6} /s, 1.0 x 10^{-6} /s, 2.92 x 10^{-5} /s, 5.0 x 10^{-4} /s, 3.4 x 10^{-6} /s, 9.5 x 10^{-6} /s, 1.1 x 10^{-5}/s. which indicates slow supply of Pb in these locations comparing to others selected locations. For the oxyanions metals the k_{-1} values for all selected soils generally exhibited a very slow resupply from solid phase to solutions, as shown in **Table 6.13.**

Table 6.12. Determined parameters of Kd, Tc and K-1 values for all studied metals in the collected soils near Sohar Industrial Region (SIR), sultanate of Oman.

Sites		AL	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
L1	K_d	9.25	1.81	3.17	3.74	17.8	33.7	12.0	74.00	20.4	24
	T_c	446.8	0.02	0.64	1350	0.04	0.05	0.02	0.01	166	2672
	K_{-1}	6.44E-05	5.49	0.12	5.11E-05	0.35	0.16	1.24	0.37	8.01E-05	4.26E-06
L2	K_d	4.23	2.38	2.78	6.24	12.61	28.6	14.65	62.44	15.86	266
	T_c	3114	0.50	0.05	0.05	0.50	0.10	0.05	279.00	0.04	848
	K_{-1}	1.7E-05	0.18	1.56	0.80	0.04	0.08	0.32	1.34E-05	0.36	1.04E-06
L3	K_d	3.79	3.47	3.23	12.95	19.67	27.1	13.40	49.62	26.24	2.04
	T_c	0.50	0.50	1.00	0.04	0.05	0.04	0.04	105	444.00	1.00
	K_{-1}	0.16	0.17	0.09	0.62	0.33	0.30	0.61	6.27E-05	2.79E-05	0.14
L4	K_d	4.06	4.14	2.22	8.80	346.1	32.75	18.84	41.85	34.0	39
	T_c	0.01	1.00	0.10	1.50	88	0.01	0.40	327	443	335
	K_{-1}	8.64	0.08	1.47	0.03	1.26E-05	1.16	0.05	2.78E-05	2.52E-05	2.92E-05
L5	K_d	3.70	5.27	2.91	9.46	208.13	13.10	16.15	91.02	33.13	23.31
	T_c	0.12	3.50	0.57	1.61	5.05	0.04	0.001	0.05	241.00	0.002
	K_{-1}	0.81	0.02	0.22	0.03	3.88E-04	0.78	24.67	0.10	5.05E-05	8.61
L6	K_d	4.06	3.34	2.32	4.19	46.3	9.51	12.3	28.78	24.44	17.08
	T_c	0.003	0.14	0.11	1.55	0.02	0.75	0.001	1573	0.02	0.03
	K_{-1}	24.42	0.64	1.07	0.05	0.29	0.04	25.5	7.01E-06	0.56	0.68
L7	K_d	3.15	2.16	2.22	1.87	57.6	11.32	7.86	69.38	26.64	65.59
	T_c	0.13	0.02	0.02	0.33	0.02	0.04	1.56	0.05	0.04	2.91E-04
	K_{-1}	0.84	7.42	7.25	0.53	0.33	0.92	0.03	0.12	0.34	20.75
L8	K_d	4.27	2.78	1.85	2.04	555.0	6.34	12.49	24.05	31.71	43.17
	T_c	0.44	0.12	0.02	0.04	0.02	0.002	89330	0.26	0.24	4.96E-04
	K_{-1}	0.17	0.89	8.67	3.60	0.03	25.6	2.99E-07	0.05	0.04	15.85
L9	K_d	3.25	9.08	1.89	1.59	400.33	9.87	10.80	74.0	22.20	33.98
	T_c	0.01	0.002	0.11	0.18	0.02	0.04	656.8	170.2	0.23	2237.0
	K_{-1}	14.71	13.8	1.06	0.78	0.03	0.68	3.55E-05	2.04E-05	0.05	3.37E-06
L10	K_d	2.73	5.18	3.03	1.72	34.15	8.88	6.41	14.34	63.4	9.25
	T_c	0.13	0.00	1.56	0.02	0.002	1.44	1.56	0.04	4180	0.03
	K_{-1}	0.85	35.5	0.06	9.11	6.48	0.03	0.03	0.65	1.28E-06	1.39
L11	K_d	3.56	5.18	3.47	1.67	83.25	7.93	7.40	33.30	63.43	55.5
	T_c	0.13	0.58	0.11	9.43E-04	0.05	8.23E-04	1.55	0.04	165.1	0.47
	K_{-1}	0.83	0.13	1.03	212.67	0.11	60.92	0.03	0.35	3.97E-05	0.02
L12	K_d	3.26	3.17	3.53	1.98	14.8	7.14	5.55	77.70	62.4	15.9
	T_c	0.13	0.13	0.39	0.15	1.45	8.12E-04	1.53	0.05	1122.0	2632
	K_{-1}	0.84	0.90	0.26	1.17	0.02	67.7	0.04	0.11	5.79E-06	9.54E-06
L13	K_d	3.6	3.5	2.9	15.86	78.11	8.71	6.66	33.30	50	9.25
	T_c	0.17	0.13	1.44	0.04	397	0.02	0.004	0.04	3811	0.01
	K_{-1}	0.66	0.91	0.09	0.73	1.44E-05	2.43	14.5	0.31	2.35E-06	6.40
L14	K_d	2.8	4.30	2.35	3.30	5.14	9.99	5.55	48.10	2.71	8.54
	T_c	0.14	0.84	0.02	0.41	0.002	0.77	0.002	0.05	0.54	1.22
	K_{-1}	0.86	0.10	7.06	0.25	31.2	0.05	31.6	0.17	0.23	0.03
L15	K_d	2.51	7.25	3.6	6.22	70.3	15.7	11.10	66.6	2.74	26.6
	T_c	0.13	0.90	0.36	0.02	314.6	0.15	4.11E-04	0.02	1369	983.90
	K_{-1}	0.83	0.04	0.21	2.14	1.34E-05	0.12	63.71	0.20	7.18E-05	1.13E-05

Table 6.13. Determined parameters of Kd, Tc and K-1 values for all studied oxyanions in the collected soils near Sohar Industrial Region (SIR), sultanate of Oman.

