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Spatial Analysis of Rare Earth Elements and Lead in Urban Soils of Greater London Authority area and Development of a New Method for Assessment of Labile Rare Earth Elements in Soils

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The thesis is submitted to National University of Ireland, Galway in fulfillment of the requirement for the degree of Doctor of Philosophy, in the School of Geography, Archaeology & Irish Studies

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Abstract

Rare earth elements (REEs) are a group of seventeen elements, comprised of the fifteen lanthanides, yttrium (Y) and scandium (Sc), which have been known as 'industrial vitamins' due to their important roles in technical progress and the development of industries. Despite the increasing interest, there is current controversy about the health benefits and toxicity of these materials during the processing and utilization of REEs. Due to long residence time in soils and their potential toxicity effects, the contamination of urban soils has received wide attention in recent years. However, little information is available on REEs accumulation in urban soils, and the spatially varying relationships between geochemical elements in urban soils have also seldom been investigated. In addition to the complex land use and heterogeneity of urban soils, the sources of heavy metals and REEs in soils can be both natural and anthropogenic, and the spatial variation of their enrichments vary over space. On the other hand, for risk assessment of metal-contaminated soils, it is important to predict the bioavailability of metals.

In this research, geographical information system (GIS) and spatial statistical techniques were applied to identify the contamination hotpots and to reveal the spatial variation of geochemical elements in urban soils of London. Meanwhile, a new method for simultaneous measurements of REEs using the diffusive gradients in thin films (DGT) was conduct in laboratory and deployment in soils. The research objectives were: (1) to investigate the concentration and distribution of lead and seven REEs in urban soils; (2) to identify contamination hotspots of REEs on sources and their influencing factors; (3) to reveal spatially varying relationship between Pb and Al in London soils and to explore the influencing factors of these elements in the study area; (4) to develop DGT for the simultaneous measurements of fifteen REE ions.

The results showed that the index of local Moran's I was a useful tool to identify contamination hotpots of Ce, La, Nd, Sc, Sm, Yb and Y in urban soils, and to classify them into spatial clusters and spatial outliers. Soil parent material was a natural factor leading to high-value spatial clusters of REEs in north and south area, while individual spatial outliers were

associated with anthropogenic sources including agricultural practices, vehicular emission and urbanization.

The relationships between Pb and Al were spatially varying in urban soils of London, with different relationships in different areas. The GWR models showed clear positive spatial relationships influenced by the natural geochemical factors found in large parklands and greenspaces in part of central, as well as southeast and southwest areas of London. Anthropogenic factors had a great impact on the concentration of Pb, leading to the weakened correlation in central London or even the changed relationship direction from positive to negative correlation between Pb and Al in the suburban area of northern London. This study highlights the value of using GWR to reveal spatially varying relationships in environmental variables.

Furthermore, a new technique was developed to measure simultaneously fifteen REE ions in this study using the diffusive gradients in thin films (DGT) with Chelex® 100 binding gel. The results showed that DGT uptakes of all REE ions were independent of pH (3-9) and ionic strength (3 mM -100 mM). The fifteen REE ions were successfully extracted by elution using 2.0 M HCl, with elution rate ranging from 86.5% to 93.8%. The capacities of Chelex® 100 DGT for measurement of the mixed elements were determined at a range of 5.39-6.75 mg cm², reflecting rapid binding dynamic to REEs in a mixed solution of the fifteen REE ions. This study demonstrates a significant advantage of Chelex® 100 DGT in simultaneous measurements of the fifteen REE ions, which could be an effective tool for the simultaneous measurements of REEs in the environment.

Keywords: Hotpot analysis, Local Moran's I, Geographically weighted regression (GWR), Spatially varying relationship, Geochemical variable, Rare earth elements, Lead, Aluminium Diffusive gradients in thin films (DGT), Chelex® 100 DGT, Soils, Urban soils

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 This thesis or any part thereof, has not been, or is not currently being submitted for any degree at any other university.

Yumin Yuan

The work reported herein is as a result of my own investigations, except where acknowledged and referenced.

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This paper would be presented in Chapter 4. My dedication in this paper accounted for 90% in reviewing literatures, exploring data and writing manuscript.

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This paper would be presented in Chapter 4. My dedication in this paper accounted for all DGT experiments, processing of the data, forming the conclusion, and writing \sim 90% of the manuscript.

3. Yuan, YM., Cave, M., Xu, HF., Zhang, CS. Exploration of spatially varying relationships between Pb and Al in urban soils of London at the regional scale using geographically weighted regression (GWR) (Submitted: Journal of Hazardous Materials)

This paper would be presented in Chapter 4. My dedication in this paper accounted for 90% in reviewing literatures, exploring data and writing manuscript.

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Abbreviations

А	The exposed surface area of the DGT device
Al	Aluminium
AIC	Akaike Information Criterion
Ba	Barium
Be	Beryllium
BaCl ₂	Barium Chloride
С	The total contents of carbon
Со	Cobalt
Cu	Copper
Cd	Cadmium
Ce	Cerium
CaCO ₃	Calcium carbonate
CaCl ₂	Neutral salts
CEC	The cation exchange capacity
Cyanex 923	A liquid phosphine oxide extractant
Cyanex272	A dialkyl phosphinic acid extractant
Chelex [®] 100	Iminodiacetic acid (sodium form)
CH ₃ COON _a	Sodium acetate
CV	Coefficient of variation
D	Diffusion coefficient
Dy	Dysprosium
DL	Detection limits
D418	Chelate ion exchanger

D001-cc	Strong Acidic Cation Exchange Resin
DGT	Diffusive gradients in thin films
Eu	Europium
EDTA	Ethylene-diamine-tetra-acetic acid
Fe	Iron
FOREGS	Forum of European Geological Surveys
Gd	Gadolinium
GPT	Formerly termed glutamate pyruvate transaminase
GOT	Formerly termed glutamate oxaloacetate transaminase
GIS	Geographical Information System
GWR	Geographically weighted regression
GLA	Greater London Authority
GPS	Global Positioning System
Но	Holmium
HNO ₃	Nitric acid
HCl	Hydrochloric acid
HF	Hydrofluoric acid
HCO ₃	Carbonic acid
HREE	Heavy rare earth elements, Gd-Lu
HSTY®-SS	Cell [®] /HSTY [®] Metal Scavenger Toolkit
НЕОРРА	1-hexyl-4-ethyloctyl isopropylphosphonic acid
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IDW	Inverse distance weighted
La	Lanthanum

Lu	Lutetium
LOI	Loss on ignition
LREE	Light rare earth elements, La-Eu
LISA	Local Indicator of Spatial Association
LA-ICP-MS	Laser ablation inductively coupled plasma mass spectrometry
Мо	Molybdenum
Mn	Manganese
MnO_2	Manganese dioxide
MREE	Medium rare earth elements
MDL	Method detection limits
MWHC	Maximum water holding capacity
М	Accumulated mass of the species in binding gel
Ni	Nickel
Nd	Neodymium
NaCl	Sodium chloride
Ν	The total contents of nitrogen
OLS	Ordinary least squares regression
PSS	Phase Poly (4-styrenesulfonate)
pC4SL	Provisional Category 4 Screening Levels
Pr	Praseodymium
Pm	Promethium
Pb	Lead
Р	Phosphorus
PM_{10}	The respirable particulate matter

r	Correlation coefficients
REEs	Rare earth element(s)
RE	Rare earth(s)
Sm	Samarium
Si	Silicon
SD	Standard deviation
SPSS	Statistical Package for the Social Sciences
SPR-IDA	Suspended particulate reagent-iminodiacetate
t	The deployment time
Tm	Thulium
ТЪ	Terbium
Ti	Titanium
TSP	Total suspended particulate matter
XRFS	X-ray Fluorescence Spectrometry
Yb	Ytterbium
Zn	Zinc
Δg	The thickness of the diffusive layer
001×7	Demineralization Ion Exchange Resin

Chapter 1 Introduction

1.1 General Introduction

With the world's urban population continuing to grow, it is important to understand the complex interactions and interrelationships between human activities and the urban environment (Wong et al., 2006). Urban environments play a supreme important role in human health and wellbeing (Liu and Diamond, 2005; Hänninen et al., 2014). Anthropogenic activities related to urbanization and industry are usually more intensive in urban areas, which may cause many problems including environmental pollution (Alloway, 1995; Gu et al., 2014a). One group of the typical contaminants in urban environment are trace metals, which are consequently useful indicators of environmental pollution (Manta et al., 2002; Sun et al., 2010). During the last decades, trace metals have been widely used by humans. Over time, increased emissions and their deposition can lead to anomalous enrichment, posing trace metal contamination of the urban environment, especially in soils. Urban soil is receiving attention as it can be the 'sink' of large quantities of pollutants including potential toxic geochemical elements which can be deposited for a long time (Ajmone-Marsan et al., 2008). Human health concern is generally associated with excessive exposures to metals via inhalation, ingestion, and dermal contact that cause harmful effects to biological organisms. Therefore, trace metal pollution in urban soils can have long-term and far-reaching effects on the environment and health.

Nowadays, urban environmental geochemistry has become an important scientific discipline. Since its establishment, it can be regarded as a field of scientific research that examines the physical, chemical, and biological conditions of an urbanized environment using the chemistry of the solid earth, its aqueous and gaseous components (Siegel, 2002). A wealth of scientific information yielded provides insights into the deposition, mobilization, distribution, and dispersion of potentially toxic metals in urban soils (Ip et al., 2004). This knowledge plays a crucial role in the assessment of trace metal contamination and in the evaluation of potential environment and health risks (Sutherland and Tolosa, 2000). In addition, it is increasingly recognized that incorporating of such information into urban planning can improve the development of healthy and sustainable urban environments (Brown, 2003; Pacione, 2003). Thus, it is necessary to further understand spatial variation of trace metals in urban soils.

Due to intense human activities in the urban area, the soil contamination and signs of the enrichment with trace metals may be masked (Sutherland, 2003; Semlali et al., 2001, 2004; Zereini et al., 2004). GIS mapping is a useful tool for estimating and quantifying the spatial distribution of trace metals in soil (Li et al., 2004; Lee et al., 2005). Contaminated sources can be assessed as soon as the transport routes and transport patterns of the trace metals are identified through distribution maps (Baker et al., 2000; McGrath and Zhao, 2003). On the other hand, monitoring the bioavailability and risks caused by trace element pollution in environment requires determination of their concentration in the soil. Soil toxicity limits are usually determined by the total concentration of such toxicity limits should depend on the bioavailability of trace metals and their possible incorporation of the trace metals into the food chain (Ross et al., 1994; Kabata, 2010). It is necessary to choose the appropriate analytical methods from the existing methods to address the specific problem of concern.

Therefore, the purpose of this study is to investigate the concentration and spatial distribution of trace metals, mainly rare earth elements (REEs) and lead (Pb), in urban soils and an understanding of spatial relationships between the environment and anthropogenic activities. At the same time, to develop a new method for assessment of labile trace metals in soils. All these efforts will be useful for setting more realistic thresholds for trace metal polluted urban soils thus allowing for more effective way for hazard assessment and better decision-making in soil management.

1.1.1 What are rare earth elements

REEs comprise a group of 17 chemical elements: lanthanoid elements lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), scandium (Sc), and yttrium (Y) (Tyler, 2004; Loell et al., 2011). As Sc and Y share similar chemical properties with REEs and are often found in the same ore deposits (Thomas et al., 2014) they are regarded as the REEs. REEs are members of Group IIIA in the periodic table (atomic number between 57 and 71), which explains the similar chemical-physical

properties (Henderson, 1984) and environmental behavior (Tyler, 2004). In geological deposits, they have been commonly classified into two groups by their atomic number and masses (Sadeghi et al., 2013): those from La to Sm (i.e. lower atomic numbers and masses) known as the light rare earth elements (abbreviated LREE) (Ryu et al., 2007) and those from Gd to Lu (higher atomic numbers and masses) referred to as the heavy rare earth elements (abbreviated HREE) (Silva et al., 2016). The term "medium rare earth elements" (abbreviated MREE) has occasionally been applied to those from Pm to Ho (Tharumarajah et al., 2011).

1.1.2 Application in industry and agriculture

As shown in Figure 1-1, the unique physical and chemical properties of the REEs enable them to be used in numerous green and high-technology products (Crow, 2011) that people use on a daily basis (Meyer et al., 2011), such as high-strength magnets, computers, cell phones, high-capacity batteries, glass additives, pigments, superconductors, color TV sets, weaponry systems, wind turbines, X-ray-intensifying screens, phosphors for electronic displays, alloying agents in metals (Moller et al., 1986; Loell et al., 2011). Weber (2012) reported that 2.2 pounds of Nd and more than 5 pounds of La are used for a Toyota Prius car, while a new generation windmill requires 1500 pounds of Nd. The REE-doped zeolites are used as fluid-cracking catalysts in the petroleum industry (Pines, 1981). Ce oxide is used in the preparation of nanotubes for the purpose of obtaining excellent electrical conductivity and thermal conductivity (Wang et al., 2005). Moreover, REEs also play an important role in national defense construction, including precision-guided weapons, communications equipment, batteries and other defense electronics. Apart from their extensive use in industries, REEs have been used in agriculture for more than 40 years (He et al., 2001; Schwabe et al., 2011). REE-based micro-nutrient fertilizers have been widely applied in plants to improve the quality of crops and vegetables (Guo et al., 1988; Diatloff, 1999; Maheswaran et al., 2001), which contain Ce, La and Nd as their main components (Xiong, 1995; Zhang et al., 2001a). Thus, it has been predicted that the global demand for REEs will explode rapidly in the coming decades.

Chapter 1 Introduction



Figure 1-1 : This histogram shows the percentages of use of REEs in the US reported by the United States Geological Survey Mineral Commodity Summary, 2017. Most computer, electric vehicle batteries and cell phone are made with REEs. Granite, marble, and gemstones are polished with cerium oxide powder. Many vehicles use REEs catalysts in their exhaust systems for air pollution control. Many motors and generators contain magnets made with REEs. (Reproduced from Gambogi, 2011).

1.1.3 Environmental and health concerns of REEs

With the increasing industrial and agricultural utilization of REEs in recent years (Chen, 2011; Haxel et al., 2002), more and more REEs are released into the environment (Livergood, 2010). REEs are scattered and accumulated as residues in soils, water and atmosphere during the mining and processing, which are posing an environmental hazard (Yang et al., 2009; Kulaksiz and Bau, 2011). Reports indicate that the surface mining activities have caused serious environmental damages, such as soil erosion, air pollution and acidification (Liu et al., 2006; Wang et al., 2014).

Because of the common presence of thorium (Th), Aluminium (Al), Barium (Ba), Beryllium (Be), Cadmium (Cd), Cobalt (Co), Copper (Cu), Iron (Fe), Manganese (Mn), Lead (Pb), Zinc (Zn), and

local riebeckite (Yusof et al., 2001), the presence of REE minerals and commodities are associated with radionuclides contaminants.

On the other hand, as shown in Figure 1-2 REEs can be accumulated or transported to soil and ground water then they can enter the food chains (Liang et al., 2013) which bring potential risks on human beings (Cao et al., 2000). As non-essential elements in organisms, the knowledge of REE accumulation and ecological effects in soil remains unclear. In recent years, the toxicological effects of REEs have been receiving more attention (Aguilar et al., 2004). Gao (2009) has reported that REEs may also accumulate in the human body through inhalation, ingestion, and even skin contact, resulting in the increase of the developmental rates of lethal diseases.



Figure 1-2 : Mobility of the contaminants is controlled by geologic, hydrologic ,and hydrogeologic environments where the mine is located along with the characteristics of the mining process and waste handing methods (Reproduced from Migaszewski et al., 2015).

1.1.4 Spatial variation of REEs and lead in urban soils

Despite a great deal of research on the environmental contamination and potential health hazards of REEs in the mining areas over recent years, there has been relatively little investigation into

their geochemical behaviour and impacts in urban soils (Teng et al., 2004; Natarajan et al., 2006). The sources of REEs in the urban soils can be both natural and anthropogenic (Hernandez et al., 2003; Rivera et al., 2015). The accumulation of REEs in surface layers of urban soils is related to the direct and indirect anthropogenic inputs (Schwabe et al., 2011). Many studies indicated that REEs have been considered as environmental indicators of vehicles and other human activities in urban areas (Zayed et al., 1999a; Cinti et al., 2002), especially where leaded gasoline is no longer in use (Kitto et al., 1992; Huang et al., 1994). Human activities not only determine the levels of soil enrichment with REEs, but also control their forms and speciation. Therefore, it is needed to investigate the spatial variation of REEs in urban soils, scientifically assess the current status of REEs contamination and explore the influencing factors on REEs accumulation and distribution in urban soils.

