

# Studying the Application and Advances of Diffusive Gradients in-Thin Films Techniques (DGTs) to Constrain Mobility and Bioavailability of Heavy Metals in Soils

Georges Martial Ndzana<sup>1\*</sup>, Alex Dortie Koleh<sup>2</sup>, Kashif Ali Kubar<sup>3</sup>, Louis Marie Bondje Bidjeck<sup>4</sup>, Etienne Bekoa<sup>4</sup>, Primus Azinwi Tamfuh<sup>1,5</sup>, Damien Henri Odigui Ahanda<sup>4</sup>, Thierry Mamert Abodo Koa<sup>4</sup>, Emile Temgoua<sup>2</sup>, Monique Abossolo-Angue Abane<sup>4</sup>, Lucien Dieudonné Bitom<sup>1</sup>

<sup>1</sup>Department of Soils Science, Faculty of Agronomy and Agricultural Science, University of Dschang, Dschang, Cameroon

<sup>2</sup>Department of Plant and soil Sciences, Faculty of Agriculture and Sustainable Development, Cuttington University Suakoko, Bong County, Republic of Liberia.

<sup>3</sup>Department of Soil Science, Faculty of Agriculture, Lasbela University of Agriculture, Water and Marine Sciences, Uthal, Balochistan, Pakistan

<sup>4</sup>Department of Earth Sciences, Faculty of science, University of Yaounde I, Yaounde, Cameroon

<sup>5</sup>Department of Mining and Mineral Engineering, National Higher Polytechnic Institute, University of Bamenda, Bamenda, Cameroon  
Email: \*georges.ndzana@univ-dschang.org

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## Abstract

The aim of this review is to investigate the application and latest developments of the Diffusive Gradients in-thin films (DGT) with a focus on the mobility and bioavailability of heavy metals in soil. Soil chemical extractions are extensively used to predict nutrients elements in the soil. However, these measurements have their weaknesses and shortcomings. Comparing DGT with conventional extraction methods, DGT is a sampling technique with significant advantages; including speciation capabilities, sensitivity, time-integrated signal, low risk of contamination and time averaged concentrations. These findings have strengthened the usefulness of the DGT technique as a potential monitoring tool for soil with heavy metal contamination. Studies which have used the DGT technique to evaluate processes important to bioavailability have been booming in the last 13 years, especially its application in soils science. Some recent studies have shown a good relationship between the measurement of metals concentrations in soil and plant by DGT, and cohesive results have been obtained from these measurements when they are based on the DGT technique. DGT is a newly established procedure to assess the bioavailability of trace elements in sediments and soils, and its applica-



tions are still in the early stage of testing. Therefore, future application of DGT is likely to include the studies of HMs contamination in soil for risk assessment and transfer rates to the food chain, as some studies have indicated the potential of DGT in these areas.

## Keywords

DGT, Gels, Mobility, Bioavailability, Soil, Heavy Metals

## 1. Introduction

Heavy metals (HMs) such as cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) generally refer to metals and metalloids having densities greater than ( $>5 \text{ g/cm}^3$ ). Although HMs may occur naturally in nature, humans may promote HMs pollution through agriculture, urbanization, industrialization, and mining (Alloway, 2013; Wuana & Okieimen, 2011; Zimmerman & Weindorf, 2010). The convertible, persistent and irreversible pollution not only degrades the quality of the atmosphere, water bodies, and soil, but also threatens the health of animals and human beings by transport through the food chain (Manisalidis et al., 2020; Sethi & Gupta, 2020). As the major sink for HMs in terrestrial ecosystem, soils polluted with HMs have been attracting more and more interests. However, assessment of eco-environmental and human risks remains limited.