Sites		V	As	Se	Mo	Sb	W
L1	K_d	3.35	7.14	6.94	7.77	111	59.5
	T_c	0.3235	1209	7038	1574	0.0005	1997
	K_{-1}	0.234	3.06E-05	5.40E-06	2.2E-05	4.92	2.3E-06
L2	K_d	0.78	5.24	7.40	21.65	139.96	88.80
	T_c	0.003	2514	6825	0.30	46	2.5
	K_{-1}	76.72	1.71E-05	4.51E-06	0.04	3.6E-05	0.0011
L3	K_d	5.6	6.1	7.63	10.79	202.9	84.8
	T_c	2	0.001	9591	0.10	0.1	0.5
	K_{-1}	0.03	51.52	4.31E-06	0.30	0.0162	0.0077
L4	K_d	2.69	6.38	7.40	7.32	174.43	84.36
	T_c	4451	0.01	7837	3851	363	839
	K_{-1}	2.35E-05	5.68	6.34E-06	1.3E-05	6.1E-06	5.4E-06
L5	K_d	3.08	21.55	3.11	8.60	78.63	78.97
	T_c	13170	473.7	22540	676.4	1006	60320
	K_{-1}	8.88E-06	3.93E-05	5.15E-06	6.7E-05	5.1E-06	8.5E-08
L6	K_d	4.27	7.65	6.22	7.4	111	209.7
	T_c	3780	7021	4196	0.773	196.7	697.8
	K_{-1}	1.85E-05	5.74E-06	1.17E-05	0.054	1.5E-05	2.19E-06
L7	K_d	5.4	10.3	5.00	5.96	19.4	172.7
	T_c	6545	2782	24490	3.11E-04	440.8	334.1
	K_{-1}	1.1E-05	1.34E-05	3.02E-06	209.06	4.56E-05	6.89E-06
L8	K_d	2.16	18.87	5.29	9.51	55.5	66.60
	T_c	9998000	1041	23190	0.035	772.4	4043
	K_{-1}	1.37E-08	1.71E-05	2.62E-06	0.992	7.94E-06	1.26E-06
L9	K_d	3.00	7.42	9.25	12.33	38.95	138.75
	T_c	14780	1745	24670	2561	0.029	1260
	K_{-1}	5.36E-06	1.92E-05	1.12E-06	7.12E-06	0.23	1.47E-06
L10	K_d	2.99	5.46	4.81	5.55	74	111
	T_c	72340	11990	22890	1667	637.51	2178
	K_{-1}	1.42E-06	4.92E-06	2.12E-06	3.48E-05	7.22E-06	1.41E-06
L11	K_d	4.16	6.30	5.55	7.74	92.50	124.72
	T_c	8331	3.83E-04	114900	2.58E-03	945.51	281.9
	K_{-1}	1.12E-05	162.5	6.11E-07	19.9	4.76E-06	1.19E-05
L12	K_d	2.84	6.44	3.7	8.33	55.50	92.5
	T_c	12750	9620	107500	136.9	773.12	267.8
	K_{-1}	9.87E-06	6.20E-06	9.25E-07	3.42E-04	9.45E-06	1.64E-05
L13	K_d	20.81	8.325	4.625	6.66	88.81	41.669
	T_c	44990	3853	6788	3.41E-03	519.80	309.5
	K_{-1}	4.70E-07	1.33E-05	1.31E-05	18.56	9.68E-06	2.14E-05
L14	K_d	4.76	5.18	7.4	8.63	137.64	70.2
	T_c	6152	638.4	2.26E-04	1.64	569.80	1570
	K_{-1}	1.20E-05	1.07E-04	216.13	0.026	4.82E-06	3.42E-06
L15	K_d	4.93	5.27	9.08	4.40	53.25	50.97
	T_c	15670	2332	9646	0.0002	7693	1133
	K_{-1}	3.64E-06	2.30E-05	3.30E-06	311.05	7.25E-07	5.14E-06

6.5. Conclusion

Four types of DGT with different membranes and binding layers, (Nafion112)-DGT, (1000 MWCO-dialysis)-DGT, OP-DGT and FH-DGT, were used to investigate the effect of chemical contaminants on the trace metals speciation around economic large ports.

More than 97% of Al and 94% of Fe were non-labile fractions in 1000 MWCO-dialysis and Nafion112 at all the selected seawaters locations in AlFahal and (SIR) ports. Both metals were dominated by negatively charged organic complexes (>1000 MWCO). The concentrations of labile Al and Fe at (SIR) are slightly higher than the concentrations at the Al Fahal port, which is consistent with the presence of industrial discharges around (SIR). The labile concentrations of Cr, Co, Ni, Cu, Cd, and Pb were generally low and not significantly difference between the sampling locations. This suggests that theses metals may be complexed strongly with organic ligands that are less labile. The measured concentrations of labile V in the FH-DGT sampler was very low at the four selected seawaters locations ranged between 4%-5% of the total dissolved concentration due to high levels of large colloidal and strong complexing ligands in crude oil.

The obtained labile species of Ni in groundwaters were ranged between 8.4 μg/L and 82 μg/L. in SIR locations. The smallest proportion of Ni labile species (11%-29%) were measured by (Nafion112)-DGT in all selected open wells. The labile Fe concentration in Wells-1 and -2 were much higher than those in Well-3 and (RIE)'s wells. The percentages of Fe measured by (Nafion112) were 15.3%, 37% and 19% of the total dissolved reflects the presence of fairly large negatively ligands. The measured Al species in (Nafion112)-DGT at all selected open wells waters were lower than those estimated by both above versions ranged from 5% - 53%. This suggests that Al species bound to large natural and negatively charged colloidal organic ligands in all studied open wells were excluded by the Nafion112 membrane. In Khadafan near (SIR), the relative Fe labile concentration in Wells-1 and -2 were much higher than those in Well-3 and (RIE)'s wells and the measured (Nafion112)-DGT-labile Fe species were very low, 15.3%, 37% and 19% of the total content in 0.45 µm filterable grab samples respectively. This is due to the presence of Fe in large colloids/particulates and negatively complexes excluded by the Nafion112 membrane. The measured As, Mo, Se; Sb, and W concentrations in FH-DGT were very low, and lower than their background concentrations in groundwater in most countries, which indicates thate the studied open wells at both sites were uncontaminated by these above oxyanions metals. However, the percentages of all targeted oxyanions labile fractions in the three studied wells in Khadafan near (SIR) ranged between 8% and 86%, which reflects the presence of iron and large organic colloidal particles that are too large to pass through the diffusive gel