Among numerous urban soil pollutants, heavy metals are regarded as contaminants owing to their toxicity and difficulty in degradation (Sun et al., 2010; Kim et al., 2015). For the health of humans and plants, the occurrence of Pb in soil is important, since it is not only toxic to human beings and organisms, but also it causes urban environmental pollution (Huang et al., 2012). After entering the soil, it can directly or indirectly affect human health through intake, inhalation or even skin contact. Many studies have shown that relatively low concentrations of Pb in blood lead to significant decrease in intelligence quotient (IQ) of children (Bierkens et al., 2012; Isaac et al., 2012). The elevated concentrations of Pb in urban top-soils are almost related to anthropogenic activities, especially the leaded gasoline exhausts (Wilkins, 1978). The spatial variation of Pb in urban soils can be used as a tracer to investigate geological and anthropogenic contributions to heavy metals concentrations in soils (Pelfrene et al., 2013) and to explore the influencing factors by the same or different sources. It is important to understand how urban development may have influenced soil quality when heavy metals enrich across city (Mcllwaine et al., 2017).

In urban areas, it is difficult to identify contamination of urban soils due to the spatial heterogeneity feature of trace metals caused by multiple environmental factors such as soil parent materials, land uses, rock type, topography and human activities (Reimann et al., 2000; Lee et al.,

2006). Since the influencing factors vary spatially, there would be different responses of trace metals to these factors in different locations (Zhang et al., 2008). They may exhibit different relationships in different areas, because of the different influences of factors in different locations (Zhang, 2006). Today, forced by the increasing environmental and health awareness of the public, assessments of a range of trace metals in urban soils (CCME, 1997; National Environmental Protection Agency, 1995) have become a requirement of the hazard assessment and soil management guidelines. Therefore, it is important to better understand the complicated relationships in urban geochemistry, especially with strong human activities which are strongly spatially variable.

1.1.5 Geographical information systems (GIS)

Geographic information system (GIS) is regarded as a powerful tool for collecting, retrieving, transforming, storing and displaying spatial data from the real world (Burrogh and McDonnell, 1998). Current GIS technology in combination with statistical techniques are widely used to display spatial variation of soil parameters. The application of GIS is beneficial for reducing costs of investigation and recognizing the contamination on sources (Liu et al., 2006; Zhang and McGrath, 2004; Zhang et al., 2009). Moreover, the geochemical maps of heavy metals and other elements can be used as a visual tool which provides an easier way to identify the potentially contaminated areas. Many studies have shown that statistical techniques (McBratney, 1996) and GIS (Korre et al., 2002) have become promising tools for the study of soil management and hazard assessment (Sollitto et al., 2010; Burrough et al., 2015). For example, a better understanding of the spatial variability of soil heavy metals and the environment can be obtained by using the semivariogram approach of geostatistics. The results which are helpful for improving eco-environment quality in a regional scale (Yang et al., 2009). Furthermore, a continent scale of potential health impacts between pyrethroids and soil or water in the European can also be obtained by overlaying the pyrethroids transport pathways with the key environmental feature, e.g. pesticide use, crop distribution, landscape and climate parameters (Pistocchi et al., 2009).

1.1.6 Diffusive gradients in thin films (DGT)

According to previous studies, the determination of total trace metal content in the soil can evaluate the environmental risk (Tack and Verloo, 1995), while only the labile metal species are available to plants (Menzies et al., 2007). Knowing the total concentrations of trace metals in soil fails to provide information for the assessment of their bioavailability to plants (Zhang et al., 2014). Many early studies have been performed to find a suitable method to estimate bioavailability of trace metal, such as chemical extraction (Pierzynski, 1998), biotic ligand model (Thakali et al., 2006), or Windermere Humic Aqueous Model (Tipping, 1998). However, metal speciation in soil solution may change during sampling and extraction when it is tested by the traditional methods (Zhang et al., 2001). In addition, these methods fail to account for the kinetics of metal resupply from solid phase to solution (Hooda and Zhang, 2008). This problem is addressed by DGT technique, which can measure the mean flux of labile species in soil directly (Zhang et al., 2001), and provide an effective approach for the measurement of bioavailable metal concentrations in situ (Zhang et al., 2013). Yet, to date, the current use of DGT measurement in studies of REEs soil pollution remains absent.

Many studies have observed relationships for DGT-labile metal concentrations in plants grown under pot and field conditions. For example, in the study of Ngo et al., (2016) the DGT technique was used to predict the bioavailability of As and Sb to *Raphanus sativus* in a contaminated soil. The result showed strongly correlations between As and Sb in R. *sativus* tissues and their DGT measured labile concentrations. The DGT application in soil for estimating As bioavailability was conducted by Dai et al., (2017) who compared the DGT with other methods in predicting As uptake by *Brassica chinensis* grown in various soils from 15 provinces in China. DGT technique showed a better correlation than other methods. Peng et al., (2017) also found a better correlation between trace metal concentrations in soil measured by DGT and trace metal concentrations in plants, indicating that DGT method can be used to predict on uptake by different plants. It would be of great interest to know if the DGT technique can also be used to evaluate the bioavailability of REEs in soil.

1.1.7 EU and Irish policies on soil contamination

There are extensive EU and Irish legislation for the prevention and control of soil pollution. For example, the EU Seventh Environment Action Programme was implemented through national environmental regulations by the Member States, whose aims are: (1) to reduce soil erosion; (2) to remediate contaminated sites and increase soil organic matter by 2020 (EC, 2013). Achieving the aims of Floods Directive (2007/EC/60) and The Water Framework Directive (2000/60/EC) (WFD) without destroying the environment relate to many actions in planning mechanisms, including land degradation, green infrastructure in place (EEA, 2016) to improve and protect soil quality. In addition, as a result of the continued use of soil, the commission adopted a Soil Thematic Strategy (COM(2006)231) on 22 September 2006 aimed at protecting soils throughout the EU. Despite the Commission decision in May 2014 to withdraw the proposed Soil Framework Directive, the Seventh Environment Action Programme recognizes that soil degradation is a vital challenge. According to the Seventh Environment Action Programme effective on 17 January 2014, the aims are adequately protecting and remedying contaminated sites of soil and committing the EU and its Member States to enhance efforts to reduce soil erosion and increase soil organic matter. Therefore, it is a key part of research in the urban soils sector to investigate the levels of trace metal and REE contamination.

1.2 Aims and Objectives

The aim of this thesis is to improve the hazard assessment and soil management of trace metals in urban soils. To better understand of the geochemical behaviour and to investigate the level of REEs contamination in urban soils of London by using GIS techniques; and to analyse the spatially varying relationships among REEs and lead thus highlighting their anthropogenic and influence factors (Facchinelli et al., 2001; Cai et al., 2015). A literature review of factors associated with the characteristics of REEs in soils that contribute to the spatial variation of REEs in urban

soils helps us to find the gap in the knowledge (Fu et al., 2001; Huo et al., 2012). And extensive laboratory experiments are carried out to fill the gap in the simultaneous measurement of REEs labile species in soils. The experiments and the application of techniques to measure labile REEs described in this thesis are believed to be the first of their kind ever conducted. The results are providing a novel method for assessment labile of REEs in the soils. To this end, the following tasks were identified:

- To investigate the concentration of seven REEs (Ce, La, Nd, Sc, Sm, Yb and Y) in the urban soils of London;
- (2) To study the spatial variation of seven REEs and other trace metals in the urban soils of London by using statistics, Local Moran's I index and GIS techniques;
- (3) To reveal spatially varying relationships between Pb and Al, Ti and Al and to explore the influences of natural and anthropogenic factors;
- (4) To assess the environmental risks associated with REEs and other trace metals in urban soils and to identify their potential contamination sources;
- (5) To develop DGT for the simultaneous measurement of the fifteen REEs.

Achievement of these specific objectives have allowed the broader objectives to be met:

- (1) The spatial pattern of Ce, La, Nd, Sc, Sm, Yb and Y in their distribution maps highlights the value of using Local Moran's I for the identification of contamination hotspots and the influence of the factors controlling REEs distribution and sources within urban soils.
- (2) The spatially varying relationships between Pb and Al in soils of the urban London suggested that GWR is an effective tool to reveal spatially varying relationships in environmental variables, providing the improved understanding of the complicated relationships in environmental parameters from the spatial aspect.
- (3) To provide a methodology for simultaneous measurement of fifteen REE ions in soils based on the data acquired using the Chelex® 100 DGT in a single assay.
- (4) To improve the hazard assessment and soil management of trace metals in urban soils.

1.3 Structure of Thesis

Chapter 2 reviews the relevant literature on factors likely to affect the spatial distribution and concentration of REEs in soils. It also describes the weathering process of REEs under natural conditions in the techniques used to investigate the spatial analysis. It reviews the measurement methods of REEs in soils and expands on how these might be applied to urban soil pollution studies.

Chapter 3 (A) describes the process of sampling and sample preparation of soil samples, which were collected from the London urban area, and a preliminary assessment of top-soil chemistry in the urban areas of the London. It also gives details of the spatial interpolation methods used to investigate the environmental behaviour and general characteristics of REEs in the urban London soils. **(B)** describes that field sampling and analytical methods for Maoniuping REEs tailing dam soils were applied in the study, and presents the results of REEs levels related to mining activities in soils samples. The contamination levels and the potential bioavailability for the REEs in soils are determined in order to assess the impact of the abandoned residues on the surrounding communities. In addition, the experimental methods used in this thesis are determined, starting with information on the measurement of REE ions in laboratory methods. The designs and operations of the nine experiments are given, with the chapter also setts out the experimental procedures used to calculate the accumulating mass of the (*M*) and the DGT-measured concentration (C_{DGT}) from the binding layer, and the gel preparation and DGT deployment. The statistical tools used to analyse the results of the experiments are presented in the chapter.

Chapter 4 comprises the published papers: "Using local Moran's I to identify contamination hotspots of rare earth elements in urban soils of London" Journal of Applied Geochemistry, 2018, 88 (167-178). This paper reports the spatial distributions of Ce, La, Nd, Sc, Sm, Yb and Y in urban London soils, inducing the spatial clusters, spatial outliers, and their influencing factors, were identified using the index of Local Moran's I and IDW. The REEs hotspots revealed in urban

soils may not only imply potential contamination required further attention, but also highlight that the Local Moran's I is an effective way to identify contamination hotspots in urban soils.

"Exploration of spatially varying relationships between Pb and Al in urban soils of London at the regional scale using geographically weighted regression (GWR)". This paper analyses the spatially varying relationships between the concentrations of soil Pb and Al in urban soils and their relationship to natural or anthropogenic impact. A GWR was used to explore the spatial relationship in the results. GWR models showed how these spatially varying relationships are varied across the study area and establish relationships between the concentration of some of these trace metals and the soil parent material and human impacts.

"Simultaneous measurement of fifteen rare earth elements using diffusive gradients in thin films" Journal of Analytica Chimica Acta. 1031 (98-107). This paper contains the development of the novel DGT measurement method for the fifteen REE ions, and demonstrates (i) significant advantages of the Chelex® 100 DGT in the simultaneous measurement of the fifteen REE ions, reflected by a wide tolerance toward environmental interferences, and (ii) deployments in contaminated mine soils verified that Chelex® 100 DGT was a feasible tool for bioavailability assessment of REE ions in soils in this study.

Chapter 5 discusses the findings of this research in relation to the objectives outlined in chapter 1 and chapter 2, and highlights the new findings of this research and their impact in expanding the base of knowledge in relation to the hazard assessment and soil management of trace metals in urban soils, and describes the contributions and advancement in the field of soil contamination.

Chapter 6 summarises the conclusions of the research and points to future work on REEs and trace metals in urban soils.

1.4 Summary of Research Papers

Paper 1: lead author

Using Local Moran's I to identify contamination hotspots of rare earth elements in urban soils of London

Yumin Yuan., Mark Cave., Chaosheng Zhang. 2018. Applied Geochemistry. 88, 167-178.

In this article, a total of 6467 top-soil samples were extracted from the British Geochemical Survey of urban London area, providing the basic data for studying the top-soil REEs distribution patterns and their environmental influencing factors. The hot spots and cool spots were identified using the index of Local Moran's I. A strong natural control of REEs was illustrated with elevated concentrations in the Alluvium, Glacial till and Clay-with-flints deposit, which was clearly influenced by the lithology. Low value clusters of REEs in the Hyde and Richmond Park were associated with the high concentration of Si. Besides the natural control, the high value outliers concentrated in the built-up area and rural areas, which indicated that soil REEs content were also affected by human activities, such as agricultural practices, vehicular emission and urbanization. The spatial patterns of REEs revealed in urban soils may imply potential contamination which is required further attention.

I am credited with analyzing the data collected by British Geochemical Survey. I am responsible for the processing of the data, forming the conclusion, and writing \sim 90% of the manuscript.

Paper 2: lead author

Simultaneous measurement of fifteen rare earth elements using diffusive gradients in thin films

Yumin Yuan., Shiming Ding., Yan Wang., Liping Zhang., Mingyi Ren., Chaosheng Zhang. 2018. Analytica Chimica Acta. 1031, 98-107.

In this article, a new method for the simultaneous measurements of fifteen REE ions was established by using the DGT technique with an improved Chelex® 100 binding gel. Five different types of ion exchange resins (Chelex® 100, D418, D001-cc, 001x7, and HSTY®-SS) were investigated. The binding kinetics of each REE ions in a mixed solution indicated a rapid uptake on the Chelex® 100 gel. The results showed that stable elution efficiencies for these REE ions by using 2.0 M HCl, independent of pH (3-9) and ionic strength (3 mM-100 mM), with capacities for mixed solution at a range of 5.39-6.75 µg cm⁻². Application of the DGT for soil analysis showed that Chelex® 100 DGT was a useful tool in simultaneous measurement of the fifteen REE ions, even in a soil with high concentrations of REEs.

I am credited with the collection of soil samples in Mianning city, China. I am responsible for the completing all DGT experiments, processing of the data, forming the conclusion, and writing \sim 90% of the manuscript.

Paper 3: lead author

Exploration of spatially varying relationships between Pb and Al in urban soils of London at the regional scale using geographically weighted regression (GWR)

Yumin Yuan, Mark Cave, Haofan Xu, Chaosheng Zhang.

This article applied GWR to analyse the spatially varying relationships between the concentration of Pb and Al in urban soils of London based on 6467 samples collected by British Geological Survey. Akaike Information Criterion (AIC) and six bandwidth parameters (rang from 1000 m to 50000 m) were used to calculate the coefficients and the local R² for GWR models. The results displayed that the relationships between Pb and Al vary across urban soils of London, with different relationships in different areas. The great impact of anthropogenic input Pb, resulted in the weakened correlation in central London or even the changed relationship direction from positive to negative correlation in the suburban area of northern London. On the other hand, the positive relationships between Pb and Al exhibited in large parklands and greenspaces in part of central, as well as southeast and southwest areas of London, which could be related to less influences from human activities. Our results highlight that GWR is an effective way to reveal spatially varying relationships in environmental variables.

I am credited to analyze the data collected by British Geochemical Survey. I am responsible for the processing of the data, forming the conclusion, and writing $\sim 90\%$ of the manuscript.

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2.1 Natural and Anthropogenic sources of REEs

The natural content of REEs in soils mainly originates from the bedrock mineralogy and lithology (Diatloff et al., 1996; Yoshida et al., 1998; Krafka, 1999), and the average total concentration of REEs in the Earth's upper crust is 0.015% of the Earth's crust (Haxel et al., 2002). In many studies the concentration of REEs in the soils of different countries have been investigated (Diatloff et al., 1996; Yoshida et al., 1998; Krafka, 1999), and their results are list in Table 2-1. The largest REE deposits are mostly associated with hydrothermal carbonate and peralkaline silicate rocks (Zhang and Shan, 2001) which are affected by hydrothermal processes (Williams-Jones, 2012). The REEs are considered as the most lithophile (rock-loving) elements (Kynicky, 2012), and the abundance of REEs occurs in more than 200 known REEbearing minerals (Chakhmouradian and Wall, 2012), such as the generally mined (Joy et al., 2003) bastnäsite REECO₃(F,OH) (53–79 wt% ∑ REO) (Zhang et al., 1995), xenotime (REE, Zr) (P, Si)O₄ (43–65 wt%) (Trifonov, 1963), monazite (REE, Th, Ca, Sr) (P, Si, S)O₄(38–71 wt%) (Richter, 2006), and Ba-REE fluorocarbonates BaxREEy(CO₃)x+yFy (22-40 wt%) (Möller, 1963) (Table 2-1). Table 2-2 showing a decreasing order of REEs content depends on the parent materials: granite > quaternary > basalt > purple sandstone > red sandstone (Zhu and Liu, 1988). Soils developed from basic igneous rock, acid igneous rock, sandstone, and shale rock usually have higher REEs contents (Vinogradov, 1959), ranging from 174 to 219 mg kg⁻¹ (Liu, 1996), while soils originated from loess and calcareous rocks (Ure and Bacon, 1978) have lower REEs concentrations between 137 to 174 mg kg⁻¹ (Liu, 1996). As can be seen in Figure 2-1, due to the large scale of mining and refining activities greatly contribute to the REEs emission in soils, the naturally occurring abundances are altered (H. Ichihashi, 1992).

mg/kg (ppm)								
Element	Atomic Number	Continental Crust ¹	Upper Continental Crust ²	Top-soils (Europe) ³	Soils (South China) ⁴	Stream Sediments (Europe) ³		
La	57	30	30	25.9	7.98-57.0	41		
Ce	58	60	64	52.2	18.3-122	83		
Pr	59	6.7	7.1	6.02	1.72-12.2	9.22		
Nd	60	27	26	22.4	6.16-40.6	36.6		
Sm	62	5.3	4.5	4.28	1.21-7.76	6.91		
Eu	63	1.3	0.88	0.851	0.19-2.36	1.15		
Gd	64	4	3.8	4.2	1.32-7.14	6.32		
Tb	65	0.65	0.64	0.638	0.28-1.15	0.958		
Dy	66	3.8	3.5	3.58	2.01-6.29	5.4		
Но	67	0.8	0.8	0.716	0.34-1.16	1.09		
Er	68	2.1	2.3	2.1	0.81-3.11	3.18		
Tm	69	0.3	0.33	0.312	0.09-0.42	0.47		
Yb	70	2	2.2	2.09	0.56-2.66	3.09		
Lu	71	0.35	0.32	0.307	0.08-0.42	0.477		
REE		144.3	146.37	125.594	40.32-260.77	198.865		
Sources: ¹ Wedepohl (1995), ² Taylor and McLennan (1985), ³ Salminen et al., (2005), ⁴ Miao								
ct al., (2000).								