The mobility of HMs such as Cd, Cu, Pb and Zn, and their bioavailability to sensitive receptors in terrestrial environments, is strongly influenced by separating the metal between the solid and dissolved fractions of the soil (mostly speak of as the Kd) (Dočekalová et al., 2012; Rieuwerts, 2015; Warnken et al., 2006). The measurement of the total metal concentration is not always, or even usually, appropriate for considerations of metal mobility and bioavailability (Dočekalová et al., 2015; Li et al., 2009a; Speir et al., 2007). These metals fractions may occur differently in the soil, and their mobility and bioavailability are governed by physical-chemical soil properties (Glaser et al., 2002) and its chemical compositions (Camobreco et al., 1996). Determining the bioavailability of heavy metal in contaminated environment is a crucial step in risk assessment for metal-polluted soils (Sungur et al., 2015; Wu et al., 2021). Metals toxicity is usually predicted from the relationships with the soil solution concentration, free metal ion in soil solution, or some functionally defined extractable fraction (Athar & Ahmad, 2002; Oorts et al., 2021; Soriano-Disla et al., 2010). It is necessary therefore, to understand the impact of the presence of heavy metals in soils and be able to develop techniques to determine its potential risks from soil contamination. In this context, the Diffusive Gradients in thin-Films (DGT) technique based on the diffusion of metals from the soil solution can be considered as an effective alternative compared to other traditional sampling procedures (Hooda et al., 1999; Zhang et al., 2001).

The use of DGT technique in soils and sediments provides unique informa-

tion relating to the system dynamic. The DGT technique was developed for in-situ measurements of trace metals elements such as: Cd, Cu, Co, Ni, Pb, Zn (Denney et al., 1999; Gao et al., 2021), which have been used to characterize soils (Cattani et al., 2008; Dočekalová et al., 2012; Nolan et al., 2005; Nowack et al., 2004), and have been extended to the measurement of metal fluxes in sediments and soils (Noh et al., 2016; Zhang et al., 2001). Since the extension of DGT to soils and sediments, the technique has been evaluated extensively in several studies of geochemical and health discipline (Nolan et al., 2005; Zhang et al., 2001). A good Predicting element availability to plants with DGT measurement has been witnessed in numerous studies (Degryse et al., 2009; Pérez and Anderson, 2009; Tandy et al., 2011). From these studies, DGT has been recognized to be suitable for the evaluation of metal bioavailability for plants. Based on the usefulness, the DGT technique has proven to be more accurate and robust than the conventional methods (Conesa et al., 2010). The DGT technique has been shown to be an effective technique for determining labile metal species in soils and sediments (Martin, 2008), and has its application to a broad suite of metals common to mine-influenced environments (e.g., Cu, Ni, Zn, Cd, Pb, Hg). The Metal values obtained using DGT also have been shown to conform reasonably well to predict the labile metal fraction using speciation models (Arevalo-Gardini et al., 2017; Unsworth et al., 2006). However, the work efficiency of DGT flux can reach higher levels when the soils moisture is at the maximum water holding capacity (MWHC) levels. The DGT technique is a relatively simple research tools which allows testing bioavailable metals and help to understand how the biota cooperate with their environment. In this review, the applications and advances of DGT technique in soil are discussed. The work begins with a brief introduction of the theory of DGT and then discusses the gels used in DGT as a key part, and the recent advances in bioavailability and toxicity of heavy metals assessed by DGT. Finally, the study makes outlook the possible aspects of DGT application in soil in future.

## 2. Theory of DGT

The DGT technique is based on the involvement of a polypropylene device comprising of two pieces, the piston and the cap. The piston works to support the gel layer that is placed inside the devices; a membrane, diffusive layer and a functional binding layer, which may vary based on the procedures and the targeted analyt being sampled (Menegário et al., 2017; Tafurt-Cardona et al., 2015). The base of the piston and membrane or diffusive layer is enclosed by the cap, which ensures the pathway of ions from the bulk solution to the inner layer through a well-defined area; while the diffusive layer forces ion transport to occur completely by diffusion, thus allowing analyt concentration to be determined (Amauri Antonio Menegário et al., 2017). DGT samplers are very easy to install and easy to use at a reasonable cost. However, detail on installation, deployment time, storage, calibration and other procedures can be varied according