For coastal sediments near the discharge point at Al Fahal port, the total dissolved concentrations of trace metals (Fe, Ni, Cu, V, As, Se and Mo) in porewaters were high at all selected locations and did not vary significantly. This is probably attributed to the high inputs originating from antifouling paints, discharges from the refinery, and oil spill. The DGT measured labile concentrations of Fe, Ni, Cu, and V were higher near the discharge point. The ratios of concentrations of DGT-labile species of Al, Cr, Co; Ni, Cu, Zn, Cd, and Pb showed slow resupply from solid phase in sediments at all selected locations ranged from 0.01-0.44. Due to the complexation with strong DOM in the areas studied, and colloidal Fe oxy/hydroxides from crude oil.

The DGT concentration of Al, Fe and Mn in soils collected from SIR ranged from (12-22 µg/L), (14-63 µg/L) and (9-17µg/L), respectively, in line with the background level. The average concentrations of the $CaCl_2$ extracted metals were relatively low in all selected soils may be due to Fe and Mn oxide minerals and ligands. The dissociation rate (k_{-1}) from the solid phase decreased with increased crude oil ligands contamination. The K_d basically controls the extent of the amount of trace metals that can be resupplied by the solid phase in soils. For 15 selected soils K_d ranged from (1.8-33) ml/g for (Al, Cr, Mn, Fe, Ni and Cu). The (K_d) values in soils samples of (L1, l2, L3, L10, L12 and L14) are low and ranged between (5-34) ml/g. For the soils collected from (L10-L13), the Kd values of Cd were higher than other locations and ranged between (50-63) ml/g. The K_d values of Pb were high at (L2, L7, L8 and L11) of 266, 65, 43 and 55 ml/g respectively. The higher values of K_d indicated that a high metals fractions retention by the solid phase through sorption reactions and low concentration available in the soil solution. The K_d values of oxyanion metals V, As, Se and Mo were low at all selected locations, while Sb and W showed in general a high average values of (K_d) in the selected soils.

Based on the C_{DGT} of studied trace metals in the selected soils around (SIR), the coastal soils can be considered uncontaminated and safe. The DGT technique has shown to be robust and reliable, which can provide the precise information regarding the quality of the seawaters, groundwaters, soils, and sediments in the Sultanate of Oman.

Chapter 7 – General conclusions and future work

This work aims to further develop and apply the dynamic speciation technique DGT (diffusive gradients in thin films) for assessing Oman's aquatic environment. The concentrations and speciation of trace metals in seawater, sediments, soils and groundwaters at Sultanate of Oman around two large economic ports with industries and refineries and near industrial regions were measured.

The work carried out in synthetic solutions with 0.5 - 0.7 M NaCl and crude oil shows that crude oil contamination contributes to the trace metals load as WSF and labile complexes. The DGT technique has been further improved by employing varying thicknesses of diffusive layers (Δg), restricted gel, different pore size (MWCO) dialysis and Nafion112 cation exchange membranes.

Firstly, the potential of DGT technique was assessed in **Chapter 3** for determining the labile speciation of trace metals in synthetic seawaters polluted with varying concentrations of crude oil OWR% under varying mixing times. The concentrations of labile metals by all versions of DGT samplers were significantly affected by the presence of oil ligands and showed an increase as well as a decrease in metal concentrations as a result of increased amounts of crude oil OWR%. Using DGT devices containing varying thicknesses of diffusive gel showed that DGT labile species increased as a function of the diffusive layer thickness in synthetic solutions with and without oil. For Cd and Cu, DGT measurements were significantly lower than those measured by resin extraction (WSF) due to complexation with large ligands which cannot diffuse across the hydrogel. The DBLs are influenced by oil ligands (apparent layer) and it is greater than the (physical layer) (δ) explained according to the Eigen mechanism. For all trace metals studied, except for Cu at high OWR (5% and 25%), the DGT technique showed similar trends as obtained by resin extraction method. DGT of varying thicknesses were validated by demonstrating a linear mass versus 1/Δg relationship for studied trace metals in synthetic seawater with and with no oil, where experiment data were compared with DGT theoretical lines. Slight deviation of Cu and huge deviation of Cd was observed.

Combination of DGT and resin extraction methods for trace metals in solutions of different OWR% is useful for further quantitatively understand the effect of crude oil ligands on trace metals fractionation in the synthetic solution of high ionic strength.

Secondly, further development of DGT for speciation measurements of trace metals in crude oil contaminated seawater using different separation membranes was achieved in **Chapter 4**. It was found to be capable to assess the influence of the crude oil ligands of various types and sizes on the lability and mobility of targeted trace metals in high ionic strength solutions in the presence of different levels of OWR%. The diffusion coefficients through filter membrane and hydro gel with Nafioin112 were much lower than those measured through filter membrane and diffusive gel with and without dialysis**,** 35 to 40 times lower for Co, 26 to 35 times lower for Pb and Zn 20 to 26 times lower for Cu, Cd and Ni. Using Nafion112 membrane or/and dialysis membrane in DGT can further understanding metal speciation in solutions of varying OWR%. The measured concentrations of Co, Cd, Cu and Zn in (Dialysis1000 MWCO)-DGT samplers were lower than those determined in 1000 MWCO Micro Float microdialysis concentrations. This is due to the existence of low molecular weight Co, Cd, Cu and Zn species, small enough to pass through the 1000 MWCO-

Micro Float microdialysis but not labile enough to be retained in the (Dialysis 1000 MWCO)-DGT samplers.