Table 2-1: REEs, atomic numbers, and abundances.



Figure 2-1 : Contaminants of concern is depend on the REE-bearing ores, the toxicity of the contaminants from the waste rocks, ore stockpiles and process waste streams (Reproduced from Gwenzi et al., 2018). The presence of excessive REEs contents in soils may have serious consequences for surrounding ecosystems, groundwater, agricultural productivity and human health (Li et al., 2013).

Table 2-2: Mean total REE content in soils from different parent materials (Liu, 1996)

Parent materials	Mean content (mg kg ⁻¹)	
Acid igneous rock	196	
Neutral igneous rock	178	
Basic igneous rock	216	
Loess	174	
Laterite	203	
Sediment rock and shale	202	
Sandstone	219	
Lime rock	137	
Purple sandstone	190	
Sand-shale stone	174	

It is widely recognized that mining activities lead to the intensive accumulation of REEs in soils (Feng et al., 2005), but fertilization is also an essential way by which REEs get into soils (Husain et al., 1980) (Figure 2-1). Scientific reports showed that phosphorus fertilizer production contains on average 45.2 mg La kg⁻¹ and 61.0 mg Ce kg⁻¹ (Volokh et al., 1990; Meehan et al., 2001). Regular uses of these fertilizers have yielded a significant increase of the REE content in cultivated soils (Todorovsky, Minkova, and Bakalova, 1997). Moreover, REE-based micro-nutrient fertilizers, which contain Ce, La and Nd as their main components (Xiong, 1995; Zhang et al., 2001a), have been widely applied to plants to improve the quality of crops and vegetables for over 20 years in China (Guo et al., 1993; Diatloff, 1999; Maheswaran et al., 2001).

In addition, the results derived from the early studies have indicated that due to poor control of collected waste and separated collection upstream (Allegrini et al., 2014), several waste ashes posed the particular risk of having Sc, Sm, and Eu accumulated in soils (Kawasaki et al., 1998). Compared with the contents of animal and horticulture waste ashes, higher values of Sc, Sm, Gd, and Tb were found in sewage sludge ashes, and Eu and Tb were observed in the tin incinerator's bottom ashes (Zhang et al., 2001a). Morf et al. (2013) and Allegrini et al. (2014) also have reported that solid residues from municipal solid waste incinerators (MSWI) contained high levels of REEs.

Atmospheric deposition with anomalous concentrations of anthropogenic REEs may enter soils (Wang et al., 2000). It has been found that the total concentration of REEs in atmospheric particulate matter in the western part of the Netherlands was 0.22-33.0 ng m⁻³ (Wang et al., 2001a). The study by Volokh et al. (1990) also showed the presence of anthropogenic La, Ce, Nd, Sm, Eu, Tb, Dy, and Lu with high values (454-1333.7 mg L⁻¹) from the snow in the area around a phosphorus fertilizer plant in Russia. Additionally, introduced in the late 1950 s (Kerr et al., 1984; Shu et al., 2015), zeolite cracking catalysts, which contain rare earth mixtures (Sousa-Aguiar et al., 2013; Shi et al., 2016), have been used by the petroleum refining industry

to produce light-weight hydrocarbons, such as gasoline and fuel oil (Doronin et al., 2015). The study performed by Nance (1977) reported the ratios of La/Sm, 20, 5.2 and 28, respectively in ambient coarse particles (diameter > 2 mm) was found in the emission form a refinery and a coal and oil-fired power plant (Olmez and Gordon, 1985).

On the other hand, in urban areas, anthropogenic activities are also considered as the influencing factors of REEs in soils (Hong et al., 2010; Liang et al., 2014). The relationships between metals in urban soils behave differently in space due to different human activities such as industrial discharges and processing (Suzuki et al., 2011; Khan et al., 2016), waste-processing plants, vehicles emissions and fertilizer use (Kučera et al., 2006). For example, London is a large city of industrialization and urbanization. It has a long history of coal using, metal mining and peat burning. Those human activities could also contribute the REEs discharges in urban soil of London.

2.2 Influencing Factors of REEs in Soil

In natural conditions, the accumulation of REEs in soils are influenced by many factors, such as their parent rocks, weathering processes, pH value, and organic matters (Cao et al., 2001; Heinz et al., 1993; Sholkovitz, 1994b). Among these factors, the soil pH value is an important factor influencing the adsorption of REEs in the environment (Gao, Zhang and Wang, 1996b). Previous study has found that increasing soil pH values causes a greater adsorption of REEs in soils (Wang et al., 2001a) as soil particles are covered with more OH⁻ ions to be formed as complexes with REE ions (such as Ln(OH)2⁺, Ln(OH)⁺₂, and Ln(OH)⁻₄) (Zhu and Xing, 1993). Gao et al. (1999c) compared the adsorption equipotential points of La and Yb under different pH conditions, and the results revealed that the adsorption capacity is lower for Yb than that for La at pH values similar to the equipotential point. Cao et al. (2001) revealed that the desorption of La, Ce, Gd, and Y in the soil was increased when soil pH decreased from 7.5 to 3.5.

REEs can be fixed in organic matter (OM) which play an important role in controlling the behaviours of REEs in soils. This is due to the protons dissociating from the carboxyl and phenolic groups of humic polymers in the soil (Beckwith and Butler, 1993) that have a high capacity of adsorbing or chelating bivalent and trivalent cations (Wu et al., 2001a). Tyler and Olsson (2002) demonstrated that the highly stable and immobile OM contributes significantly to the mobility and transport of the REEs because of the amounts and shares of dissolved organic carbon (DOC) in the soil (Nikonov et al., 1999). Shan, Lian and Web (2002) found that the rate of La, Ce, Pr, and Nd with organic acids followed the order of citric acid > malic acid > tartaric acid > acetic acid = $Ca(NO_3)_2$. It is in the same order of the stability of the REE complexes as that the formation of organic acids have (Shan, Lian and Web, 2002). Dong et al. (2001) identified that the absorption and desorption of Eu³⁺ had a significant correlation with the humic and fulvic acids, and in the case of column experiments on Eu³⁺ from sand, Eu was detected in the eluent only when DOM was added in the system (Nagao et al., 1998). The adsorption of Ce to bentonite was obviously lower than humic acids (Brown, 1969).

Base on previous studies, the adsorption rate of REEs to Manganese dioxide (MnO₂) and FeOOH (Koeppenkastrop and DeCarlo, 1993) is fast and strong, and REEs adsorption reactions are very swift in Iron (Fe) and Manganese (Mn) concretions as described by Fleet (1984). Gao et al. (1999b) reported that the adsorption rate was fast at the beginning when it was controlled by the diffusion rate. In addition, Fedorf and Fendorf (1996) demonstrated that REEs was adsorbed to the oxides of minerals. The results of their experiments indicate that the surface precipitation of sodium hydroxide on pH was the main adsorption mechanism of birnessite (Wang et al., 2000). Their results also confirmed that the complex surface of monomeric and small multinuclear mineral species in a goethite significantly controlled the retention of La (Fedorf and Fendorf, 1996). Dong et al. (2001) reported the main adsorption mechanism of alumina on a red soil was bentonite, which was formed by bridged hydroxy lanthanide complexes.

2.3 Health Effects of REEs

According to the Hodge-Stemer classification system, REEs are generally considered as neither essential elements for life nor strongly toxic elements in the environment (Haley, 1979). The rapid increase of the exploitation and utilization of REEs, has caused the harmful effects and health hazards of REEs transferred to human as inhalation and ingestion (Haxel et al., 2014; Chen and Zhu, 2008) may cause the REEs accumulate in blood, brain and bone (Feng et al., 2000; Yuan et al., 2003).

2.3.1 Effects on lung

An early study by Vogt et al. (1986) provided evidence that the REEs pneumoconiosis was not only a long-term lung disease but also more likely to occur in people exposed to rare earth dust. The Ce fine particles accumulated in the lungs may result in interstitial disorders, emphysema, and severe obstructive injury and may reduce carbon monoxide diffusion (Nemery, 1990). The case of Dufresne et al. (1994) reported workers who had died of cancer at various sites had higher than average measured concentrations of elemental Ce, La and Nd in the lungs. Even though the toxicity of REEs is only slightly potential pathologic compared with other well-documented fibrogenic dusts (Richter, 2003), the biological effects of occupational exposure to the REEs are still unclear. Hence, due to the health of workers (Pairon et al., 1994), respiratory intake of REEs particles at occupational exposure worksites is strictly restricted (Neizvestnova et al., 1994).

2.3.2 Effects on liver

The studies of Arvela et al. (1976, 1980) found that the liver's declining function could be associated with high exposure levels of REEs, especially for LREE. Liver is a tissue that can contain a large amount of bioavailable REEs, which has already been reported in various

studies (Zhu et al., 2005). A specific decrease in liver microsomal enzymes activity was reported by Arvela and Karki (1971), who found that the liver endoplasmic reticulum was changed by injecting La, which played an important role in drug metabolism and detoxification. Similar results were observed by Magnusson (1963) and Tuchweber et al. (1976), who demonstrated the formerly termed glutamate pyruvate transaminase (GPT) and formerly termed glutamate oxaloacetate transaminase (GOT) of liver specific enzyme activity was increased after the injection of REEs.

2.3.3 Effects on bone

According to a study by Moskalev (1985), REEs are bone-seeking elements. Bone is not only the second largest deposition tissue of REEs in the human body (Damment et al., 2003) but also related to both the organic matrix and the inorganic minerals of the bone. The long biological half-lives of REEs in bone provide an important basis for environmental monitoring (Evans, 1990). Although no toxic effects of REEs have been found on bone structure, mineralization defects have been reported by Damment and Shen (2005) and Freemont et al. (2004) after administering high-dose lanthanum carbonate to rats.

2.3.4 Effects on brain

Certain neurological effects of REEs have been found after direct injection La³⁺ into brain tissue to produce similar analgesic effects of opiates (Harris et al., 1975). Furthermore, the study on the effects of lanthanides on nerve cells was conducted by Evans (1990), who found that due to the blood-brain barrier, lanthanides can not enter the central nervous system (Joy and Finn, 2003); however, it was related to the interaction with Ca²⁺ in the transport processes (Weinemann et al., 1984). Besides, the case study of Zhuang et al. (1996), who compared the brain tumor tissue of patients with astrocytoma with normal human brain tissue, showed high

levels of La, Ce, Gd, and Lu in the brain tumor tissue, which provided a feasible correlation for the hypothesis that REEs were involved in tumorigenesis (Liu et al., 2013).

2.4 Spatial Analysis for REEs in Soil

The sources of REEs are complex (Facchinelli et al., 2001). Meanwhile, due to the heterogeneity of urban soils, concentrations of REEs vary over space (Luo et al., 2007). A better understanding of the spatial distribution and sources of REEs in soils (Aquino et al., 2015; Silva et al., 2018) will provide approaches to reduce concentrations and minimize human exposure (Azevedo et al., 2015). Spatial analysis of REEs in soils reveals spatial changes and helps to identify REE hotspots and their sources (Wang and Liang, 2016). This approach not only assists in exploring the influencing factors on REE distribution but also building spatial variability maps for identifying areas subject to environmental impact. Moreover, it a crucial step in delivering future environmental policies that affect human health and environmental protection. For example, Li et al. (2015) investigated 9 heavy metals accumulations and spatial distributions in road dust around a REEs mining area in Inner Mongolia, China, and confirmed that the concentration and distribution of As in the soils was influenced by the industrial activities. Pb and Mn in road dust were the main contributors to the anthropogenic source. The results also indicated that the road dust was contaminated by all investigated metals to varying extents, which might pose a potential hazard to children living near the REE tailings area for a long time and should be given more attention. Allajbeu et al. (2016) studied the atmospheric deposition of rare earth elements in Albania. The spatial distribution patterns of all tested REEs coincided with the locations of the steel and oil industry, indicating that the enrichment of REE in the atmospheric deposition was influenced by strong wind and anthropogenic source. Positive Nd, Gd, Eu, and Tb anomalies were also found. The HREE enrichment was intensified by the coal-enriched soil dust and the physiologic in organic material of moss tissue.

2.5 Historical Measurements Methods of REEs

The total concentration of REEs in soil is widely acknowledged in geochemistry as an important tool to provide valuable information about overall pollution levels (Nolan et al., 2003; Degryse et al., 2009), but it fails to provide sufficient information for estimating the bioavailability of REEs depending on the chemical speciation of REEs in soils and plant species (Zhang and Shan, 2001). Many efforts have been made to understand the potential mobility and bioavailability of REEs, such as single and sequential extraction procedures (Tessier et al., 1979; Quevauiller et al., 1993). Considering that under soil-weathering conditions, the water-soluble and exchangeable metal species are greatly mobile and available to plants (Hooda et al., 2008), assessing the bioavailability of metals in soils, therefore, efforts should concentrat on these available fractions. For this purpose, many single extraction methods have been developed and applied to investigating the bioavailability or toxicity of metals in soils (Das et al., 1995; Rauret, 1998). Generally, extraction methodologies, including neutral salts as Calcium chloride (CaCl₂) (Novozamsky et al., 1993) and Sodium nitrate (NaNO₃) (Snaka and Dolezal, 1992), diluted or mild acids (0.1 M HCl) (Baker and Amacher, 1982) and organic extractants including Diethylenetriaminepentaacetic acid (DTPA) (0.005 M) (Haq et al., 1980; Norvell, 1984; Brun et al., 2001), organic extractants ethylene-diamine-tetraacetic acid (EDTA) (0.005-1 M) (Haq et al., 1980; Hammer and Keller, 2002; Chaignon et al., 2003) have been widely used due to their ability to form water-soluble and well-defined complexes with metals cations.

Feng et al. (2005) compared the extraction methods, including DTPA, EDTA, CaCl₂, and NaNO₃ for the evaluation of bioavailability of heavy metals in soil. The significantly correlated relationship between the extractable amounts of Cr, Cu, Zn, and Cd and the metal content of barley roots was analyzed by the rhizosphere-based method. The results indicated that the CaCl₂ extraction method was also able to assess the bioavailability of Cr and Zn, while the EDTA extraction method be used to assess the bioavailability of Zn. The DTPA extraction method was good for assessing the bioavailability of Cu and Zn, but the correlation coefficients of Cu and Zn were relatively poor. In contrast, the DTPA and EDTA extraction

methods were suitable only for calcareous or for acidic soils, respectively. The CaCl₂ and NaNO₃ extraction methods were only suitable for exchangeable metals.

Zhang and Shan (2001) studied the accumulation behaviour of La, Pr, Ce, and Nd in winter wheat and their speciation in soil by using RE-based fertilizers. The fractionation of fertilized and unfertilized soil was divided into three stages of sequential extractions: water soluble and exchangeable and carbonate bound (B1), Fe-Mn-bound oxide (B2), and organic sulfide bound (B3). The results showed that the contents of REEs in B1 fraction significantly correlated with those in roots. In the fertilized soil, the REEs mainly exist in B2 and B3 while less amount in B1. The correlation coefficient was found between 0.6519 and 0.7410 when the amount of fertilizer in the soil was less than 20 mg/kg.