to the needs, and environments (Ernstberger et al., 2002; Mengistu, 2009). For the deployment of the devices in soil, the unit is placed in close contact with wet soils using twist and turns methods or inserted into sediments (Hanousek et al., 2016). The labile forms of chemical elements diffuse through the filter and diffusive gel and are absorbed on the binding gel (Zhang and Davison, 2001, 2015). As the unit is being deployed, there is a diffusive boundary layer (DBL) that is formed between the diffusive layers, the diffusive gel and filter membrane and the resolution (Zhang et al., 2014b). After all the deployment time, a linear concentrations gradient is well established between the solution and the binding gel (Martin, 2008; Mason et al., 2005). The DGT technique works with Fick's first law of diffusion, which monitored the diffusion of dissolved species such as Cd, As, Mn, Cu, Pb, Zn, etc. By adding a membrane-diffusive layer, which could also control and restrict the flux accumulated in an ion-exchange resin (Luo et al., 2010; Zhang et al., 2014b). Assuming the concentration gradient of the ions remains constant during deployment time ( $t$ ), the flux  $F$  ( $\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ ) of an ion through the diffusive gel layer is given by (Equation (1)) and the concentration of ions measured by the DGT ( ${}^c\text{DGT}$ ) can be calculated using Equation (2) (Huynh et al., 2012).

$$F = DC\Delta g \quad (1)$$

$${}^c\text{DGT} = M\Delta gDtA \quad (2)$$

where  $D$  is the diffusion coefficient ( $\text{cm}^2\cdot\text{s}^{-1}$ ) for a given metal ion,  $C$  is the bulk concentration of an ion,  $A$ , the area of hydrogel membrane ( $\text{cm}^2$ ) exposed to the bulk solution, and  $M$ , the mass of metals (ng) accumulated in the diffusive layer over time,  $t$ (s).

Until now, various types of materials have been evaluated as diffusive layers within the DGT samplers for the purpose of assessing the labile species of heavy metals in soil (Dočekalová & Divis, 2005; Menegário et al., 2017).

### 3. Development of Binding Gels for Measurements

As discussed above, the first demonstration of DGT potential as predictor of bioavailability was shown in 1999 (Hooda et al., 1999), and its application for bioavailability assessment in soil is still in its early stage of development. There are several different materials that have been defined and proposed by many researchers for application as DGT binding layers (Table 1). These binding layer however, comprises of solid resins that are combined into a gel matrix, for example, polyacrylamide to form a binding layer (Heidari et al., 2016). In expanding the range of analyt determined in a single DGT deployment, mixed binding layer (Mason et al., 2005), and multiple binding layer (Naylor et al., 2004) samplers have been developed. In order to use solid material as a binding agent within a DGT binding layer, the material must be meaningfully small particle size to allow simple and evenly combined into a gel matrix. As shown in Table 1 with different binding agents, many options are employed to consider which binding layer can be used for a particular geometry. The DGT suitability

**Table 1.** Development of binding gels for measurements of various dissolved chemicals in soil.

Analyst(s)	Binding gel	Binding capacity or max. Concentration	References
Metals	Chelex-100 resin	$5 \times 10^{-4}$ M Cd, 10-h deployment	(Zhang and Davison, 1995)
Phosphorus	Ferrihydrite	(Fe oxide, based on Fe (NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O) 2 µg P cm <sup>-2</sup> (0.4 mg·L <sup>-1</sup> ), 24-h deployment	(Ding et al., 2010; Zhang et al., 1998a)
Sulphide	Silver iodide	(AgI) 1 µmolcm <sup>-1</sup> (62.6 µmol·L <sup>-1</sup> , 15 h)	(Teasdale et al., 1999)
Radioactive caesium	Ammonium	molybdophosphate 2.3 mg of stable Cs (equivalent to 7 GBq137Cs or 108 GBq134Cs)	(Murdock et al., 2001)
Phosphorus	Zr oxide	(based on ZrOCl <sub>2</sub> ·8H <sub>2</sub> O) > 100 µg P cm <sup>-2</sup> (>20 mg·L <sup>-1</sup> ), 24 h deployment	(Ding et al., 2010)
Sulphide	(simultaneous measurements with metals)	AgI in gel (combined use with Chelex × 100 resin) N/A	(Motelica-Heino et al., 2003)
Arsenic, phosphorus and metals	Titanium dioxide	(Metsorb~12 µg P cm <sup>-2</sup> (2.5 - 5 times higher than ferrihydrite)	(Bennett et al., 2010)
Phosphorus and cations	Ferrihydrite and Chelex-100	(mixed binding layer, MBL)12 µg Pongel (2.52 cm <sup>2</sup> , 850 µg·L <sup>-1</sup> ); 75 µg Mn in gel (3 mg·L <sup>-1</sup> ), 24 h deployment	(Mason et al., 2005)
Phosphorus and sulphur	Zr oxide-silver iodide	(AgI) ~80 µg P cm <sup>-2</sup> (>20 mg·L <sup>-1</sup> ), 24 h deployment	(Ding et al., 2012)
Potassium and phosphorus	Mixed Amberlite and ferrihydrite	450 µg K on gel (2.54 cm <sup>2</sup> ); 1.2 mg P L <sup>-1</sup> , 8-h, deployment	(Zhang et al., 2013)
Phosphorus and iron	Zr oxide-silver iodide	(AgI) 90 µg P cm <sup>-2</sup> and 75 µg Fe cm <sup>-2</sup>	(Xu et al., 2013)
Arsenic	Zr oxide	159 µg As (III) and 434 µg As (V) in Fresh water per	(Sun et al., 2014)