Thirdly, the effect of crude oil and aging time on the trace metals availability in soils of different properties was investigated in **Chapter 5**. Both factors were found to significantly influence the measured metal concentrations of DGT-labile, extractable by $CaCl_2$ and soil solutions. Increases of crude oil treatments in soils promoted the formation of non-labile species of Cu and Pb and limited the availability of both metals. Values of labile pool size, K_d, and R (ratio of C_{DGT} and C_{soln}) were calculated and the kinetic parameters (response time Tc and desorption rate k_{-1}) were obtained using DIFS (DGT Induced Fluxes in Soils and sediments) model. The trend changes for k_{-1} values of studied metals in three selected soils were influenced by crude oil amendemnets and aging time. Therefore, risk assessment of a wide range of soil types is likely to be more effective when using a technique such as DGT, which accommodates the kinetic limitation.

Fourthly, the developed dynamic speciation technique DGT was used for assessing water quality and soil quality in Sultanate of Oman **Chapter 6.** Four versions of DGT devices with different membranes, OP-DGT, (1000 MWCO)-DGT, (Nafion112)-DGT and FH-DGT for speciation measurements were deployed in seawaters, grounwaters, soils and sediments.

The study clarified the picture of chemical contaminants and their effect on the trace metals concentration and speciation around these economic regions. Based on findings, the measured concentrations studied trace metals in Nafion112-DGT and (1000 MWCO-Dialysis)-DGT devices were much lower than total concentrations by ICP-MS because they a dominated by large and negatively charged organic complexes. The measured concentrations of labile V were very low at the four selected seawaters locations due to high levels of large colloidal and strong complexing ligands from crude oil contamination. The concentrations of labile Al, Ni, Zn and Fe at (SIR) are slightly higher than the concentrations at the Al Fahal port, which is consistent with the presence of industrial discharges around (SIR). The concentrations of Cr, Co, Ni, Cu, Cd, and Pb in all used DGT versions were generally low and not significantly difference between the sampling locations because they complexed strongly with oil organic ligands that are less labile. The FH-DGT-labile V species was very low at all selected seawaters due to the formation of large colloidal and strong complexing ligands in crude oil. In Khadafan near (SIR), the relative Fe, Mn and Ni labile concentration in Wells-1 and -2 were much higher than those in Well-3 and (RIE)'s wells. The measured As, Mo, Se, Sb, and W concentrations in FH-DGT were very low, and lower than their background concentrations in groundwater in most countries, which implies that all selected open waters wells in Muscat and Sohar were uncontaminated by these above.

For coastal sediments near the discharge point at Al Fahal port, the total dissolved concentrations of trace metals (Fe, Ni, Cu, V, As, Se and Mo) in porewaters were high at all selected locations and did not vary significantly due to the high inputs originating from antifouling paints, discharges from the refinery, and oil spill. The C_{DGT} of Fe, Ni, Cu, and V were higher near the discharge point.

The DGT concentrations of Al, Fe and Mn in 15 soils collected from SIR were in line with the background levels. The K_d values of oxyanion metals V, As, Se and Mo were low at all selected locations, while Sb and W showed in general a high average values of (K_d) in the selected soils. The dissociation rate (k_{-1}) from the solid phase decreased with elevated oil ligands contamination. The (K_d) values of Co in soils samples of (L1, l2, L3, L10, L12 and L14) are low and high for Cd and Pb. The

K_d values of oxyanion metals V, As, Se and Mo were low at all selected locations, while Sb and W showed in general a high average values of (K_d) in the 15 selected soils.

The obtained Tc values of all trace metals in selected metals were low, indicating a very fast supply of metals. For oxyanions metals they obtained Tc values were generally high in all selected soils, which suggest a poor buffering of these metals from the solid phase to soil solution. The Tc values of all trace metals in selected metals were low, indicating a very fast supply of metals. For oxyanions metals, the obtained Tc values generally high in all selected soils, which indicates a reduction of resupply from the solid phase to soil solution due to low content of these metals in soils. Based on the C_{DGT} of studied trace metals in the selected soils around (SIR), the coastal soils can be considered uncontaminated and safe.

The work has demonstrated that DGT technique is robust and reliable tool that can be used to assess the effect of crude oil ligands on the concentrations of available trace metals species in seawater, groundwater, sediments and soils.

Future work.

Although wide investigations on the DGT development has been performed in this study, further studies using DGT with different membranes are needed to assess the effect of crude oil ligands on the trace metals speciation.

(i) Application of these developed DGT versions to different types of crude oils under varying mixing rate, temperature, salinity, pH, photo-oxidation and separation time to gain more understanding on the performance and usefulness of DGT.

(ii) Using dialysis membranes of smaller pore size in the range 100-500 (MWCO) in DGT for more selectivity and efficiency for metals fractions discrimination in crude oil contaminated marine systems and groundwaters.

(iii) Two different applied levels of crude oil (2% and 8% v/w) often had no significance effect on Cd and Pb labile metals concentrations in studied soils. Therefore, it is necessary to point out that future work need to be conducted on crude oil contaminated soils using higher concentration and different types of crude oil to obtain a more complete picture on the assessment of the influence of oil ligands on trace metals speciation in soils extremely contaminated with crude oil.

(iv) Further studies are recommended to extend for assessing the levels of trace metals, organic compounds and pesticides in seawater, groundwaters, sediments and soils around all economic ports, industrial and agricultural practices in Sultanate of Oman using DGT dynamic technique.

(v) Develop a framework and standards that assists development of criteria for the protection of Omani environment.

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Appendixes

Appendix (A)

Table1.1- Crude analysis the results of Oman crude oil analysis using the 389 UOP method using wet ashing and ICP-OES, provided by Petroleum Development Oman (PDO).