2.6 Application of DGT for Metals in Soil

It is well known that, in traditional methods of testing soil solution, metal speciation may change during extraction and sampling and the kinetics of metal resupply from solid phase to solution are not considered (Hooda and Zhang, 2008). Meanwhile, the bioavailability of metals in soil is dependent on both their concentrations in the soil solution and their rate of transport through the soil (Davison and Zhang, 2012). The diffusive gradients in thin films (DGT) is a novel in-situ device that measures directly the mean flux of labile species in soils to the device during the deployment (Zhang et al., 1995; Zhang et al., 2001). Therefore, it provides a promising approach for the measurement of bioavailable metal concentrations in soils (Zhang et al., 2001). Since the invention of the technique by Bill Davison and Hao Zhang in 1993 (DGT Research Ltd. 2014), the DGT has been used extensively to measure labile species in water (Alfaro-De la Torre et al., 2000; Murdock et al., 2001; Zhang et al., 2004; Unsworth et al., 2006; Paller et al., 2019), sediment (Harper et al., 1998; Downard et al., 2003; Motelica-Heino et al., 2003; Naylor et al., 2004; Campbell et al., 2008; Huang et al., 2019), and soil (Zhang et al., 2004; Ma et al., 2006; Li et al., 2019) environment (Zhang and Davison, 1995). A typical

DGT device uses a binding layer overlaid by a diffusive layer and filter (Xu et al., 2013). The binding layer is usually a hydrogel impregnated with Chelex resin or an analyte-specific adsorbent (Ding et al., 2010; Mundus et al., 2011). As shown in the Figure 2-2 and Figure 2-3, there are two types of holders configurations that are commonly used in DGT technique (Ding et al., 2016). One is a dual-mode holder used for solution and soil tests (Figure 2-2), and the other DGT holder is a flat-type one used for analysis of sediments (Figure 2-3).



Figure 2-2: DGT holders used for measurements in solution and soil. (A) and (B) are the 'O-shape' ring and recessed base of the DGT core in the holder, respectively. (C) is the hollow base for accommodation of the DGT core. (D) and (F) are the two different assembled forms of the DGT core and the open cavity for measurements in solution/water and soil, respectively. (E) and (G) are the cutaway views of (D) and (F), respectively. Reproduced from Ding et al. 2016.



Chapter 2 Literature review

Figure 2-3: DGT probes used for measurements in sediment. (A), (B) and (C) are the flat base, the window frame, and their assembled form for the two types of probes, respectively. (D) is the cutaway view of the bottom of (C) loaded with binding gel, diffusive gel and filter membrane, reproduced from Ding et al. 2016.

As shown in the Figure 2-4, in the uptake process, chemical element concentrations in solution go through the diffusion layer to the binding phase, which establishes a constant concentration gradient in the diffusive layer (Zhang et al., 1995; Davison and Zhang, 1994, 2012) (Figure 2-2). Previous studies have demonstrated that the measurement of DGT provides a better correlation to plant uptake than any other measurements (Zhang et al., 2001; Song et al., 2004; Nolan et al., 2005; Koster et al., 2005). The reason is that DGT uptake lowers the heavy metal

concentrations in the pore water near the DGT unit (Roulier et al., 2008; Perez and Anderson, 2009), which induces the heavy metal desorbed form the soil into the pore water at the same time (Zhang et al., 2001) (Figure 2-2). Therefore, it provides a promising method to measure the metal available from the complete soil system (Nowack et al., 2004; Lehto et al., 2006). Zhang et al. (2014) summarised the availability of DGT for many different purposes, which extends to in-situ measurement (Harper et al., 1998), monitoring (Scally et al., 2003), labile and bioavailable concentrations (Zhang et al., 2001) and fluxes, speciation (Monbet et al., 2008; Roig et al., 2011), and a high spatial resolution (Santner et al., 2015) and 2D concentration images (Ding et al., 2015).

A study conducted by Degryse et al. (2009) evaluated the accuracy of assessing the element bioavailability by DGT from soil to plant root. The results found that if plant uptake is low, competitive cations may affect the plant uptake more than DGT flux, and the diffusive transport of element from soil to the plant roots is most accurate when its uptake rate is limited. The correlation between the DGT flux and plant uptake may not be well due to the plants has little affinity with the element or the plant uptake is saturated by a large supply. Besides, a number of studies also have reported the effective capacity of a binding gel layer may be affected by pH (Ding et al., 2010), ionic strength (Xu et al., 2013), competitive ions (Mundus et al., 2011), and soil moisture (Panther et al., 2011). Conesa et al. (2010) determined the presence of high concentration of other competitive cations may hinder the accumulation of metals by the chelating resins, especially when pH value is low in mine tailings. Moreover, Hooda et al. (1999) also found soil moisture is another significant influencing factor of DGT measurement in soils. In their experiments, they found that not only the membrane needs the soil to be moist enough to maintain contact, but also the DGT flux reached the highest level when the soil moisture content was at the maximum water holding capacity (MWHC) level (Tankere et al., 2012). Therefore, the above influencing factors should be taken into account when assessing bioavailability using the DGT results.





Figure 2-4 : The kinetic process of DGT absorption and soil response. And the relationship between the process of plant and DGT absorption (Reproduced from Nanjing Easysensor Environmental Technology Co., Ltd).

Summary of the development of the binding agents extensively used for specific measuring cationic metals in the Table 2-3. The first and most frequently used binding agent is an iminodiacetate chelating resin (Chelex® 100), which has been developed for the measurement of a large number of metal ions, e.g, Cu, Ni, Zn, Cd, and Mn (Davison et al., 1994; Zhang et al., 1995; Zhang et al., 1998). A similar layer using suspended particulate reagent-iminodiacetate (SPR-IDA) has been reported for the measurement of trace metals (Co, Ni, Cu, Zn, Cd, Pb) with analysis using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (Warnken et al., 2004). Li et al. (2003) developed a solution phase poly (4-styrenesulfonate) (PSS) binding layer for the measurement of Cu and Cd in synthetic water. Specific measurement of some cationic metals has been made using other binding

agents (Mengario et al., 2010; Divis et al., 2005; Gregusova et al., 2011). Due to the great DGT capacities, strong tolerance to competitive ions, and chemical stability, the Chelex® 100 gel seems to be the most popularly used as a binding gel in DGT measurement (Mason et al., 2005; Huynh et al., 2012; Wang et al., 2016).

Analyte type	Binding layer (Bing agent)	Analytes	Reference
Cations	Chelex ®100 resin	Zn, Ni, Cu, Fe, Mn and Cd	Davison and Zhang 1994; Zhang et al., 1998
	Suspended particulate reagent-iminodiacetate (Spr-IDA)	Co, Ni, Cu, Zn, Cd and Pb	Warnken et al., 2004
	Poly (acrylamide-co-acrylic acid) (PAM-PAA), Whatman P81, Poly (4-styrenesulfonate) (PSS), Polyvinyl, alcohol (PVA), and sodium polyacrylate (PA)	Cu and Cd	Li et al., 2002; Fan et al., 2009
	Saccharomyces cerevisiae, and thiol-polyvinyl alcohol (PVA-SH)	Cd	Menegario et al., 2010; Fan et al., 2009
	Spheron-Thiol, Duolite GT73, and Iontosorb AV-MP resin	Hg	Divis et al., 2005; Divis et al., 2009
	Ammonium molybdophosphate (AMP), and copper ferrocyanide (CFCN)	Cs	Murdock et al., 2001; Li et al., 2009
	Spheron-Oxin® chelating ion-exchanger	U	Gregusova et al., 2011

Table 2-3: Summary of the development of the binding layer used in DGT (Wang et al., 2016)

2.7 Summary

The literature review has discussed the characteristic, occurrence, and geochemical behavior of REEs and their potential environmental effects in soils and health, and has provided in detail with their spatial distribution and influencing factor in soil. REEs will gain more importance in our future life due to their unique properties that are constantly demanded by various new technologies. Thus, understanding the spatial distribution and influencing factors of REEs in urban soil is critical for research on urban geochemistry. Despite a great deal of research on heavy metals pollution in urban soils over the past few decades, very little has been managed to identify the specific anthropogenic activities that have attributed to the REEs contamination. Moreover, considering the heterogeneity of urban soil that caused by a mixture of natural and anthropogenic controls, we address this research gap by studying the spatial variation and spatial distribution of REEs, using GIS and spatial analyses approaches to identify contamination and to explore influencing factors.

On the other hand, studies related to the extraction of REE ions generally use traditionally methodologies such as neutral salts, mild acids, and organic extractants. To date, the sampling device for simultaneous measurement of REE ions using DGT is also scarce. In our present work, we address this gap by developing DGT for the simultaneous measurement of the fifteen REEs.

Reference

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3.1 Research (A) Part

3.1.1 Study area description

The Greater London Authority (GLA) stands on the River Thames in the south-east of England, consisting of Cretaceous and Palaeogene bedrock and an overlying of Quaternary superficial deposits in some areas. This area is described in detail by Sumber (1996) and Ellison et al. (2004). A simplified geology with surface soil parent material (PM) map (Miles and Appleton, 2005) was used for the study (Figure 3-1). The Cretaceous chalk of the London Basin (Figure 3-2) is a typically fine-grained white limestone that is covered by the Chalk Group in the north-west and by older Cretaceous formations in the south (Hancock, 1975). Overlying the Chalk is the younger Palaeogene deposits, which is not only the main part of the central London Basin but also the most extensive clay formation in London (Bristow et al., 1997), of which is extensively in the north-west and along the southern sector of the London. The lower parts of the White Chalk in the south-east comprise white chalk with little seams of flint nodules (Bristow et al., 1997). The Thanet Sand Formation is the oldest Palaeogene deposit located in the south and south-east, which is dominated by silty, finegrained sand (Sumber, 1996). Above the Thanet Sand Formation lies the Lambeth Group, consisting of silty clay, pebble beds and fine-to medium-grained sands (Ellison et al., 2004). The Clay-with-flints is the heterogeneity that crops out extensively in the north-east and southeast of the London, lying on the Chalk (Katherine et al., 2011). It is the weathering of the Palaeogene and earlier Quaternary deposits, composed of clay with large unworn flint cobbles, sandy clay and reddish-brown clayey silt (Sumber, 1996; Katherine et al., 2011). River terrace deposits in the London and forms a central belt extending north into the Lee valley, which is the most widespread type of superficial deposit (Ellison et al., 2004).



Figure 3-1 : Simplified soil parent material map of the London region (GLA = Greater London Authority).



Figure 3-2 : The geological structure of the London region reproduced from Sumbler (1996).

3.1.2 Soil sampling and sample analysis

In the Greater London Authority (GLA) area, a total of 6467 urban topsoil samples were collected by the British Geology Survey from 2005 to 2009 (Knights and Scheib, 2010). The soil sampling was collected from a depth of 5 to 20 cm after the removal of any surface litter. Sampling was carried out in each 1×1 km square from the GLA area, with a sample site in each of the four 500×500 m quadrants (Johnson et al., 2005) (Figure 3-3). At each site, the composite sample consisted of 4 soil cores taken from 20×20 m square at four corners and the centre, according to a non-probability systematic design (BGS, 2011; Flight and Scheib, 2011). All the soil samples were air-dried, disaggregated, and sieved through a nylon sieve with 2 mm apertures and sub-sampled by coning and quartering. The total concentrations of 48 chemical elements were determined in the < 2 mm for each sample by wavelength dispersive X-ray fluorescence (XRF) spectrometry. Loss on ignition (LOI at 450 °C) and pH were also determined (Ferreira et al., 2017). Details of survey methodology, sample preparation, analytical methods, and quality control procedures were provided by Allen et al. (2001), Johnson (2005) and Johnson (2011), but we summarize the key points here.



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Figure 3-3 : Location of top-soil samples in urban London area (N= 6467).

3.1.3 Data analysis

3.1.3.1 Representative descriptive parameters

The parameters of Range, Variance, and Standard Deviation (SD) were calculated to describe the spread of a distribution. In fact, a larger SD indicates a greater difference between the values of the variable and a greater dispersion of a dataset. For comparing data sets with different units or wildly different averages, the Coefficient of Variation (CV) is used to describe global variability (Gallardo and Parama, 2007), which refers to the ratio of the SD to the average. We also calculated the percentage of Minimum, 5%, 25%, 75%, 95%, Maximum in this study.

3.1.3.2 Correlation analysis

Correlation analysis is commonly used to measure the degree of linear correlation between variables with appropriate statistical parameters. A scatterplot is the most frequently used tool for two quantitative variables (Yamane, 1973). A high correlation implies that two or more variable have a strong relationship with each other, while a weak correlation means that the variables are poorly related. In addition, in order to describe the degree of linear correlation between variables more accurately, the correlation coefficient can be used to study correlation (Koch and Link, 2002).

3.1.4 The inverse distance weighted (IDW) interpolation

The inverse distance weighting (IDW), a deterministic spatial interpolation model, is one of the most widely used by geoscientists and geographers. IDW estimates values at un-sampled points by summing the weighted contributions from the sampled points within a selected number of neighbours of the un-sampled location (Robinson and Metternicht, 2006). The assumption is that sampled points closer to the unsampled point are great than those farther away so that the weight is inversely proportional to the p^{th} power of the distance between the unsampled point and the sampled points (Krivoruchko, 2011). The IDW weights is as follows:

$$\lambda_i = \frac{1/d_{i0}^p}{\sum_{i=1}^N 1/d_{i0}^p}, \quad \sum_{i=1}^N \lambda_i = 1,$$

Where d_{i0} is the distance between locations Xi and X_0 , p is a power parameter; N represents the number of sample points used for the estimation; λ_i is the weight of the ith sample point; The weights for the measured locations used in the prediction are scaled so that their sum is equal to 1(Isaaks and Srivastava, 1989).

3.1.5 Spatial outlier and spatial cluster analyses

In urban environment, soils are heavily disturbed by human activities. Due to the land use is complicated and the sources of imported soils are often unknown (Zhang et al., 2009), the potential contaminated sites of top-soils with trace metals may be masked (Coby et al., 2006). When studying urban soil pollution, it is important to identify the hotspots of pollution. It implies that high levels of pollution compared with the surrounding area. Meanwhile, it is worth to note that potential contaminated sites behave as 'outliers' in an urban geochemical database (Zhang et al., 2009), which are distant from the rest of the data. The high-value outliers play an important role in contaminated land investigation, especially when the values have exceeded the soil guideline values which should be paid more attention and further investigations could be needed for environmental management. In comparison with various other methods for hotspot analysis, spatial scan statistics (Ishioka et al., 2007), Getis's G index (Getis and Ord, 1992), Tango' C index (Tango, 1995; Zhang and Lin, 2006) Local Moran's I index (Ansenlin, 1995) seems to be a prevalent one. It can not only identify spatial clusters with high or low values but also reveal spatial outliers (Lognley and Tobon, 2004).

In this study, the method of local indicator of spatial association (LISA) was applied. According to Zhang et al. (2008b), there are a few factors affecting the Local Moran's I index analysis, including data transformation, weight function, and the extreme values. Considering checmial components in soils are compositional data, which may lead to spurious correlation (closed effect) in traditional statistical analysis, the centred-log-ratio (clr) transformation method was applied. Data transformation also helps to reduce the influences of extreme values (Zhang et al., 2008). To investigate the effects of different distance bands on the LISA reults, four distance bands ranging from 500 m to 2000 m were considered. Based on the spatial patterns of Ce, La, Nd, Sc, Sm, Yb, and Y, it seems the distance band of 1000 m was appropriate, which not only revealed the major spatial clusters in the north and the sourth parts, but also allowed other patterns to emerge. When using Local Moran's I index to analyze the spatial patterns, in order to obtain reliable and stable results in this study, all the factors were taken into account.

Local Moran's I index (Anselin, 1995; Getis and Ord, 1996) can be expressed:

$$I_{i=\frac{Zi-\bar{Z}}{\sigma^2}}\sum_{j=1,j\neq i}^n [W_{ij} (Z_j - \bar{Z})],$$

Where \overline{Z} is the mean value of Z with the sample number of n; Z_i is the value of the variable z at location I; Z_j is the value at the other locations (where $j \neq i$); σ^2 is the variance of z; and W_{ij} is the inverse of the distance d_{ij} between Z_i and Z_j , defined as a weight (Zhang et al., 2008).

A high positive Local Moran's I means that the target location under the study has similar value to its neighborhood. Two types of spatial clusters, high-high clusters (high values with high value neighborhood) and low-low clusters (low values with low value neighborhood) were identified by Local Moran's I. Meanwhile, a high negative Local Moran's I value indicates a potential spatial outlier. Spatial outliers are significantly different from the value of its surrounding locations, including high-low (a high value in a low value neighborhood) and low-high (a low value in a high value neighborhood) (Lalor and Zhang, 2001). Therefore, Local Moran's I index not only can be clustered both spatial clusters and spatial outliers but also can be standardized so that its significance level can be tested based on an assumption of a normal distribution (Anselin, 1995; Levine, 2004).

3.1.6 Spatially varying relationships analyses

In order to better understand the complicated relationships in urban geochemistry, especially with the influences of human activities which are strongly spatially variable, the concept of 'spatially varying relationship' deservers more attention (Brunsdon et al., 1996; Fotheringham et al., 1996). The traditional way of analysing relationships is to use statistical methods, such as correlation analysis and ordinary least square (OLS) regression. However, these methods

are producing 'average' or 'global' parameters to estimate the spatial relationships (Ali et al., 2007), which are reflected equally over the whole region. Therefore the impacts of local variations could be hidden (Bacha, 2003; Geri et al., 2010). In light of this, a local spatial statistical technique named geographically weighted regression (GWR) has been receiving increasing attention in geographical analyses (Brunsdon et al., 1996; Fotheringham et al., 2002; Deller and Lledo, 2007; Waller et al., 2007).