study have revealed that, binding layer suitability depends on the environment in which it will be deployed, with many of the binding layer only appropriate to freshwaters owing to the high concentrations of potentially competing ions present in more complex environments like seawater (Conesa et al., 2010; Panther et al., 2013b). The Solute measured by DGT accurately relies on the strength of interaction with the binding layer. However, these binding layers have been compared with different materials to assess trace metals in sediments and soils. It is not possible to show all the working performances of every binding layer described; only the binding layer which have gained a widespread and application which have stood the test of time are considered. These includes: Chelex-100, ferrihydrite, Metsorb, zirconium dioxide (ZrO<sub>2</sub>), 3-mercaptopropyl functionalized silica, AG50W-X8 and XAD18. These DGT binding layers have been extensively evaluated with different materials in several researches for trace elements (Fang et al., 2021). This is done to determine whether these binding materials are capable of accumulating analysts of concern (Uptake). For example, (Panther et al., 2010) evaluated Metsorb and Ferrihydrite DGT for measuring dissolved reactive phosphorus in freshwater environment for deployment time up to four days. Their work revealed that, while both techniques (binding layer, ferrihydrite and Metsorb) accurately measured the analysts of concern over the four days deployment period, only Metsorb DGT was capable of mea-

asuring the Dissolve Reactive Phosphorus (DRP) in seawater after four-days. However, the ferrihydrite DGT techniques underestimated the DRP in the freshwater by 31%. (Bennett et al., 2010) work revealed that the measurements of Mn by chalex-100 experienced similar limitations in synthetic seawater, underestimating Mn concentration by 49% after four-days of deployment. They concluded that accurate measurement of Mn was possible with longer deployment time, up to 48h. Suggesting that the short-term validations reported in many literatures may not reveal these limitations of the binding layer. Of all the above mentioned DGT binding layers, the chalex-100 DGT have stood the test of time to measure heavy metals in soils. Chalex-100 as a DGT binding layer has proven to be effective in measuring heavy metals in contaminated soils.

## 4. Resin Gel

Originally, the DGT technique was developed for *in situ* measurements (Davison & Zhang, 2012; Scally et al., 2003). Since then, the DGT technology has developed rapidly. Significant progress has been made within two aspects of the technology, which include the development of new binding gel and the 2D high-resolution measurements (Davison & Zhang, 2012; Sochaczewski et al., 2007). It is well established that the Chelex resin can take up trace metals, as it contains paired with iminodiacetate ions which act as chelating groups in the binding polyvalent metals ions. Accordingly, the binding agent for the first DGT was the chelex resin (Davison & Zhang, 2012; Mason et al., 2005). After that, the ferrihydrite gel with a strong affinity for phosphorus was used to measure labile phosphorus (Zhang et al., 2014a; Zhang and Davison, 2015) and silver iodide was included in the gel to take up sulphide (Teasdale et al., 1999). However, the radioactive caesium was adsorbed by a gel containing ammonium molybdo-phosphate (Li et al., 2009b; Murdock et al., 2001; Puy et al., 2014).