Reporting required	Standards	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct
Effluent quality											
- Arsenic	0.1 mg/l	0.96	0.10	0.09	0.02	0.12	0.11	0.119	0.032	0.236	0.13
Aluminium as Al	5.0 mg/l	0.10	0.14	0.10	0.13	0.21	0.29				
- Cadmium	0.01 mg/l	0.03	<0.002	0.00	<0.002	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
- Chromium	0.05 mg/l	0.00	0.00	<0.01	<0.01	<0.01	<0.01	<0.01	0.002	<0.01	0.01
- Copper	0.2 mg/l	0.00	<0.01	0.01	<0.01	0.02	0.01	0.014	0.021	0.012	0.02
- Cyanide	0.1 mg/l	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
- Iron	1.5 mg/l	0.46	<0.05	0.55	0.08	0.72	2.56	2.35	1.49	1.82	1.66
- Lead	0.08 mg/l	0.00	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.002	<0.01	0.01
- Mercury	0.001 mg/l	0.00	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
- Nickel	0.1 mg/l	0.01	<0.01	0.01	<0.01	0.01	0.01	0.016	0.017	0.012	0.02
- Selenium	0.02 mg/l	0.05	0.09	0.11	0.03	0.08	0.03	0.030	<0.01	<0.01	<0.01
- Silver	0.01 mg/l	0.00	<0.01	0.04	<0.01	<0.01	<0.01	<0.01	0.005	<0.01	0.02
- Vanadium	0.1 mg/l	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
- Zinc	1 mg/l	0.03	0.10	0.04	0.01	0.18	0.02	0.014	0.060	0.075	0.07
- Sulfide	0.1 mg/l	9.22	15.30	18.45	1.47	10.84	13.61				
- pH	6 - 9	7.1	7.1	7.1	7.5	7.5	7.2	7.1	7.1	7.6	7.4
COD	200 mg/l	800.0		610.0	400.0	505.0	530.0	375.0	350.0	887.5	618.5
BOD	20mg/l	88.0		70.0	89.0	79.0	82.0	184.5	179.0	560.0	370.0
- Oil & Grease	15 mg/l	114	134	520	99	100.0	120	83.0	12.0	13.0	12.0
- Carbolic acids (phenols)	0.002 mg/l	<0.05	1.6	1.0	4.2	0.7	0.8	<0.05	<0.05	<0.05	<0.05
- Nitrogen nitrates	15 mg/l	2.6	0.7	0.4	<0.02	<0.02	<0.02	<0.02	0.9	0.7	0.8
- Nitrogen Ammoniacal	1 mg/l	14.00	25.3	1.3	8.4	6.6	6.1	7.8	6.8	9.3	8.1
Total phosphorus	2 mg/l	0.8	6.4	0.5	2.4	6.4	7.5	1.7	<0.5	1.5	1.0
Conductivity	µ Seimans	123.00		108.0	122.0	148.70	125.00	128.25	119.25	87.25	103.00
Total Suspended Solids	30 mg/l	150.00	117.00	227.0	416.0	237.0	199.00	283.00	86.00	108.00	97.00
Total dissolved Solids	1500 g/l	79.90		70.2	79.8	74.25	81.25	64.25	77.50	56.71	67.00
Feacal Coliform	000 counts/100r	0.00	0.00	0.0	0.0	0.0	0.00	0.00	0.00	0.00	0.00
Boron mg/	1.0 mg/l	0.32	0.68	4.84	1.2	8.7	9.82	11.23	1.76	8.23	5.00
Barium mg/	2 mg/l	7.30	4.71	3.40	0.8	5.3	6.45	9.45	0.04	7.45	3.75
Beryllium	0.3 mg/l	0.00	<0.005	0.01	<0.005	0.00	0.00				
Cobalt	0.05 mg/l	0.01	0.01	0.01	<0.01	<0.01	<0.01				
Lithium	0.07 mg/l					12.50	12.50				
Molybenum	0.05 mg/l	0.00	<0.01	<0.01	<0.01	<0.01	<0.01				
Tempereture	<10 degree above ambient temp.				24.00						
Nitrogen organic as N	5 mg/l	9.23				5.01	9.23				
Total Nitrogen	15 mg/l	25.90				71.30	70.00				
Sulphide (total as S)	0.10 mg/l	9.22				10.84	13.61				
Viable Nematode Ove (per litre)	<1										
Organo halogens	<0.001										
Pesticide or their by products	<0.001										
Organosillcon compounds	<0.001										
Organocopper compounds	<0.001										
Organolin compounds	0 mg/l										
Oil discharged into the sea	kg/month										
	tonnes/month	#VALUE!									

Appendix (B)