The GWR model takes the samples within a defined neighbourhood into the calculation by giving more weights to nearby samples than those further away (Wheeler & Paez, 2007; Zhang et al., 2011). The GWR thus creates regression models to explore how one dependent variable changes in response to one or more independent variables at the local scale (Osborne et al., 2007; Tu, 2011). A series of results such as local regression coefficient, the local residual, and the local R2 value for each location under analysis can be calculated (Cleveland, 1979; Brunsdon et al., 1996). The geographically weighted regression can be expressed:

$$y_{i} = \beta_0 (u_i, v_i) + \beta_k (u_i, v_i) x_{ki} + \varepsilon_i$$

This means that, at every loction $i(u_i, v_i)$, $\beta_0(u_i, v_i)$ is the intercept for location i, $\beta_k(u_i, v_i)$ is the local regression coefficient for the independent variable at location I, ε_i is an independently normally distributed random error with mean zero and constant variance σ^2 . The local regression coefficients can be estimated by using the weighting function as:

$$\beta(u_i, v_i) = (X^T W(u_i, v_i) X)^{-1} X^T W(u_i, v_i) Y,$$

Where $\beta(u_i, v_i)$ represents the unbiased estimate of β , and $W(u_i, v_i)$ is the weighting matrix to ensure that observations near the specific point have larger weighting values.

Considering the sample sites are located in border areas (Zhang et al., 2011), the adaptive kernel type was selected as the weight function. Based on previous studies, the bandwidth

plays an important role in controlling the parameter for GWR results (Guo et al., 2008; Gao and Li, 2011). The Akaike Information Criterion (AICc) (Akaike, 1973) was first used to be the bandwidth, which is effective to find the 'optimal' bandwidth in the GWR model (Fotheringham et al., 2002). However, the spatial patterns of the two variables were too noisy for exploration of the influencing factors. We have investigated the effects of different bandwidths from 100 m (very short) to 50000 m on the results. When the bandwidths increased from 5000 m to 50000 m, similar spatial patterns were observed for those bandwidths. The bandwidth of 50000 m seemed to be too large with many details eliminated for the size of the study area. So, we selected only six bandwidths in this paper for comparison. On the other hand, this study focuses on the spatial patterns into consideration with the R^2 and AICc of GWR models, it seems that the bandwidth 5000 m was compromised choice, which retained not only sufficient details of the underlying spatially varying relationships in the study area but also with relative high R^2 and small AICc values.

3.1.7 Data transformation

Based on previous studies, the high skwness and outliers of raw data affect not only the spatial continuity of variogram function (Zhang et al., 1995; Zhang and Selinus, 1998), but also the prediction accuracy (Hergert et al., 1995). Therefore, when the raw data sets do not follow normal distribution, it is necessary to transform raw data to a normal distribution (Clark and Harper, 2000), which can solve the non-normality problem and limit the influences of outlier on statistical analyses (Gringarten and Deutsh, 2001).

3.1.7.1 Centre log-transformation

Considering that geochemical data are typical compositional data, the covariates for each observation that adds up to a constant 100% may lead to spurious correlation in traditional statistical analysis (Pawlowsky-Glahn et al., 2016). Among a few log-ration techniques proposed for treating the compositional data (Aitchison, 1986; Reimann et al., 2012; McKinley et al., 2016), such as the pairwise log-ratio transformation, the additive log-ration transformation, and the centred log-ratio transformation (clr) seems to be widely used (Aitchison, 1986). For comparison, the results may offer a resonable number of single or low component maps by using the (clr) transformation, especially their higher geochemical stability in the study area. For the British Geochemical Survey sample it would seem a wise approach to Fe₂O₃, CaO, P₂O₅, SiO₂, Al₂O₃ and TiO₂, with the exception of LOI to avoid the soil water content and a large number of the missing value of SO₃ problems (McKinley et al., 2016).

For example, x = [x1,x2,...,xi], the (clr) transformation is calculated by the following equation (Aitchison, 1982):

$$\operatorname{Clr} (\mathbf{x}) = \operatorname{clr} [\mathbf{x}\mathbf{i}]$$
$$\operatorname{clr} [\mathbf{x}\mathbf{i}] = [\ln \frac{x\mathbf{i}}{(H_{x\mathbf{i}})^{1/\mathbf{i}}}]$$

Where *i* is the number of covariates in the set of compositional data and *xi* the value of each covariate; each value in the set of the compositional data is replaced with an alternative value.

3.1.7.2 Normal score transformation

In some cases, variables still failed to follow the normal distribution, which may relate to tied values, size fo sample numbers, detection limit problems, and mixture of populations (Zhang et al., 2005). A power transformation called "Normal score transformation" is effective in pushing positively skewed distributions towards normality (Figure 3-4). The transformation ranks the raw data in ascending order. The z-scores of cumulative probability (i-0.375)/(n+0.25) can be used to calculate the expected normal values, where *i* is the rank in increasing order and *n* is the number of samples (Blom, 1958).



Figure 3-4: Histograms of La concentrations in urban soil of London: a) raw data of 6467 data set; b) Clr-transformed data of La; c) Normal-score transformed data of La.

3.1.8 Data treatment with computer software

All the results were stored in Microsoft Excel spreadsheets. Raw data were analysed with different software packages. The descriptive parameters were calculated with Microsoft Excel and SPSS for Windows (version 21.0). The correlation analyses and descriptive statistics were carried out with SPSS. The centred log-ratio (clr) transformation and box-and-whisker plots were performed by R. All maps were produced using GIS software ArcMap (version 10.3),

and the Local Moran's I index was calculated using GeoDa (version 0.95i, Spatial Analysis Laboratory, 2007).

3.2 Research (B) Part

3.2.1 Study area description

3.2.1.1 Mianning County of Sichuan Province, China

Mianning County of Liangshan Yi Autonomous Prefecture of Sichuan is located at the east edge of the Tibetan Plateau and north-east section of Hengduan Mountains (Shi, 1993). The area is dominated by mountains and is higher in the north and lower in the south. It belongs to subtropical monsoon climate, featured by clear separation into dry and wet season, abundant but unevenly distributed precipitation (more in the north and less in the south), and an average temperature of 13.8°C (Yuan et al., 1995). Maoniuping REEs deposit is located at Maoniuping of Senrong Township of Mianning County, which is about 30 km away from Mianning County town (Niu and Lin, 1995a). The mine area is about 5 km², which is 3.5 km long from north to south and 1.5 km wide from west to east (Niu and Lin, 1995b). The deposit is located at the west part of Xikang-Yunnan axis and to the west of the cut-off zone of Anning River (Yuan et al., 1995). It is the youngest endogenic rare earth deposit known in China, and the ore type mainly includes bastnaesite, cheykinite and synchysite (Yang et al., 2000). According to the survey, it has a proven total reserve of REEs of over 2.5 million tons, ranking the second in the country. The deposit is over 400 m underground at the thickest position. Although the current mining depth has reached 100 m, more than 2/3 of the reserve is still available for exploitation (Niu and Lin, 1994).

3.2.1.2 Geology of Maoniuping REEs tailing dam

The Himalayan Mianning-Dechang (MD) REE belt is located in the western margin of the Yangtze platform, consisting of an Archaean-Proterozoic metamorphic crystalline basement and an overlying sequence of Proterozoic clastic and carbonate rocks (Cong, 1988; Luo et al., 1998). The western margin of the Yangtze platform underwent the Permian rifting, forming a north-south trending paleo rift zone (Zhong et al., 2001), which is related to the East Indosinian-Asian collision zone formed since Paleocene (Yin and Harrison, 2000). Accompanying Cenozoic collisional orogeny, a series of Cenozoic strike-slip faults and a set of NE-, NNE- and NNW- trending folds developed in the eastern Indo-Asian collision zone (Lou et al., 1998; Hou et al., 2006a). There are more than five carbonatite-alkalic complexes in the MD belt (Chung et al., 1998), which are all controlled by Cenozoic strike-slip faults (Wang et al., 2001).

The geology of the Maoniuping complex and associated REE mineralization is controlled by a series of NE-NNE trending faults (Hou et al., 2009) (Figure 3-5), and intruded a NS-striking Yanshanian granite pluton with a U-Pb age of 146 Ma (Yuan et al., 1995). The REE orebodies are hosted largely in the nordmarkite stock, carbonatite sills (Xie et al., 2009), and to a lesser extent in the undated rhyolite and altered Yanshanian granite; they are overlain by a Triassic coal-bearing sequence (Hou et al., 2009).



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Figure 3-5 : The map of the Maoniuping REE deposit, hosted in a carbonatitesyenite complex, is the second largest light REE deposit in China.

3.2.2 Soil sampling

A total of sixty-five surface soil samples were collected at approximately a 0-20 cm depth at locations around the Maoniuping REEs mine tailing. At each point, five samples were collected and uniformly mixed. According to the position of mine tailing and the main transportation road direction, these samples were collected from areas along the road direction. The soil samples were collected in four days from 8 am to 6 pm during the periods of May

16th-19th, 2017. The coordinates of the sample location, as shown in Figure 3-6 were recorded with a portable GPS. The basic properties are shown in Table 3-1. After the collection, all samples were immediately stored in a portable cryostat and transported to the laboratory.



Figure 3-6: Map of the study area and sampling sites (N=8)

Soil samples	рН	CEC ^a (cmol kg ⁻¹)	Organic matter (g/kg)	Total REEs (mg kg ⁻¹)
Mining agil	5.97	9.63	6.28	30971.64
Mining son	7.00	9.61	6.61	1950.74
Tailing soil	7.99	8.8	5.78	19635.24
	7.32	39.2	4.03	1657.24
Dead soil	5.45	24.9	80.99	17.43
Road soll	4.63	45.4	130.43	1330.47
A ' 1/ 1 '1	7.32	3.17	12.76	10854.57
Agricultural soli	4.9	27.6	38.85	348.18

Table 3-1: Selected physical-chemical properties of the soil samples used in this study

^a CEC, cation exchange capacity.

3.2.3 Soil sample preparation and sample analysis

Soil samples were air-dried at 40°C and sieved to 2 mm. Additionally, a part of the sample was finely ground to $< 200 \ \mu$ m. All investigations were carried out in the laboratories of the College of Architecture and Environment of Sichuan University and State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, China.

Total contents of REEs were extracted from finely ground soil (< 150 μm) by using aqua regia digestion according to GBW07303 (obtained from the Perambulation Institute of Physical Geography and Geochemistry of the Geological and Mineral Ministry, Langfang, China). 0.1 g of ground soil sample was digested in Fisherbrand PTFE Crucibles with acids (typical mixture: 15 mL HNO₃, 5 mL HF, and 3 mL HCO₄). An electric heating plate was used

for heating the samples. After digestion, the samples were evaporated to dryness on a hot plate. Referring to GBW07303, the aqua regia digestion does not necessarily match the total content of an element since what the extraction yielded is different for each element and also may differ according to the type of matrix. Then, the residues were dissolved in 1-2% HNO₃ to yield the sample solutions. The concentrations of the REE ions in the liquid phase were determined directly by ICP-MS (laser ablation-inductively coupled plasma-mass spectrometry).

The pH was determined with 0.01 M CaCl₂ with a pH meter (NY-T 1377-2007). The soil solution ratio was 1: 2.5. The pH-values were delegitimized before calculating means (Carter, 1993).

Total contents of carbon (C) and nitrogen (N) were examined on finely-ground samples by a C-N-S analyser with a Thermal Conductivity Detector (Instrumental Criteria Subcommittee, 2005). Inorganic carbon was calculated from the carbonate content by multiplying the factor 0.1199. The amounts of organic carbon (Corg) resulted from the difference between (C) and inorganic carbon (ASTM D5291).

Particle size distribution was determined by the Laser Diffractometry sand fractions, 2- 0.02 mm, silt fractions, 0.02- 0.002 mm, and clay fractions, < 0.002 mm according to Beuselinck et al. (1998).

The cation exchange capacity (CEC) was determined by standard methods (Rhoades, 1982). CEC of the soils with pH < 7.0 was determined by the BaCl₂ method, while the CEC of soils with pH > 7.0 was determined by CH_3COON_a method.

Content of potentially bioavailability (1) One Chelex® 100 DGT unit was sequentially composed of a Chelex® 100 binding gel, agarose diffusive gel and the Durapore PVDF

membrane (Sun et al., 2014; Zhang et al., 2017). These layers were fixed in the new dual-mode plastic holder (Ding et al., 2016). The 30 g of soil was conditioned at approximately 70% of the maximum water holding capacity (MWHC) for 48 h ($24 \pm 1^{\circ}$ C) (Sun et al., 2014; Zhang et al., 1999). The soil pastes were then poured into the open cavity of the assembled DGT devices. After 24 h, the gel disc was eluted with 1.8 ml of 2.0 M HCl for 16 h to extract REE ions bound in the gel and analyzed by ICP-MS (Figure 3-7).

(2) REEs were extracted by shaking 2.0 g of soil in 20 ml of 0.01 mol l^{-1} CaCl₂ in a 50 ml plastic centrifuge tube for 3 h (Novozamsky et al., 1993). Meanwhile, the content of potential bioavailability REEs were determined by EDTA method for comparison (Ure et al., 1993). The REEs were extracted by shaking 2.0 g of soil in 20 ml of 0.05 mol l^{-1} EDTA and its pH was adjusted with ammonia solution to 7.0 in a 50 ml plastic centrifuge tube and the suspension was shaken for 1 h (Wear and Evans, 1968).



Figure 3-7 : Schematic illustration and photos of the process of DGT measurement. a) moisture content of soil samples. b) configuration of the new DGT holder. c) filling of the soil sample into the open cavity. d) standing of the soil-loaded DGT unit.

3.2.4 DGT experiments

A DGT for simultaneous measurements of fifteen REE ions and a new elution procedure. The present study investigated for the first time the detailed performance characteristics of the DGT equipped with a Chelex® 100 binding gels for the simultaneous measurement of fifteen REE ions. To test the validity of DGT measurement for REEs, five different types of ion exchange resins (Chelex® 100, D418, D001-cc, 001×7, and HSTY[®]-SS) were selected for the initial investigation of their adsorption performance for the REEs, based on the results of uptake efficiency and accumulation masses of M which the binding agent Chelex® 100 was chosen for DGT use. A series of validation experiments, including the binding kinetics of each element in mixed solutions and the tolerance of ionic strength and solution pH, were conducted to examine the DGT responses under laboratory conditions. Meanwhile, the DGT capacities were measured and field application in soils were tested.

3.2.5 DGT Calculation

There are three Equations to obtain the accumulation mass of REE ions, the C_{DGT} of REE ions, and the diffusion coefficients of all the REE ions through the Chelex® 100 DGT units composed of the Chelex® 100 binding gels, the diffusive agarose gel, and PVDF filter membrane (Figure 3-8).



Figure 3-8 : Schematic view of a DGT device equipped with the Chelex® 100 binding gel, an agarose diffusive gel and a PVDF membrane layer for simultaneous measurements of fifteen REE ions.

The DGT-measured concentration (C_{DGT} , μ g L⁻¹) was calculated by using the standard DGT equations (1) and (2) (Zhang et al., 1995):

$$M = \frac{Ce \left(Ve + Vg\right)}{fe} \tag{1}$$

Where *M* is the mass accumulated in the gel (μ g); *Ce* is the concentration of the analyte in the eluent solution (μ g L⁻¹); *Vg* and *Ve* are the volumes of the gel and the eluent (mL), respectively, and *fe* is the elution efficiency (Wang et al., 2017; Wang et al., 2016; Tian et al., 2011).

$$C_{\rm DGT} = \frac{M \cdot \Delta g}{D \cdot A \cdot T} \tag{2}$$

Where *M* is determined by eq. (1); Δg is the thickness of the agarose diffusive gel (cm); *D* is the diffusion coefficient of the analyte through the diffusion layer (Wang et al., 2016), and *A* is the exposed surface area of the DGT device (cm²).

The effective diffusion coefficient (D, cm²s⁻¹) of the fifteen REE ions were calculate by Eq. (3) (Wang et al., 2017)

$$D = \frac{slop \cdot \Delta g}{csol \cdot A \cdot 60} \tag{3}$$

With the slope of the linear regression of the *M* for each element (ng) obtained, accumulated in the binding gel over time (s); the thickness of the diffusive layer (diffusive gel and filter membrane) (Δ g, 0.09 cm), the area for diffusion (A, 3.14 cm²), and the concentration of the solution (C_{SOL} , ng mL⁻¹).