### 4.1. Oxyde Gel

In recent study, (Sun et al., 2014; Zhang et al., 2014a) Zr oxide gel was developed to measure phosphorus and inorganic arsenic with high capacities. The hydrous zirconium oxide (Zr oxide) has been combined with silver iodide to measure both phosphorus and sulphide (Sun et al., 2014; Sun et al., 2013); and combined with Chelex to measure phosphorus and iron (Xu et al., 2013). The mixed Amberlite and ferrihydrite gel has been recently developed to measure potassium and phosphorus (Zhang et al., 2013, 2014b). Recently, it has been found that the capacities of the Zr oxide DGT for As in freshwater and seawater were 5 - 19 times and 3 - 13 times more than those reported for the commonly used ferrihydrite and Metsorb DGTs, respectively (Sun et al., 2014; Zhang and Davison, 2015). In addition, a titanium dioxide gel-assembled DGT has been used to simultaneously measure arsenic, phosphorus and metals in soil (Bennett et al., 2010; Fauvelle et al., 2015; Panther et al., 2013a; Zhang et al., 2014a). The first material used in DGT to fabricate the binding layer was the polyvalent metal chelating resin Chelex-100 (Dočekalová and Divis, 2005). It needs to be men-

tioned that the DGT method has recently been developed to measure organic and inorganic compounds (Sun et al., 2014; Sun et al., 2013). However, the DGT technique measures directly the mean flux of labile species in soils to the device during deployment. Thus, providing a novel and promising approach for the measurement of bioavailable metal concentrations in soils (Lehto et al., 2006; Zhang and Davison, 2015).

## 4.2. Other Gels

In addition to measuring individual chemical elements, DGT techniques for concurrent measurements of multiple elements have been established, that is, Zn, Mn, Fe, and As (Naylor et al., 2004; Zhang et al., 2014a). Two separate gels of silver iodide and Chelex-100 were used together to measure sulphide and metals in sediments (Motelica-Heino et al., 2003; Zhang et al., 2014a). A mixed binding layer (MBL) containing a mixture of ferrihydrite and Chelex-100 was developed to measure phosphorus and cations (Mason et al., 2005; Zhang et al., 2014a). Furthermore, various types of materials (e.g. polyacrylamide gel, agarose gel, dialysis membrane, Nafion membrane, chromatography paper and filter paper) have been evaluated as diffusive layers within the DGT samplers (Menegário et al., 2017). Recently, the development of DGT methods has been to use ion imprinted binding layers, wherein the analyte is sorbed to the ligand to improve species retention, this approach has been successfully carried out for Cd (II) Pb(II) (Dong et al., 2014; Stanley et al., 2016; Sui et al., 2016). The development of new binding gels enables DGT technique to analyze diverse analytes in an environment, particularly those of environmental importance (Davison and Zhang, 2012; Huang et al., 2016). In addition, the primary limitations of the technique include the limited functional pH range (pH 5-9) and the limited application to certain metals/metalloids (Divis et al., 2009; Martin, 2008). However, (Galceran and Puy, 2015) show that it is possible to interpret quantitatively the proportions of metals penetrating into the rear of the binding layer in terms of the dissociation kinetics of metal complexes with humic substances using DGT. Even though the application of DGT for metals analyses is well established, it still needs to be extended to other elements. Despite all the above-described DGT advantages on the study of bioavailability, the development of a DGT technique and its validation by an established model for interpreting data obtained from a particular measurement remains a challenge in the study of DGT. Therefore, a comprehensive and standardized DGT method is required to ensure that the DGT results are measured using different binding gels in different environment.