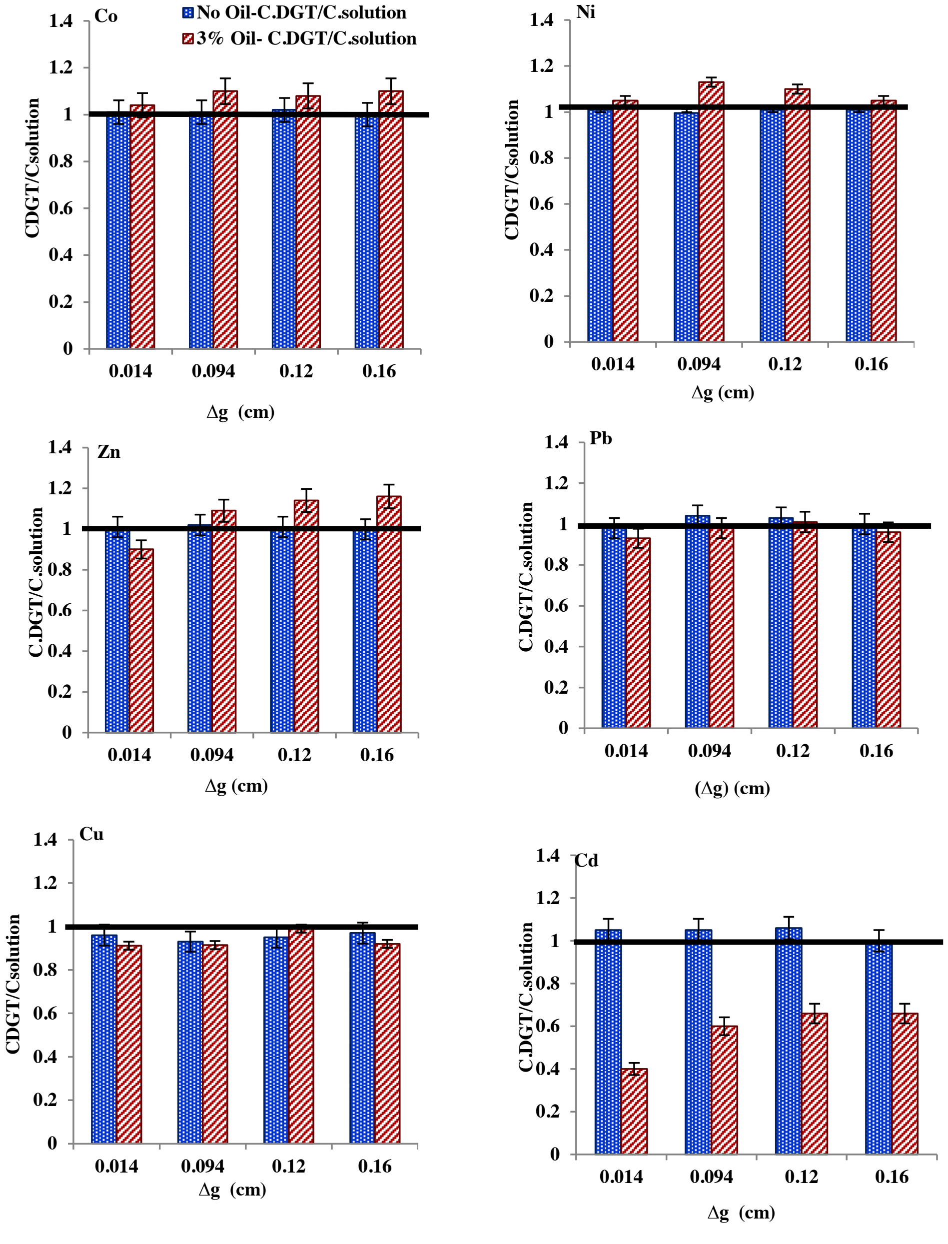
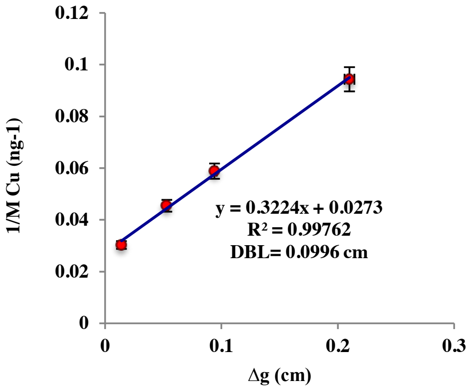


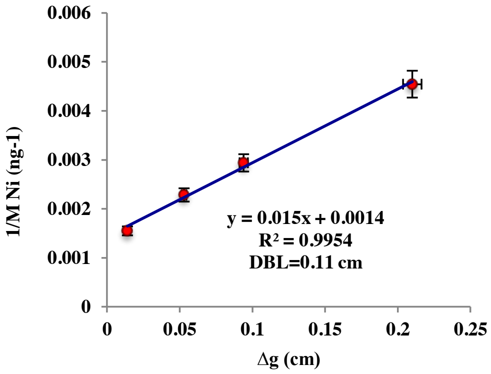
Figure 1. The ratios of the measured $C_{DGT}/C_{solutions}$, using varying thicknesses hydro gels in the synthetic solution with and without oil 3% OWR, w/v, where the DBL thicknesses is included using the effective area for the soil devices 3.08 cm^2.

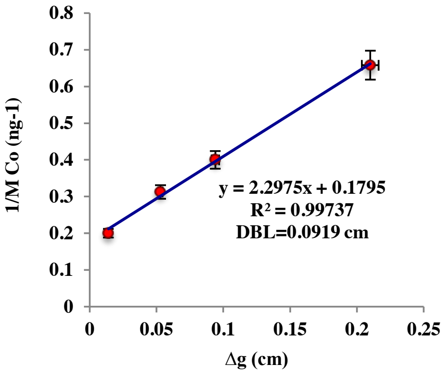
Appendix (C)

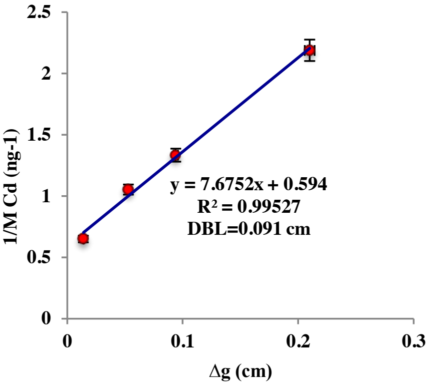
The measured diffusive boundary layer (DBL) around two industrial regions in Sultanate of Oman ((Rusyl Industrial Estate, (RIE)) and (Sohar Industrial Region, (SIR)) was determined at 6 open wells water.

Well-1-(RIE)