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Chapter 4 Research Papers

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4.1 Using Local Moran's I to identify contamination hotspots of rare earth elements in urban soils of London

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Using Local Moran's I to identify contamination hotspots of rare earth elements in urban soils of London



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ABSTRACT

Rare earth elements (REEs) in urban soils are receiving more attention because of their increased use in modern technology. Up to now, there is little information about the spatial patterns of REEs and their influencing factors in urban soils. In this study, based on the British Geological Survey "London Earth" geochemical survey data containing a total of 6467 soil samples collected from the urban area of London, the spatial distributions of Ce, La, Nd, Sc, Sm, Yb and Y, and their influencing factors were investigated. The element Sc is included in this study as related element. Urban samples were collected at a depth of (0 -20 cm), and total concentrations of 48 chemical elements were determined in the <2 mm size fraction of the topsoils using X-ray Fluorescence Spectrometry (XRFS). Spatial clusters and spatial outliers were identified using the index of local Moran's I, showing elevated concentrations of REEs in the northwest, northeast and southern parts of the study areas while all the 7 REEs exhibited generally similar spatial patterns: high values were mainly located in soils over Alluvium, Glacial till and Clay-with-flints deposits, demonstrating the close relationships between REEs and the lithology. Meanwhile, hotspot analysis revealed high values of REEs in public parks, private golf clubs, wetlands and agricultural lands especially in Hillingdon, Enfield, Brent, Harrow, Croydon and Bromley. Soil parent material was identified as the primary source for larger spatial patterns of natural origin, while smaller spatial patterns were associated with anthropogenic sources including agricultural practices, industrial activities, vehicular emission and urbanization. The REE hotspots revealed in urban soils may imply potential contamination requiring further attention.

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1. Introduction

The rare earth elements (REEs) are a group of seventeen chemical elements comprising the 15 lanthanides elements (lanthanum to lutetium), scandium (Sc) and yttrium (Y) (Henderson, 1984; Loell et al., 2011), and are of increasing economic importance, because their unique properties are proving to be indispensable and essential for a number of new technologies. Over the past decades, there has been a sharp emergence in demand for REEs with a consequent increase in anthropogenic REE discharges to the environment (Volokh et al., 1990; Chua and Sharma, 1998; Liang et al., 2005). After excessive REEs enter soils, they can be transported to ground water, accumulate in the soil surface, and then enter humans through ingestion, dermal contact or inhalation

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http://dx.doi.org/10.1016/j.apgeochem.2017.07.011 0883-2927/© 2017 Elsevier Ltd. All rights reserved. (Abrahams, 2002; Meza-Figueroa et al. 2007; Guo et al., 2012; Liang et al., 2014; Benhaddya and Hadjel, 2014). Due to their long residence time in soils and their potential toxicity, the contamination of urban soils has become more important in recent years (Harrison et al., 1981; Schuhmacher et al., 1997; Li et al., 2001; Wang et al., 2005; Li and Huang, 2007; Rashed, 2010). Several studies have shown that elevated concentrations of REEs in urban soils, not only influence the quality of the local environment, but also pose a potential human health risk (Husain et al., 1980; Ichihashi et al., 1992; Raghunath et al., 1999; Feng et al., 2000; Yuan et al., 2003; Chen and Zhu, 2005; Liang et al., 2005). For instance, REEs can accumulate in human brains via blood circulation, which may induce neurotoxic effects (Hollriegl et al., 2010; Rim et al., 2013), cause lung diseases when inhaling dust and metal fumes (USEPA, 2012), and afflict patients with diseases such as leukemia, cancer, and birth defects of children (Ismail et al., 2001; Liang et al., 2014; Rim et al., 2013). In addition, high exposure levels of REEs may lead to liver function decline (Wei et al., 2013). Due to the rapid

development of modern technology, the need of these elements has increased significantly in industry, and consequently anthropogenic REEs could emerge as a severe environmental problem in cities and significant source of contamination of urban soils (Carrero et al., 2013).

The origins of REEs in urban soils include natural and human sources, like other trace metals. In most areas, the concentrations of REEs in soils are mainly determined by the natural sources of local geology weathered to form the parent materials (Liu, 1988; Beckwith and Bulter., 1983; Dong et al., 2001; Hu et al., 2006; Schulin et al., 2007). On the other hand, the influences of human activities include mining, waste disposal, fertilizer, coal and fuel combustion and industry processes may cause elevated concentrations of REEs in soils (Zhang and Shan, 2001; Lou et al., 2012b; Szolnoki et al., 2013). For example, through the phosphate fertilizers, approximately 85 tonnes of neodymium (Nd) were discharged into the environment in the Netherlands in 1994 (Sneller et al., 2000). In the USA, the catalyst emission of REEs into atmosphere by petroleum refineries (Mizohata, 1986; Dzubay et al., 1988). In particular, as noted by Kertis and Yudowich (2009), coal fly ashes can be regarded as one of potential sources of REEs, which contain 445 ppm of REEs on an average global basis. Therefore, it is important to understand the background variation of REEs in urban soils at a variety of scales from continental (Salminen et al., 2005; Reimann and Garrett, 2005) to local, as in this study.

Due to the complex land use and heterogeneous nature of urban soils, the concentrations and distribution of REEs vary over space (Goovaerts, 2000; Legret and Pagotto., 2006; Mmolowa et al., 2011). When evaluating the potentially toxic elements from a specific area, it is necessary to assess the current status of REEs contamination and explore the factors that have influences on REE accumulation and distribution in urban soils (Liang et al., 2014; Zhao and Hazelton., 2016). Mapping based on geographical information system (GIS) in conjunction with statistical methods are useful approaches to describe the spatial distribution of contamination and to explore possible contamination sources in urban soils (Liu et al., 2006; Tiwari and Rushton, 2010). The local Moran's I index has been identified as an effective method to identify contamination hotspots (Zhang et al., 1995; Anselin, 2001; Overmars et al., 2003). This index examines the individual locations based on a comparison with the neighbouring samples, which has been successfully applied in environmental research and planning (Mc Grath and Zhang, 2003; Zhang and Mc Grath, 2004; Brody et al. 2006)

London is located in the south east of Great Britain. It has a long history of the use of coal, industrialization and urbanization (Royse et al., 2012). Metal mining and peat burning have already existed over several millennia in the British Isles (Mighall et al., 2002; Meharg and Killham, 2003; Oldfield et al., 2003), which could have resulted in trace element discharges directly in soil and emissions into the atmosphere which eventually deposit into soil. But the pre-industrial status of trace elements in soils is not obvious particularly in urban soils where the history of land use is complicated and thus the potential sources of contaminated soil are difficult to unravel (Leung et al., 2008; Xu et al., 2013a, 2013b; Yang et al., 2013). Moreover, research into REEs in urban soils and the information on the impacts of REEs on human health are still lacking, especially the spatial distribution of REEs in topsoils. This information is very important in order to identify contamination hotspot areas and assess the potential polluting sources in an urban region. The demand for REE-based materials is an increasing trend and it is an urgent mission for Britain, to give priority to the development of new sources of REEs outside of China and greater recycling from priority waste streams (Erecon, 2014). Supervision and control of the extent and severity of soil contamination and the

potential sources of REEs in urban soils is thus significant for urban environmental management. The aim of this study was to identify contamination hotspots of Ce, La, Nd, Sc, Sm, Yb and Y in the urban soils of London city using the local Moran's I index and GIS. The objectives were to: (i) investigate the concentration of seven REEs in urban soils; (ii) identify contamination hotspots by these REEs in the soils in the city of London; and (iii) explore the influencing factors of these REEs in the study area.

2. Materials and methods

2.1. Study area and soil samplings

The London Earth field survey of a total of 6467 soil samples were collected at a depth of 5-20 cm and a sampling density of four samples every square kilometre from the city of London and London Boroughs (GLA) during 2005-2009 (Johnson et al., 2005; Knights and Scheib, 2010). Each sample comprised of a composite sample, consisting of 4 soil cores taken from 20×20 m square at four corners and the centre, for the purpose of achieving a grid of high density sample coverage for the entire GLA with samples spaced about 500 m apart (BGS, 2011; Flight and Scheib, 2011). All soil samples were air-dried and then passed through a nylon sieve to <2 mm and sub-sampled by coning and quartering. Subsamples were further ground in an agate planetary ball mill (50 g), with 95% of the material finer than 53 µm. The total concentrations of the 48 chemical elements were determined for each sample by wavelength dispersive X-ray fluorescence (XRF) spectrometry, together with loss on ignition (LOI at 450°) and pH in all the urban samples. Sample preparation, detection limits, and quality control procedures are described in Allen et al. (2011) and Johnson (2011).

2.2. Local Moran's I

Moran's I involving global and Local Moran's I, is commonly used to study spatial autocorrelation. In this study, Local Moran's I index was used as a local indicator of spatial association (LISA). It was calculated for every sampling location to reveal the degree of spatial autocorrelation (Anselin, 1995). It is also a widely used tool for identifying contamination hotspots in urban soils, as well as classifying them into spatial clusters and spatial outliers (Zhang et al., 2008). Local Moran's I index (Anselin, 1995), is expressed as:

$$I_i = \frac{zi - \overline{z}}{\sigma^2} \sum_{j=1, j \neq i}^n [W_{ij}(z_j - \overline{z})],$$

Where I_i represents the Moran's I coefficient; z_i represents the variable (here REE) at location i; \bar{z} is the mean value of the variable with the sample number; z_j is the value at other locations (where $j \neq i$); σ^2 is the variance of z, and W_{ij} is the spatial weight which can be represented based on a distance weighting between z_i and z_j (Zhang et al., 2008).

A positive local Moran's I value refers to the location under study which has similarly high or low values as its neighbours and then the location is called a "spatial cluster". On the other hand, a negative local Moran's I value indicates a potential spatial outlier which is different from the values of its surrounding locations (Lalor and Zhang, 2001). In this study, the Local Moran's I was applied to identify the spatial clusters and spatial outliers of each of the seven REEs based on 9999 permutations at the significance level of p < 0.05. Various distance bands for the weight function were tried with the REEs, The results from the distance band of 1000 m were chosen, which not only revealed the spatial clusters in the city centre, but also allowed other general patterns to emerge

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Table 1	
Descriptive statistics of REFs in topsoils of urban soils in London $(n - 6467 \text{ unit in mg kg}^{-1})$	

	Min	25%	Mean	Median	75%	Max	SD	CV	Ske	DL	% <dl< th=""><th>FOREGS</th></dl<>	FOREGS
Ce	18	43	50.9	49	57	238	12.9	166.1	2.3	1	0	48.2
La	3	20	25.2	24	29	130	8.8	76.6	2.5	1	0	23.5
Nd	0.5	17	22.3	21.4	26.1	122.8	8.7	76.2	2.8	4	0.07	20.8
Sc	0.2	6	8.3	7.9	10.2	33.3	3.2	10.2	0.6	3	2.59	~
Sm	0.1	2.3	3.6	3.4	4.7	25.8	2	4.1	1.7	3	39.4	3.9
Yb	0.1	1.3	1.9	1.8	2.4	8.8	0.9	0.8	0.8	1.5	31.6	1.9
Y	4.8	17	21.1	20.4	24.1	132.9	7.6	58.2	4.3	1	0	~
pH	2.8	5.6	6.2	6.6	7	8.3	1	1	-1	0.01	0	~
LOI	0.71	5.9	7.8	7.3	9.1	58.7	3.1	9.9	3.5	0.01	0	~

SD: standard deviation; CV: coefficient of variation; DL: detection limits.

(Zhang et al., 2008).

2.3. Inverse distance weighted

The inverse distance weighted (IDW) interpolation estimates values at un-sampled points using weighted average of the sampled points within a selected number of neighbours of the unsampled location (Robinson and Metternicht, 2006). In IDW, the value of W_i can be estimated from data using the following equation:

$$W_i = \frac{1/d_i^p}{\sum_{i=1}^n 1/d_i^p},$$

Where *n* is the number of neighbouring points used for the calculation, and *p* is a positive real number called the power parameter (typically, p = 1 or 2), d_i means the distance between the sampled location and the un-sampled location for which an interpolated value is sought (Isaaks and Srivastava, 1989).

Based on the spatial correlation between scattered points, as the simplest spatial interpolation method, the IDW method is widely applied in soil geochemical mapping (Shepard, 1964; Wackernagel, 1998). In this study, the power of 1 and the number of neighbouring

samples of 16 were chosen in order to show smooth spatial patterns of the pollutants and reduce the 'bulls-eye' effect. A 'quantile classification' was applied to allow the REEs concentration values to reveal their spatial patterns.

2.4. Data transformation and computer software

To limit the influences of outliers and to exhibit the pattern of that element relative to the average behaviour of other elements in this compositional dataset, a centred log-ratio (clr) transformation (Mckinley et al., 2015) was employed for the data. The centred log-ratio (clr) transformation and box-and-whisker plots were carried out in R, an open source software. SPSS (version 21.0) was used for the descriptive statistics. All maps were produced using GIS software ArcMap (version 10.3), and the Local Moran's I index was calculated using GeoDa (version 0.95i, Spatial Analysis Laboratory, 2007).

3. Results

3.1. REEs concentrations in urban soils

There is no information available on the background values for REEs concentrations in urban soils of the London. Therefore, we



Fig. 1. Spatial distribution map of soil La concentrations in London soils.

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Fig. 2. The LISA maps of soil (a) Ce, (b) La, (c) Nd, (d) Sc, (e) Sm, (f) Yb, (g) Y (Distance Band = 1000 m).

Table 2							
Numbers of soil samples identified a	as spatial	outliers	and	spatial	clusters	based o	п
LISA method.							

REEs	Not significant	High-high	Low-low	Low-high	High-low
Ce	3758	1059	1199	165	286
La	3602	1094	1383	119	269
Nd	4046	909	1096	127	289
Sc	4364	1154	517	200	232
Sm	5116	573	326	153	299
Yb	5018	667	337	178	267
Y	3887	854	1341	115	270

High-high clusters: high values in a high value neighbourhood.

Low-low clusters: low values in a low value neighbourhood.

Low-high outliers: a low value in a high value neighbourhood.

High-low outliers: a high value in a low value neighbourhood.

used the statistical parameters of REEs concentrations in European soils data for FOREGS to evaluate REEs contamination in our samples (Salminen et al., 2005; Martiya et al., 2013). The descriptive statistics (minimum, maximum, mean, median, standard deviation (SD), coefficient of variation (CV), skewness and detection limits) for the raw data of the REEs and selected soil properties (pH, LOI) are summarized in Table 1. The median concentrations of Ce, La, Nd, Sc, Sm, Yb and Y in the study area were 49, 24, 21.4, 7.9, 3.4, 1.8 and 20.4 mg/kg⁻¹, respectively. According to the median concentrations of REEs in European (Table 1), the results indicated that REE concentrations in London urban soils did not reach the environmental and health risk thresholds. Table 1 shows the accumulation order of REEs in all samples in descending order was Ce > La > Nd > Y > Sc > Sm > Yb. In addition, the coefficient of variation (CV) can be used to compare in relative terms the variability of the same property under similar values of variances and different means (Wang and Liang, 2015). Based on the coefficient of variation (CV), the variability of La, Nd, Sc, Sm, Yb and Y was moderate with the CV fluctuating from 0.7% to 76.5%. The highest CV of soil Ce concentration was 166.2% (Table 1) indicating that Ce could be enriched in some parts of the study area.

3.2. Spatial distribution of REEs

The spatial distribution map of La in the urban areas of London city is shown in Fig. 1. The spatial distribution maps for Ce, Nd, Sc, Sm, Yb and Y are shown in Appendix (Fig. A1). Due to their similar chemical and physical properties and close behaviour in the environment (Henderson, 1984; Tyler, 2004a; Hu et al., 2006b) all 7 REEs displayed similar spatial patterns showing the elevated values in the northwest, northeast and south parts. Sc exhibited slightly elevated values in the central area. Low values of REEs were located along both sides of the River Thames. Of particular note, are the large areas of elevated and low concentrations reflecting the influences of natural factors. Meanwhile, a large amount of scattered elevated values can also be observed surround by relatively low values, indicating the presence of potential spatial outliers, which are discussed in more detail in the following sections.

3.3. Spatial-cluster and spatial-outlier analysis

For Local Moran's I results for the centred log-ratio transformation data of Ce, La, Nd, Sc, Sm, Yb and Y concentrations in London soils (Fig. 2), most of the REEs in soil showed generally similar spatial patterns. About 40% of the REEs in samples of soil belonged to the significant spatial clusters including high-high and low-low spatial patterns, except for Yb and Sm with smaller percentages (Table 2). For soil La, Ce, Nd and Sc, the northwest and



Fig. 3. Simplified soil parent material map of the London region (GLA = Greater London Authority).

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Fig. 4. Hotspots of REEs overlaying on simplified soil parent material map of the Greater London Authority (GLA).

southern regions of the study area were dominated by High-high patterns, and the low-low spatial clusters were located in the central area. It is worth noting that the Local Moran's I index is sensitive to outliers (Zhang et al., 2008). In the maps for the 7 REEs, most of the high-low outliers were located close to the Low-low cluster in the central area. There were some high-low outliers in the northern and eastern part of city. Spatial outliers in the city centre, west and northeast parts were in accord with their high concentrations (Fig. 1).

4. Discussion

4.1. Geogenic factors

4.1.1. Bedrock

All seven REEs had very similar spatial patterns, with a large number of hotspots simultaneously located in the northwest and southern parts of the study area, while most of the cool spots of the REEs are found in the middle of the study area (see Figs. 1 and 2).



Fig. 5. LISA map of soil La in the London city (Highlighting hotspots and cool spot of La).