## 5. Metals Bioavailability and Toxicity in Soil Using DGT

### 5.1. Bioavailability

The applications of DGT to assess the bioavailability of heavy metals in soils have received attention worldwide. A trend that can be observed linked to the

development of new methods based on the DGT technique, is the prediction of available metals based on the comparison of the DGT results with others methods for specific analysts (Menegário et al., 2017). Presently, there is an increasing body of research focusing on the use of the DGT technique for predicting the bioavailability of metals and toxicity (Menegário et al., 2017). The Labile and small complexes of metals are the forms that allowed metal to be able to pass through cell membranes and therefore, they are commonly the most bioavailable and harmful to biota (Turner et al., 2012). However, as these metals are the ones sampled by the DGT technique, some studies have been carried out to assess the possibility to use DGT to predict the bioavailable metals and their toxicity to human (Tandy et al., 2011; Tella et al., 2016). Some recent studies on bioavailable metals in soil using DGT and some plant species (Table 2). The DGT technique has been developed mostly for toxic cationic divalent trace metals but, it has also been expanded to test the bioavailability of plant nutrients such as: phosphate, potassium, uranium, methyl mercury, arsenate, molybdate, and most

**Table 2.** Examples of recent studies on metals availability in soil using DGT and some.

Elements	Species/soils	Findings	References	
Mn	Different Scandinavian agriculture soils	It is unlikely that the DGT techniques can be used to accurately predict the plant availability of Mn in crop production. DGT prediction of plant availability was best in anaerobic compared to aerobic soils. However, DGT can be a valuable tool in understanding factors affecting Mn availability.	(Mundus et al., 2012)	
Cd, Cu, Pb and Zn	Sorghum bicolor; Lactuca sativa	The DGT technique was fairly predictive of bioavailability in the greenhouse but not in the field.	(Agbenin and Welp, 2012)	
Pb, Zn, Cu and Cd	Triticum aestivum	DGT and leachate concentrations in combination with bioassays in undisturbed soil cores can be used to account for metal bioavailability in soil.	(Mundus et al., 2012)	
Cd, Zn	Taraxacum officinale and Plantago lanceolate	DGT did not perform better than soil solution, as Cd and Zn uptake in the plant was not limited by diffusion	(Muhammad et al., 2012)	
Cd, Zn	Rice ( <i>Oryza sativa</i> )	Due to the inherent heterogeneity of the rice rhizosphere soils, deployment of DGT in dried and homogenized soils offers the best possibility of a soil screening tool.	(Williams et al., 2012)	
Cu, Zn and Cd	Various vegetables	DGT can be used for the general evaluation of the risks associated with soil contamination with Cu, Zn and Cd in field conditions.	(Senila et al., 2012)	
Hg	Rice ( <i>Oryza sativa</i> )	DGT can predict the bioavailability of methyl mercury in rice paddy soil, and the DGT method can provide a quantitative description of the rate of uptake of this bioavailable methyl mercury.	(Liu et al., 2012)	
Zn and Cd	Salix smithiana clone	Single extraction with the DGT value of Cd was not able to predict shoot Cd removal on the tested soils.	(Puschenreiter et al., 2013)	
Cu	Soil solution	The DGT allowed a representative estimation of the amount of Cu available in the soil.	(Garrido and Mendoza, 2013)	
Cu	Fontinalis antipyretica	Tatiana Garrido and Jorge	The DGT approach was demonstrated to be a dynamic in-situ measuring technique that can be used as a surrogate of bio-indicators if the cationic correction is taken into account.	(Ferreira et al., 2013)
Phosphorus	<i>Lycopersicon esculentum</i> , <i>Triticum aestivum</i>	P deficiency assessed by yield response to P fertilizers; DGT provided excellent separation of responsive and nonresponsive soils.	(Mason et al., 2008; Mason et al., 2010)	