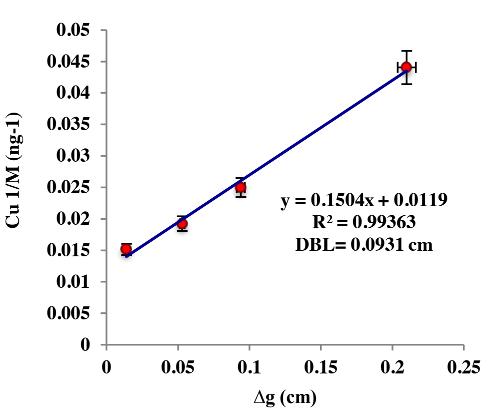


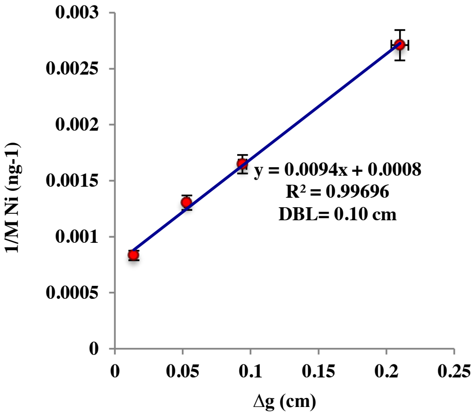


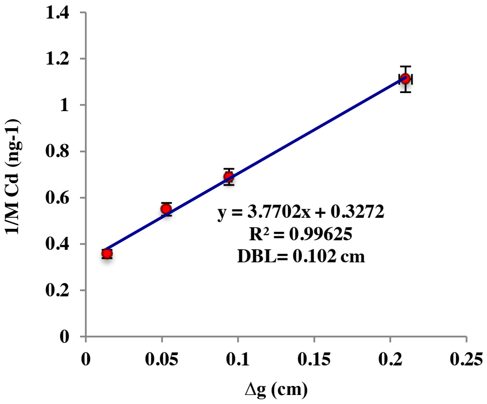




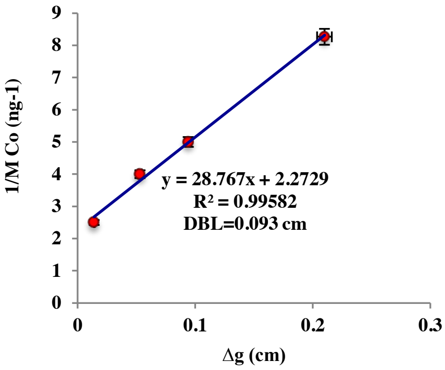
Well-2 (RIE)


Cu 1/M (ng-1)
0.05
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.05
0.1
0.15
0.2
0.25
Δg (cm)
y = 0.1504x + 0.0119
R² = 0.99363
DBL= 0.0931 cm

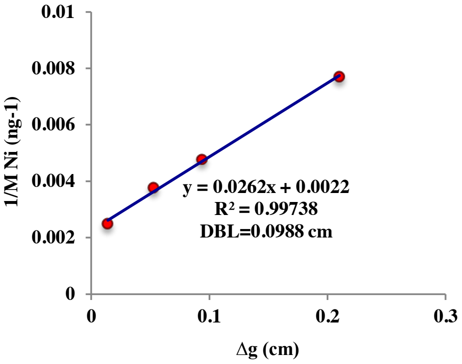

1/M Ni (ng-1)
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
0
0.05
0.1
0.15
0.2
0.25
Δg (cm)
y = 0.0094x + 0.0008
R² = 0.99696
DBL= 0.10 cm


1/M Cd (ng-1)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.05
0.1
0.15
0.2
0.25
Δg (cm)
y = 3.7702x + 0.3272
R² = 0.99625
DBL= 0.102 cm

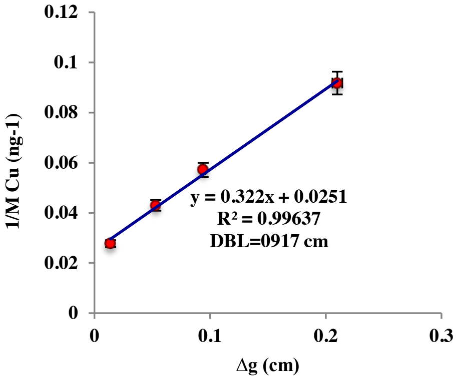
Well 3- (RIE)



9
8
7
6
5
4
3
2
1
0
1/M Co (ng-1)
y = 28.767x + 2.2729
R² = 0.99582
DBL=0.093 cm
0
0.1
0.2
0.3
Δg (cm)

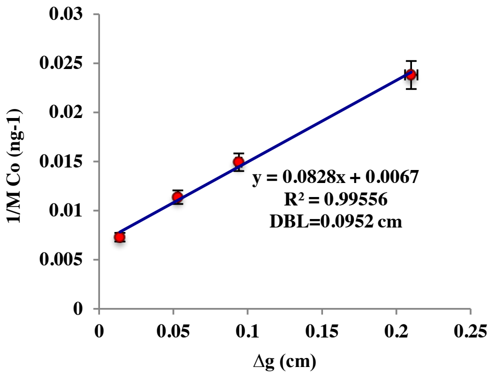


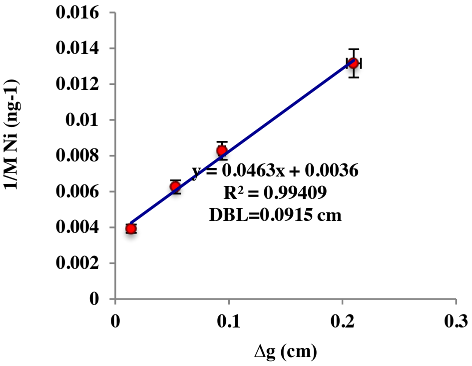
0.01
0.008
0.006
0.004
0.002
0
1/M Ni (ng-1)
y = 0.0262x + 0.0022
R² = 0.99738
DBL=0.0988 cm
0
0.1
0.2
0.3
Δg (cm)

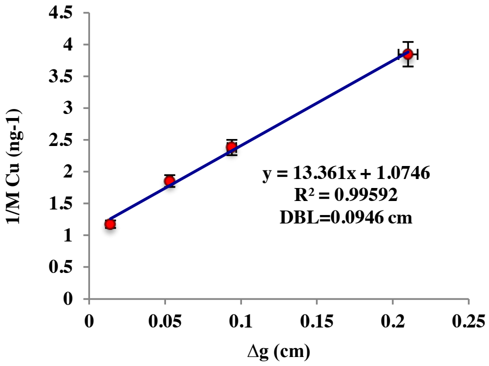


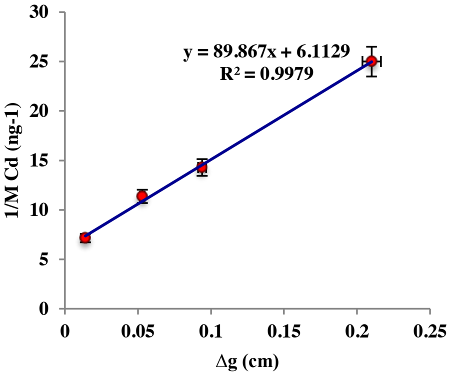
0.12
0.1
0.08
0.06
0.04
0.02
0
1/M Cu (ng-1)
y = 0.322x + 0.0251
R² = 0.99637
DBL=0917 cm
0
0.1
0.2
0.3
Δg (cm)