Fig. 6. LISA maps for (a) Al_2O_3 , (b) TiO_2 (Distance Band = 1000 m).

This pattern corresponds to the soil parent materials in the study area, with the samples plotted on their underlying rock types (Figs. 3 and 4). Soils from the White chalk subgroup, Clay-withflints and Thames Group (clay) areas displayed the highest REE concentrations among all the rock types, followed by the Alluvium and Brickearth areas. The elevated REE concentrations are associated with the Chalk and the predominantly chalky deposits developed over carbonate rocks due to weathering, mineralization and transportation processes. The Chalk of the London Basin is typically a fine grained white limestone made mainly from organically precipitated aragonite (Hancock, 1975), which are present in the GLA area to the south and west. Compared with chalk, flint is a very hard, brittle, siliceous material formed in bands in the more carbonate-rich chalks, which is a very widespread deposit, covering south and upper east of the Basin. Ca minerals may have bound most REEs in the earth's crust during magmatism and hydatogenetic processes (Alessandro et al., 2009), as a result a large number of REEs in soil minerals emerge in the form of carbonates. REEs are hydrolysed in the soil, and the amorphous hydroxyl groups, RE (OH)²⁺, are adsorbed to the surfaces of clay minerals and Fe-Mn oxides in soils (Zhu and Xing, 1992). According to the result, the close association between carbonate rocks and REEs was clearly revealed by the LISA results (see Fig. 4).

Furthermore, The LISA maps of Al₂O₃ and TiO₂ illustrate the high concentrations in top-soils over the London Clay (Thames Group clays), Clay-with-flints and Alluvium, as well as particularly low concentrations in most of the River Terrace deposits, Plateau Gravels and the Thanet Sand Formation (see Fig. 6). Zones highly enriched in those elements indicate that REEs are probably either adsorbed by clay minerals or bound to Fe- and Mn-(hydr) oxides and or fixed within crystal lattice of ilmenite (Liu et al., 2006; Giusti, 2013). The positive correlation between REEs and Ti in weathering profiles indicate that the released REEs are fixed by clay minerals and Fe-ox-ides/hydroxides (Middelburg et al., 1988). Previous studies also support the result that clay minerals in surface sediments also impact the adsorption of trace metals in combination with Fe, Mn amorphous oxides, and even some of which may cover clay surfaces (Bradl, 2004). Thus, the high level of those trace metal concentrations may be the consequence of the higher clay content in the subsoil of the northwest and south part of the study area. It is not unreasonable to assume that soil parent material and weathering process are a natural factor leading to enrichment of REEs in



Fig. 7. LISA maps for (c) SiO₂, (d) pH (Distance Band = 1000 m).

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soils of this district.

4.1.2. Influences of pH and soil type

The LISA map of La, Nd, Sm and Y shows that a cool cluster in Richmond upon Thames (see Fig. 2). Richmond Park, in the London borough of Richmond upon Thames, has little history of industrial activities. The reason for the cool pattern is not only related to the lack of anthropogenic activity in this area, but also due to the pH and soil type. The majority of Richmond is underlain by River Terrace deposits which vary in age and thickness, and are composed mainly of gravels and sands. The LISA map of SiO₂ (see Fig. 7) reveals a large of high-high cluster located in Richmond Park, which also indicates low content organic matter. This occurs because as the SiO₂ percentage rises with an increase of sandstone in sandy soil there is a decrease, by dilution, of organic matter and CaCO₃ (Bear, 1964). Owing to the dissociation of protons from the carboxyl and phenolic groups of humic polymers in the soil, studies (Beckwith and Bulter, 1983) show that organic matter contributes dramatically to the adsorption of REEs. Thus, the sandy soil containing the high concentrations of SiO₂ is likely to be depleted in REEs and other trace metals. The overall spatial pattern of pH in London city is illustrated in Fig. 6, and a clear cool pattern of soil pH in Richmond Park is observed. The soil pH value is another essential consideration affecting the adsorption of REEs (Dong et al., 2001; Gao et al., 1999). When soil pH is high, the surface of soil particles are charged with more OH- ions, so that dissolved REE ions can easily form complexes, such as Ln (OH)²⁺ and Ln (OH) (Zhu et al., 1993). Therefore, adsorption of REEs generally increases

with higher soil pH values. The maps of SiO2 and pH, and cool patterns of REEs in the topsoil, clearly show the influence of soil types and pH on REE content.

4.2. Anthropogenic factors

4.2.1. Influences of fertilizer application

Relatively high concentration of Ce, La, Nd, Yb and Y hotspots are also found in parks, wetlands and agricultural lands especially in Hillingdon, Hounslow and Enfield (see Fig. 2). They present, some scattered High-high cluster and High-low outliers of these five REEs in farmlands and wetlands (Figs. 2 and 5), indicating similarities in their origins. We also observed a larger concentration of High-high clusters of P in the central of London, especially accumulating along the banks of the main river (Fig. 8). It is widely recognised that the P-fertilizers are an important path for REEs and metals get into agricultural soils (Buckingham et al., 1999; Hu et al., 2004; Pang et al., 2002). With a annual agricultural input rate of 300 kg ha⁻¹ of P-fertilizers, about 30–170 g REEs ha⁻¹ will inevitably enter the soil (Todorovsky et al., 1997). The map of P shows high clusters in Hillingdon, Hounslow and Enfield areas, which do not contain intensive vehicular-related activities, but does contain agricultural activities. This may indicate that REEs are probably derived from the use of phosphate fertilizers. In addition, the spatial patterns of other trace metals (Cu and Zn, see Fig. 8) that are also associated with phosphate fertilizer show the same high-high clusters as the LISA maps of Ce, La, Sc, Yb and Y, which points to Pfertilizer being the source. This is also supported by of the study of



Fig. 8. LISA maps for (e) P_2O_5 , (f) Cu, (g) Pb, (h) Zn (Distance Band = 1000 m).

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Fig. 9. Box-and-whisker plots display the total concentration of (a) Ce, (b) La, (c) Nd, (d) Sc, (e) Sm, (f) Yb, (g) Y related to different distances from the city centre:5 km, 10 km, 20 km and 30 km. Boxes depict 25th, 50th (median), and 75 percentiles and whiskers minimum and maximum values, outliers ($^{\circ}$).

Nicholson et al. (2003), which shows that phosphate fertilizers are an important source of heavy metals entering agricultural soils in England and Wales, especially Cu, Zn and Cd. This implies that the spatial distribution patterns of REEs in farmland and wetland soils could be attributed to the application of phosphate fertilizers.

4.2.2. Influences of industrial activities

Local Moran's I index is sensitive to spatial outliers, especially to the high-value ones when used in highlighting potential contamination in environmental contamination studies (Zhang et al., 2008). For soil REEs, some scattered High-high cluster and High-low outliers are found in areas of Redbridge, Newham, Barking, Dagenham, and Rainham (see Fig. 2). This indicates that the REEs concentration may be affected by scattered sources. Based on field investigation, some landfill, metal recycling and cement plants are located in these areas. According to other authors, leachate generated in waste landfill contains a high concentration of heavy metals, most commonly Fe, Cd, Cu, Zn and Ni (Elwali et al., 2008), and other trace elements (Aulin, 1998; Östman et al., 2006). The LISA maps of Cu, Pb, Zn and REEs show high value clusters in the vicinity of landfill, metal recycling and cement plants in the study area (see Fig. 8). This suggests that industrial and waste landfill may also be related to REEs enrichments. As already discussed in the case of Richmond Park, soil pH is also important in controlling translocation of exogenous REEs in the environment (Heinz and Perkins, 1993; Cao et al., 2001) as high pH increases the absorption of REEs, thus decreasing their mobility (Liang et al., 2014). As expected, the soil pH cluster map shows a clear high-high spatial cluster in Newham, Barking, Dagenham and Rainham area, and soil Cu, Fe and Zn have very similar spatial patterns, with hotspots located in the same areas (Fig. 8). This indicates that hotspots with high concentration of REEs in the Dagenham, Rainham, Redbridge and Barking could be attributed to the landfill, municipal dumps and small-scale metal recycling.

4.2.3. Influences of vehicular emission

In the LISA maps of the 7 REEs, many scattered High-low outliers are found in central of London (see Fig. 2), especially Ce, La, Nd and Y. Because the REEs share similar chemical and physical properties they represent a geochemically coherent group, suggesting a similar source origin for these trace metals. Moreover, it can be seen from the LISA maps of Cu, Pb and Zn that three metals displayed similar spatial patterns: relatively high-concentrated of high-high cluster in the central of city and low-low cluster around in rural area, decreasing with the increasing distance from the centre. Nicholson et al. (2003) reported that atmospheric Zn deposited on soil accounted for the largest amounts of metals from the atmosphere in England and Wales, followed by Cu and Pb. Similar patterns of these metals and REEs were evident (Figs. 2 and 8) indicated the strong influence of vehicular emission (Culbard et al., 1991; Manta et al., 2002). Additionally, London is one of the oldest industrialised cities in the world, which has undergone rapid economic development in past centuries. The increasing population and traffic volume in the city of London have inevitably caused an increase in local anthropogenic emission during the urbanization. Therefore, this study also employed the Box whisker plots of the Ce, La, Nd, Sc, Sm, Yb and Y in London soils. Based on the boxplots results, the total concentration of each REE was classified into four groups using a criteria value of rescaled distance between 5 and 10 km from the centre of London to rural area (Fig. 9). These boxplots share a common trend: the soils at distance of 20 km and 30 km from the centre exhibited relatively high REEs concentrations. As mentioned earlier, REEs in the rural areas were strongly enriched by soil parent material rather than anthropogenic sources. However, it is interesting to note that soil samples within 10 km distance from the centre contained a few high value outliers, especially Ce, La, Nd and Y where a few high value outliers were found at distance of 5 km. Previous studies have suggested that Cu, Pb and Zn concentrations in the urban park soils may be related to the location and the history of parks (Li et al., 2001) (Huang et al., 1994). show that REE in exhaust fumes is derived from REE elements used in the catalytic converters of petrol engines. The Ce, La, Nd and Y of the soil samples within the central of London area show the large number of High-low outliers compared to the rest of the soils studied in more rural areas (Fig. 2). Therefore, our finding further indicated that vehicular emission may play a part, in addition to urbanization may contribute to Ce, La, Nd and Y in urban soils from the central area. While the above factors have been explored in this study, it needs to be noted that it still a difficult to establish a causal relationship between contamination hotspots and the influencing factors based on spatial distribution patterns (Volokh et al., 1990; Todorovsky et al., 1997).

5. Conclusions

This paper highlights the value of using Local Moran's I for the identification of contamination hotspots in urban soils. The spatial patterns of Ce, La, Nd, Sc, Sm, Yb and Y in their distribution maps showed similar trends to the LISA maps revealed by Local Moran's I. Moreover, this paper also highlights the influence of the factors controlling REE distribution and sources within urban soils. Soil parent material was an important factor leading to the natural enrichment in REEs of soils in the city of London with large scale spatial patterns. Based on previous research as well as the spatial analyses of the study area, the results indicated that REEs enrichment in urban soil may have complex sources, the most likely factors are from the agricultural practices, waste disposal, metal recycling, vehicular emission and urbanization.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.apgeochem.2017.07.011.

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4.2 Exploration of spatially varying relationships between Pb and Al in urban soils of London at the regional scale using geographically weighted regression (GWR)

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Highlights

Relationships between Pb and Al in urban soils of London was spatially varying;

Positive and negative relationships between were found in north and south areas, respectively;

Anthropogenic factors weakened the relationships in central London;

Large parks and greenspaces reserved the positive relationships between Pb and Al;

GWR is effective in revealing spatially varying relationships in urban soils.

Abstract

Exploring the spatially varying relationships of urban soil geochemistry based on statistical analysis is an effective way to improve our understanding of the geochemical characteristics of the given study area. In this study, geographically weighted regression (GWR) was applied to reveal the spatially varying relationships between Pb and Al in urban soils of London based on 6467 samples collected by the British Geological Survey. The local R² and coefficients were calculated using the Akaike Information Criterion (AIC) and six bandwidth parameters ranging from 1000 m to 50000 m. Results showed that the relationships between Pb and Al were spatially varying in urban soils of London, with different relationships in different areas. The negative relationships between Pb and Al were found in the northeast and north areas and weak relationships were located in central areas, implying the links with the impact of anthropogenic activities on Pb concentration, while road traffic, industry activities and construction in centre of London may be linked to the weakened or changed direction of the relationship. However, positive relationships between Pb and Al were found in large parklands and greenspaces in the southeast and southwest as well as a small area in

central London, due to less influences from human activities where the natural geochemical signatures were preserved. This study suggests that GWR is an effective tool to reveal spatially varying relationships in environmental variables, providing an improved understanding of the complicated relationships in environmental parameters from the spatial aspect, which could be hardly achieved using conventional statistical analysis.

Keywords: Geographically weighted regression (GWR), Spatially varying relationships, Geochemical variable, Urban soil, Lead, Aluminium

1. Introduction

Heavy metals are important chemical components in soils. For the health of humans and plants, some heavy metals such as Pb, Cd and Hg belong to the non-essential elements (De Miguel et al., 1998; Kabata-Pendias, 2004), which are considered as contaminants because of their toxicity and difficulty in degradation (Zhang et al., 2012). In natural conditions, concentrations of geochemical elements in soils are affected by parent materials (Alloway, 1995; De Temmerman et al., 2003; Aelion et al., 2009; Ballesta et al., 2010; Cai et al., 2010), as a result of geological and pedologic processes that rule soil formation (A. Castrignano et al., 2000). In urban areas, additional sources of heterogeneity are caused by anthropogenic activities. Moreover, due to the complex and heterogeneous nature of urban soils, the spatial distribution of geochemical elements is affected by multiple factors (Franco-Uria et al., 2009; Qishlaqi et al., 2009; Yang et al., 2007; Lv et al., 2013), resulting in different relationships among them in different locations (Zhang et al., 2007; Lv et al., 2013). Therefore, it is necessary to find an efficient way to reveal such spatially varying relationships between geochemical elements in urban soils across local areas, which would be helpful to better understand the complicated relationships in urban geochemistry as well as to reveal their association with influencing factors.

The traditional statistical methods, such as correlation analysis and ordinary least square (OLS) regression, produce 'average' or 'global' parameters to estimate the spatial relationships (Ali et al., 2007), which are reflected equally over the whole region. Therefore, the impacts of local variations could be hidden (Bacha, 2003; Batisani & Yarnal, 2009; Geri et al., 2010). In light of this, an important contribution of geographically weighted regression (GWR) is to build regression models to explore how one dependent variable changes in response to one or more independent variables at the local scale (McMillen, 1996; Fotheringham et al., 1998; Leung et al., 2000a; Yu and Wu, 2004; Deller and Lledo, 2007; Waller et al., 2007). The GWR model takes the samples within a defined neighbourhood into calculation by giving more weights to nearby samples than

those further away (Wheeler & Paez, 2007; Zhang et al., 2011). The GWR results depend on the observations that are in close proximity to the subject point, so they reveal the relationships within the neighbourhood (Fotheringham et al., 2002; Foody, 2004; Bickford and Laffan, 2006). Thus, the GWR can be used to explore the spatially varying relationships between variables (Tu, 2011).

Among heavy metals, of particular interest is the spatial variation of Pb in urban soils, not only because it contains high toxicity, but also it can be strongly influenced by human activities. For example, industrial discharges (Mattuck and Nikolaidis, 1996; Aelion et al., 2009), vehicles emissions (Sansalone and Buchberger, 1997) and construction are considered as the major influencing factors of Pb in urban soils (De Temmerman et al., 2003; Zhang, 2006; Delbecque and Verdoodt, 2016; Wu et al., 2019). In addition, previous studies have reported that there are inter-concentrations between different heavy metals and each other which may be due to adsorption of heavy metals on the oxides, such as Pb retention was correlated to clay contents (Korte et al., 1976; McKenzie, 1980; King, 1988; Alloway, 1990). To date, the use of Pb gasoline for vehicles has declined in many countries, while the concentrations of Pb in the urban soils remain a concern because the anthropogenic sources of Pb are particularly dense in the urban environment (Clark et al., 2006; Rawlins et al., 2012). Despite other potentially toxic elements that could also be interesting for investigation, this study focuses on Pb, which could be helpful for us to seek the links with the influencing factors.

In this study, the GWR was applied to explore the spatially varying relationships between Pb and Al in urban soils of London. The chemical element Al was chosen as the independent variable for the dependent variable of Pb. The reason why Al was chosen was because not only it has been commonly used as a reference element of lithogenic origin in multivariate statistical analyses, but also its shares similar features as Pb under the natural environment where they are strongly bound by fine-particles of clay minerals (Spark, 2010). The hypothesis is that the relationships between Pb and Al are expected to be spatially variable. The element Pb could vary in relations to Al depending on the natural and anthropogenic influences which are varying at different locations. However, this positive correlation may be disturbed or changed by anthropogenic influences, as Pb is strongly influenced by human activities. Another element Ti was chosen as the dependent variable of Al for comparison. The element Ti and Al have been frequently used as reference elements, as they are components of minerals resistant to chemical weathering, and they are less affected by anthropogenic factors (Sezgin et al., 2003; Tylmann, 2004). The relationship between Pb and Al. The objectives of this study were: (1) to reveal the spatially varying relationships between Pb and Al in London soils at the regional scale; (2) to investigate the effects of different bandwidths on the results of

GWR for the purpose of identifying spatial patterns of the spatially varying relationships; and (3) to explore the associations between the spatially varying relationships and the related influencing factors.