recently been used to understand the effect of nanoparticles in the soil environment (Davison and Zhang, 2012; Dočekalová et al., 2015; Huang et al., 2017). The concentration of these heavy metals measured by DGT is associated with labile species, including free ions and kinetic resupply of ions from the solid phase, which are considered to be bioavailable (Zhang et al., 1998b). Recently, Zhang and Davison (2015) reviewed the use of DGT for studies of speciation and bioavailability. During this study, however, key reports over decades were examined and discussed, by giving an environmental perspective to the theory of DGT (relating to measurements of metal complexes) and the ability of DGT to obtain *in situ* information was discussed. In addition, the relationships between DGT measurements in soil and plant uptake were deeply discussed. In order to determine trace element species, the methods based on the DGT technique are mostly used (Menegário et al., 2010; Menegário et al., 2017). While it is true that, DGT might not be expected to be a universal tool to predict bioavailable metals in soil and sediment, for examples, the measurement of labile species have aided predictions to where it have emerged (Degryse et al., 2009; Smolders et al., 2009). In a recent study, (Johnson et al., 2012; Menzies et al., 2005) reported that, the redox-driven layering in sediments makes them a particularly challenging environment for predicting and assessing bioavailability and toxicity, but, again, there are some encouraging recent results (Zhang and Davison, 2000). (Salzberg et al., 2012; Simpson and Batley, 2003) also reported that, there is no single technique that can be expected to imitate the range of processes that may be operating during biological uptake. Many studies involving bioavailability of trace elements to DGT measurement have been investigated thoroughly with focused on the uptake of trace metals such as: Cd, Cu, Zn, Ni and Pb by plants, using standard DGT device with a chelex resin layer, but very few studies have compared bioavailability with DGT for other elements (Shahid et al., 2016; Tandy et al., 2011; Wang et al., 2016). For example, (Wang et al., 2014) measured as concentrations in forty-three different soils collected in China with different extractions procedures, including DGT and soil solution measurement. It was concluded that, the DGT-measured and soil solution concentrations of As give a good prediction of the plant As concentrations and show much better than the acid digestion extraction procedures. It has been recognized by many researchers that, in the conventional methods of testing soil solution, metal speciation may change during sampling and extraction and the kinetics of metal resupply from the solid phase to solution are not considered (Koster et al., 2005; Zhang et al., 2014a). Furthermore, the bioavailability of metals in a given soil is reliant on both, their concentrations in the soil solution and their rate of transport through the soil (Zhang and Davison, 2000; Zhang and Davison, 2001). With little exclusions, most of the reports concerning with DGT and bioavailability in soils have focused on measuring the concentrations rather than uptake fluxes (Ahmed et al., 2013; Luo et al., 2013). Up till now, it has been used by (Mason et al., 2010; Menzies et al., 2005) for predicting yield responses of tomato cultivated at high P

levels and for predicting wheat responses to different P fertilizers formulations (Menzies et al., 2005). Recently, (Mason et al., 2010; McBeath et al., 2007) showed that the DGT technique was able to predict the growth response of wheat when cultivated under a range of P conditions.

## 5.2. Metals Toxicity and DGT

Previous studies by measuring Cd uptake using spinach in solution in the absence or presence of synthetic ligands concluded that, at constant free ion activity and constant total Cd concentration, the uptake of metal increased with increasing dissociation rate of the complex, and correlated well with DGT measured concentrations, which strongly suggest that Cd uptake by spinach was limited by diffusion (Degryse et al., 2012). They further reported that, direct uptake of the complex was predicted to be a major contribution only at milli molar concentrations of the complex or at very large ratios of complex to free ion concentration. The “true  $K_m$ ” for uptake of  $Cd^{2+}$   $Zn^{2+}$  was estimated at  $<5$  NM. Uptake of Cd by spinach in nutrient solution and the DGT-measured diffusion flux as function of free ion concentration for solutions with 40mMNaNO<sub>3</sub> or NaCl. The free ion concentration was identical; the total Cd concentration was three-fold larger NaCl solution with 68% of Cd complexes with chloride. Similar observations were made for Cd uptake by rapeseed Brassica napus (Dai et al., 2017; Sungur et al., 2015). Although the uptake is related to the DGT measurements for both plant species, there were differences in uptake between the plant species. In non-buffered solutions, the Cd uptake flux was larger for spinach than for rapeseed. In buffered solutions with slowly dissociating complexes, the uptake flux was larger for rapeseed. The other way of saying this is that, the contribution of the slowly dissociating complexes to the uptake, relative to the contribution of the free ion, was larger for rapeseed than for spinach (Degryse et al., 2012). (Tandy et al., 2011; Wang et al., 2016; Yao et al., 2016) reported that the DGT method predicted the responsiveness of Cd bioavailability in complex contaminated soil. They concluded that the DGT technique is a physical surrogate for plant uptake, thus offering the possibility of a simple test procedure for measurement of bioavailable metals in soil. A few studies have compared Cu concentration with DGT-measured concentrations as well as other potential predictors (Tella et al., 2016). For example, (Sun et al., 2010) examine the total Cu and soil solution concentration. In this study, it was demonstrated that there are strong correlations between DGT and plant concentrations in a wide range of soil for Cu uptake by plants. The author further concluded that, Cu concentration in shoots of wheat were rather weakly correlated with DGT-measured concentrations and were, surprisingly, better correlated with the total Cu in the soil. (Agbenin and Welp, 2012; Balistrieri and Blank, 2008; Luider et al., 2004) compared the labile Cu determined by DGT technique with the uptake of Cu in trout gills. However, it was then concluded that, there was an influence of organic matter in Cu uptake by trout gills as well as Cu concentrations determined