(SIR)-Well 1

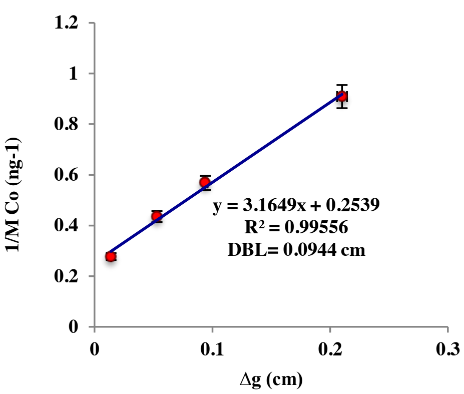

0.03
0.025
0.02
0.015
0.01
0.005
0
1/M Co (ng-1)
0
0.05
0.1
0.15
0.2
0.25
Δg (cm)
y = 0.0828x + 0.0067
R² = 0.99556
DBL=0.0952 cm

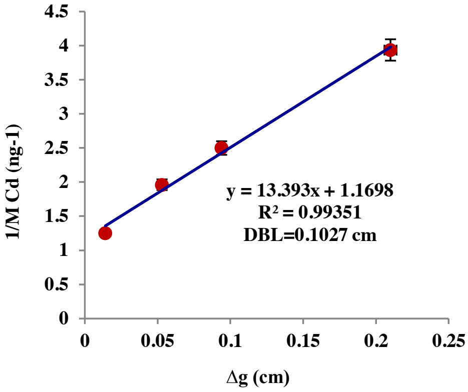

0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
1/M Ni (ng-1)
0
0.1
0.2
0.3
Δg (cm)
y = 0.0463x + 0.0036
R² = 0.99409
DBL=0.0915 cm

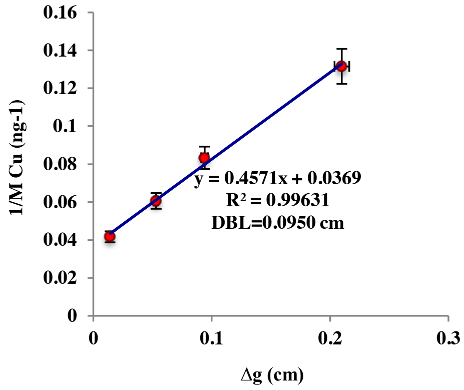

4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
1/M Cu (ng-1)
0
0.05
0.1
0.15
0.2
0.25
Δg (cm)
y = 13.361x + 1.0746
R² = 0.99592
DBL=0.0946 cm


30
25
20
15
10
5
0
1/M Cd (ng-1)
0
0.05
0.1
0.15
0.2
0.25
Δg (cm)
y = 89.867x + 6.1129
R² = 0.9979

(SIR)- Well-2


1.2
1
0.8
0.6
0.4
0.2
0
1/M Co (ng-1)
y = 3.1649x + 0.2539
R² = 0.99556
DBL= 0.0944 cm
0
0.1
0.2
0.3
Δg (cm)


4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
1/M Cd (ng-1)
y = 13.393x + 1.1698
R² = 0.99351
DBL=0.1027 cm
0
0.05
0.1
0.15
0.2
0.25
Δg (cm)


0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
1/M Cu (ng-1)
y = 0.4571x + 0.0369
R² = 0.99631
DBL=0.0950 cm
0
0.1
0.2
0.3
Δg (cm)

(SIR)-well -3

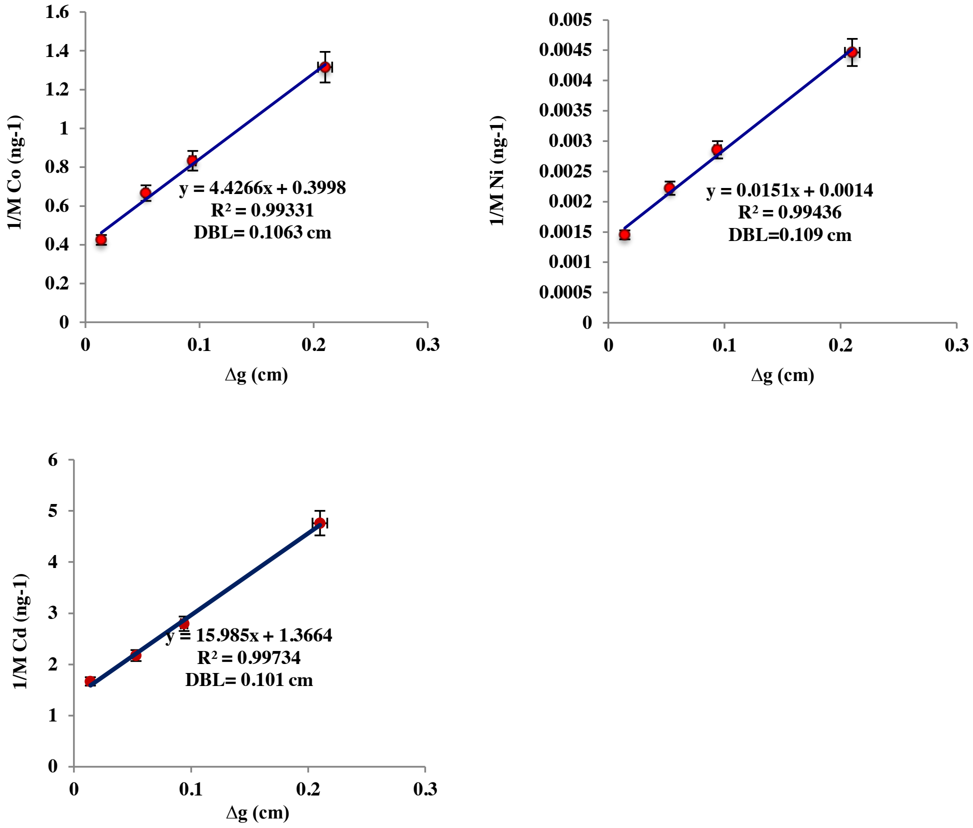


Figure 1. DGT results for Co, Ni, Cu and Cd in selected well~~s~~ waters at RIE in Muscat and SIR in Sohar, plotted as 1/mass of versus the diffusive layer thickness (Δg; cm).