by DGT. Similar results were reported for Cu binding to organic matter measured by DGT and fish gill bio-indicators (Luider et al., 2004). Commonly, the plant availability of Cu, Zn, and P in soil is highly dependent on kinetics of release from the solid phase, the DGT technique is expected to be superior to extraction techniques especially when diffusional supply is limited (Larner et al., 2006). So far Cu and Zn have only been measured by this technique in contaminated soil e.g. (Song et al., 2004; Tandy et al., 2011) and not in agricultural soils with trace levels of these elements. DGT assessment of bioavailability is mostly accurate under conditions where the diffusive transport of an element from the soil to the plant roots is rate-limiting for its uptake (Degryse et al., 2009; Zhang et al., 2014a). If the uptake by plant is low, competitive cations may affect the plant uptake, while they have no effect on the DGT flux (Zhang et al., 2014a), whereas the labile complexes do not contribute to the plant uptake but they are measured by the DGT technique. This denotes that, when the plant has little affinity for the element or when the supply is large and the plant uptake is saturated, the DGT flux and plant uptake may not correlate well (Zhang et al., 2014b).

## 6. Summary and Outlook

The DGT techniques have been considered as a potential monitoring tool for soil with heavy metal contamination. The technique involves using a specialized-designed passive sampler that houses a binding gel, diffusive gel and filter membranes. During deployment, the elements or compounds pass through the membrane filter and diffusive gel and are assimilated by the binding gel in a rate-controlled manner. However, the post-deployment analysis of the binding gel can be used to determine the bulk solution concentrations of elements or compounds using a simple equation. There is no reverse diffusion of the analyte back into the solution which is assumed to occur during deployment of the DGT device. Bearing in mind the difficulty of environmental chemistry, it is not surprising that the ability of DGT to predict bioavailability and toxicity is variable. High solute concentrations are usually associated with conditions of toxicity. There is a substantial literature showing that under these conditions the biotic ligand model applies, which denotes that uptake is affected by the free ion concentration and competition with other ions for the biotic ligand.

In conclusion, there is great promise for the use of DGT in soils, particularly with respect to help understand the uptake processes and for predicting the uptake, or requirements for, nutrients when their concentrations are low, which indicates deficient conditions. As a surrogate of plants, DGT is capable of measuring heavy metal concentrations in the soil. However, DGT is not considered to be a universally applicable tool for the prediction of bioavailability of metals in soil and sediments. Moreover, there is no single technique that is expected to imitate the wide range of processes that may be functioning during biological uptake. DGT is no exception, but it does imitate some significant processes that may be dominant in some situations. Future applications of DGT are likely to include the

studies of heavy metals contamination in soil for risk assessment and transfer rates to the food chain, as some studies have indicated the potential of DGT in these areas. Further investigation in these areas will help the development of DGT as a tool for assessing metals bioavailability in soils and sediments and the risk associated with its contamination which poses health issues on human and animals. The DGT technique has also been used, in combination with some materials to assess the bioavailability of heavy metals in soils. There is a great promise for the use of DGT in soil, particularly understanding the uptake processes and for predicting the uptake, or requirements for nutrients when the concentrations are low, which indicates deficient conditions

### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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