2. Methods

2.1.Geology and soil geochemistry data

The bedrock geology of the Greater London Authority (GLA) showed a wide range of Cretaceous and Palaeogene bedrocks in the north and south areas (Miles and Appleton, 2005; British Geological Survey, 2011) (Fig. 1.). Palaeogene bedrocks in the north area were composed of the Bagshot Formation, Thames Group (clay), Lambeth and Thanet sand Formation. The White chalk, Grey Chalk and Thanet Group (sand) belonging to Cretaceous deposits were found in the south area. Quaternary superficial deposits occurred in the central area with the most extensive alluvium, river terrace deposits and brickearth. Relatively small patches of Clay-with-flints and Head (clay-silt) were found in the south area.

In the GLA study area, a total of 6467 topsoil samples were collected on a grid system by the British Geology Survey at a density of 4 samples per km². Each composite sample was obtained by collecting 5 subsamples from the centre and corners of a 20 m square at each sampling site. Top-soil samples were collected at a depth of 0-20 cm, after removal of surface vegetation, litter and rootlet zone (usually < 5 cm). The nominal sampling depth is therefore 5-20 cm (Johnson, 2005). Analyses were performed for total concentrations of 48 elements by X-ray fluorescence spectrometry (XRFS) and loss on ignition (LOI at 450 °C) and pH. Detailed information for sampling and quality control is available in Allen at al. (2011) and Johnson (2011).



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Fig. 1. Geology map of the London region

2.2.Land use data

The land use data used in this study is the GLUD 2005 obtained from the website of the London Data store (http://data.london.gov.uk/). Five simplified land use classes: farm-land, industry, greenspace, built-up and others were generated using ArcGIS[®] software (Fig. S1).

2.3.Geographically weighted regression

The GWR reveals the spatially varying relationships between the dependent and independent variables, and a set of location specific parameter estimates. Based on Fotheringham et al. (2002), the GWR model with one independent variable can be expressed as:

$$y_i = \beta_0 (u_i, v_i) + \beta_1 (u_i, v_i) x_i + \varepsilon_i$$

Where u_i and v_i are the coordinates of the *i*th location, and $\beta_0(u_i, v_i)$ is the local intercept for *i*th location, $\beta_1(u_i, v_i)$ is the estimated local regression coefficient for the *i*th location and ε_i is the random error at the *i*th location. As data included in the calculation are geographically weighted, the local intercepts and local regression coefficients are different at different locations, which is different from OLS where these parameters remain the same for the whole dataset. The parameters are estimated from:

$$\beta(u_i, v_i) = (X^T W(u_i, v_i) X)^{-1} X^T W(u_i, v_i) Y,$$

Where β (*u_i*,*v_i*) represents the unbiased estimate of β , *W* (*u_i*,*v_i*) is the weighting matrix which acts to ensure that observations near the specific point have larger weighting values.

In practice, the bandwidth is the key controlling parameter for GWR results (Guo et al., 2008; Gao & Li, 2011). The process of choosing the weighting matrix is important to predetermine an optimum bandwidth. The optimal bandwidth for GWR was determined by minimizing some model fit diagnostic, such as cross-validation (CV) score (Bowman, 1984) or the Akaike Information Criterion (AIC) (Akaike, 1973). Considering the soil sampling sites on a generally regular grid, in order to calibrate the spatial weighting function and determine the optimal bandwidth for the models used in this study, both AIC and fixed distance bands ranging from 1000 to 50000 m were applied for comparison. Considering that the results of local regression coefficients only represent the slop coefficients (Gao and Li, 2011), a local correlation coefficient (r_i) was calculated to reveal the correlation between the dependent variable (Pb) and independent variable (Al). The formula can be expressed as:

Coefficient
$$(r_i) = \sqrt{R_i^2} \times \frac{\beta 1(ui, vi)}{\beta 1(ui, vi)}$$

Where R_i^2 is the local deterministic coefficient from GWR model, and β_1 (u_i, v_i) is the local regression coefficient. The local correlation coefficient is equivalent to Geographically Weighted Pearson Correlation (GWPCC), which is based on the concept of local statistics (Kalogirou, 2014).

2.4.Data transformation and computer software

A normal score transformation was applied to the data for GWR analyses due to the non-normality and skewness problem of the raw data (Zhang et al., 2008a). All maps were produced using ArcGIS (ver.10.4) software. The conventional statistical analyses were carried out using SPSS (ver. 21.0).

3. Results and discussions

3.1.Basic statistics for Pb and Al concentrations in London soils

The basic statistics for Pb and Al concentrations in urban soils of GLA are listed in Table 1. The 90th percentile of Pb 606 mg/kg had exceeded the provisional Category 4 Screening Levels for lead (pC4SL, 130-330 mg/kg for residential) (SP1010, 2014). The large difference between the percentiles implied that there were strong variation and heterogeneity of Pb concentrations in soils over the study area, with the range from 10.8 mg/kg to 10000 mg/kg. Meanwhile, the mean value for Pb was significantly much higher than the median, implying that there were high value outliers or extreme values which skewed the distribution of the data set. The variation of Al was also strong, ranging between 0.4% and 11%.

Table 1. Basic statistics of Pb and Al concentrations in urban soils of London (Al: in %, Pb: in mg/kg).

Element	Min	10%	25%	Median	75%	90%	95%	Max	Avg	StdDev
Pb	10.8	60.9	97.3	180.1	340	606.2	857.1	10000	295.6	430.4
Al	0.4	2.6	3.2	4.0	5.1	6.3	6.9	11	4.2	1.5

3.2. Spatial distribution of Pb and Al

The spatial distribution maps for Pb and Al concentrations in London soils based on inverse distance weighted (IDW) interpolation are illustrated in Fig. 2. The relatively low values of Pb concentrations were located in the north part and some small areas in the southeast, where rock types Thames Gp, White Chalk and Clay-with-flints were located (Fig. 1). Elevated values of Pb concentrations were observed in the central part of GLA, indicating that the topsoil Pb was dominantly influenced by anthropogenic factors which are also spatially variable. The high values of Pb in the central areas may be associated with the high traffic volume, especially in the central area where is highly urbanized with an extensive road network. In order to investigate the influences of traffic on Pb concentration, the road buffer zones (0-50 m, 50-100 m, 200-400

m, 400-600 m) were generated using the buffer tool in ArcGIS, according to the major roads of London downloaded from Geofabrik (2016) (Fig. 3). Sites closer to major roads had higher Pb concentrations, and the reduction is up to 65% if the distance is 500 m away from the road (Fig. 3). These results are in agreement with previous studies showing that the concentrations of Pb in soils increased with traffic volume while decreased with the distance from the roads (Thorpe and Harrison, 2008; Pant and Harrison, 2013; Wang et al., 2017). Moreover, Appleton and Cave (2018) reported that the bombing of UK increased Pb and other heavy metals spread on the soils and deposition of airborne particulates during the period 1940-41. In residential areas across the UK, Pb concentrations in domestic garden soils were consistently higher than those in soils of public parks (Thornton et al., 1990), indicating that the historical construction as well as lead-based paints were also likely to be contributory factors (Milke et al., 2001).

Another important influencing factor is industry. Relatively high Pb concentrations were also associated with the impact of industrial development especially in the Thames and Lee valleys. There is a decreasing trend in Pb concentration with the increase of distance away from the nearest industrial sites within 2000 m. Beyond this distance, Pb concentration remained stable (Fig. 4). Elevated Pb concentrations were also associated with other industrial activities such as landfill, metal recycling and transport functions, located in Redbridge, Newham, Barking, Dagenham, and Rainham. On the other hand, relatively low values were found over the major parks, with little impact from the significant urban development throughout the 200-300 years history of London (Knights and Scheib, 2011; Scheib et al., 2011; Appleton et al., 2018). High concentrations of Al were observed in the topsoil of north London where London clay was the dominant soil parent material, while low concentration was found in the central and south areas, which are associated with the Alluvium, River terrace deposits, Plateau Gravels and Chalk (Fig. 1).





Fig. 2. Spatial distribution maps in London soils: a) Pb; b) Al.

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Fig. 3. a) The median and mean of topsoil Al, and b) The median and mean of topsoil Pb with distance from the nearest road. Data grouped into 0-50 m, 50-100 m, 200-400 m, 400-600 m.



Fig. 4. The median and mean of topsoil Pb with distance from the nearest industry site. Data grouped into 0-500 m, 500-1000 m, 1000-1500 m, 1500-2000 m, 2000-2500 m, 2500-3000 m, 3000-5000 m.

3.3.Effects of bandwidth

To investigate the effects of different bandwidths on the GWR results, the AIC and six bandwidths ranging from 1000 m to 50000 m were considered (Fig. 5). AIC was used to find the "optimal" bandwidth at the local scale. A number of scattered patterns were observed in the whole study area when the AIC method was

chosen (Fig. 5a). Compared with the results from AIC, when the shortest bandwidth of 1000 m was used (Fig. 5b), the spatial patterns of GWR results were quite noisy, with a large number of small scattered patterns in the whole study area. When the bandwidth increased to 3000 m, some small scattered patterns in the north area disappeared. These small scattered patterns were merged in several large patterns near the city centre. The patterns became much simpler and clearer when the bandwidth increased from 5000 m to 50000 m, showing similar and consistent spatial patterns for the 4 bandwidths (Figs. 5c, 5d, 5e, 5f and 5g). With the longest bandwidth of 50000 m used in this study, most details of local spatial variation disappeared. Comparisons of R^2 and AIC_C between the AIC and six bandwidths are displayed in Table S1. The R^2 values of the GWR models with the AIC, 1000 m, 3000 m and 5000 m bandwidths were all higher than those with longer bandwidths, with their AICc values showing an opposite trend, demonstrating that the GWR models with short bandwidths performed better in modelling the relationships between Pb and Al (Huang et al., 2017). However, the short bandwidths revealed more details with noises making it hard to identify the largescale patterns. The moderate bandwidth of 5000 m appears to be a compromised choice among all the bandwidth parameters tested, with relatively high R², low AICc while clearly depicting the large-scale patterns of the underlying spatially varying relationships in the study area, with fewer noises. Our interpretation of the results will focus on this bandwidth.



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Fig. 5. Spatial patterns of (1) local regression coefficient and (2) Local R² for different bandwidths: a) AIC, b) 1000 m, c) 3000 m, d) 5000 m, e) 10000 m, f) 20000 m and g) 50000 m, respectively.

- 3.4. Spatially varying relationships between Pb and Al revealed by GWR
- 3.4.1. Local regression coefficients and local R^2

The variation of local regression coefficients for the independent variable Al and the spatial patterns of local R^2 are already shown in Fig. 5. The local regression coefficients are the slope values showing how strongly the changes of the explanatory variable Al impacts the value of the dependent variable Pb locally. Both positive and negative local regression coefficients were found, demonstrating the existence of both positive and negative correlations between Pb and Al in London soils at the local scale.

Negative regression coefficients were located in the north part of London, varying from -0.05 to -0.6. A clear directional feature was observed extending in the west-east direction. The high absolute values of regression coefficients indicated that Pb concentrations changed more rapidly with the change of the Al in the north edge area. The decreasing trend of the absolute values of regression coefficients towards central London showed the slower changes of Pb with the change of Al. Some interesting positive local relationships with Al were identified in southeast and southwest part of London. Relatively high regression coefficients (0.1-0.3) were found in large greenspace areas and low regression coefficients (0-0.1) were shown around in some built-up areas (see Fig. S1), indicating the relatively more rapid changes of the values Pb in large greenspace areas than those in the built-up areas.

The relatively high values of local R^2 were located in the north area, indicating that the local linear regression model performed well in this area. In central London and the south area, the local R^2 were generally low, implying the linear relationships between Pb and Al were weaker in these areas, and thus the variation in Al values explained a smaller percentage of the variation in Pb. These areas were more affected by human activities. There were three areas with relatively higher R^2 values in the southeast, southwest and the centre, respectively. These areas are lined with the locations of large parks and greenspace, which is relatively less interfered by anthropogenic activities which are highly spatially variable.

3.4.2. Local correlation coefficient (r_i)

For the convenience of exploration of the spatially varying relationships between Pb and Al in this study, the local results from GWR for the dependent variable Pb were used to calculate local correlation coefficients (r_i) . The spatially varying relationships between Pb and Al in London soils were clearly revealed by the local correlation coefficients and its significance levels (Figs. 6 and 7), showing negative correlations in the

northeast and north area, positive correlations in two areas in southwest and southeast, while relatively weak correlations in central London, except for a small area in the city centre with positive correlations.



Fig. 6. The spatial distribution of local correlation coefficients (r_i) between Pb and Al.





1) Northeast and north area (Area A): The negative correlations (p < 0.01) in the northeast area extended from northeast to the north (Fig. 6 and 7). This is in line with the spatial distribution patterns of Pb and Al (Fig. 2): high values of Al were located in the north side, with a decreasing trend towards central London, while high values of Pb were distributed in central London, with a decreasing trend towards the north (including northeast and northwest). The spatial variations of the two elements were in clearly opposite directions, resulting in their negative correlations in this area. The high values of Pb in central London could be related to human activities including industries, traffic and construction. On the other hand, under natural conditions, Al concentrations were controlled by geology, with high values in line with the distribution of Thames Gp (clay) in the north area. This result was supported by the positive correlations between Ti and Al in the whole study (see Fig. 8).

2) Two areas in southeast and southwest (Areas B1 and B2): positive correlations (p < 0.01) were found in two areas of southeast and southwest London, respectively (Fig. 6 and 7). Clear spatial patterns of both the low values of Pb and Al could be identified in these two areas from the Fig. 2, with a generally increasing trend in their surrounding areas. The consistent spatial distribution patterns for the two elements resulted in their positive correlations in these two areas. This result was related to the distributions of parent materials (PMs) and parklands. Both low value of Pb and Al was presented in top-soil samples overlying Alluvium, River Terrace Deposits, Thanet Sand Formation as well as White Chalk containing a large number of quartzite clasts and gravelly-sand PMs with larger particle sizes (Fig. 1, Fig. 2). It is well known that the adsorption properties of sand soils to metals are weak due to the presence of high silicate in quartzite clasts and gravelly-sand parent materials (Kern, 1994; Homann et al., 1998), which contribute to both low Pb and low Al values. Moreover, the large parks and greenspace areas may also plaid a role in relatively low concentrations of both Pb and Al, especially the sandy Richmond Park in the south-west as well as Greenwich Park and Blackheath in the southeast of London. These areas were less influenced by anthropogenic activities which had been historically protected for the past 200-300 years.

3) Central London (Area C): The weak correlations (p > 0.05) between Pb and Al were observed in soils of central London, with obviously high and strongly variable Pb values and low and strongly variable Al values (Fig. 2). As mentioned before, Al concentrations tended to be high in clay-rich PMs while low in Alluvium, River Terrace Deposits, which were associated with gravels and sandy PMs. Except for north London with high Al values, the spatial distribution of Al in central London were generally low and variable. On the other hand, Pb concentrations in central London was strongly affected by anthropogenic activities with elevated values. Compared with geology, the elevated Pb values were spatially random, mixed and complicated. Therefore, the correlations between Pb and Al were interfered and weakened in central London by anthropogenic activities in general.

4) A small area in City Centre (Area D): positive correlations (p < 0.01) were observed in a small area in central London (Fig. 6 and 7). The spatial pattern of both relatively low Pb and Al values can be identified in this area, with the increasing values in their surrounding areas. The spatial variations of the two elements were in the same direction, resulting in their positive correlations in this area. As mentioned before, the low value of Al in central London could be related to the Alluvium and River Terrace Deposits, while the relatively low values of Pb could be related to small parklands (i.e. The Vitoria park and Queen Elizabeth Olympic Park) as the soils of these parklands had retained a more natural geochemical signature than the surrounding built-up areas over the same PMs.

3.4.3. Comparison between spatial relationships of Pb-Al and those of Ti-Al

Our hypothesis is that if Pb were not affected by human activities, the relationships between Pb and Al should be generally similar to those between Ti and Al. Therefore, we used the spatial patterns of correlation between Ti and Al to "mimic" the natural relationships between Pb and Al assuming Pb concentrations were not affected by human activities. This approach will be helpful for us to establish the links between the spatially varying correlations between Pb and Al and the influencing factors. In addition to the spatial distribution map of local correlation coefficients between Pb and Al (Fig. 6), such a map for Ti and Al was also produced (Fig. 8). As expected, the correlations between Ti and Al were much less spatially variable, with all the local correlation coefficients being high and positive. Such a result further confirms the strong anthropogenic influences on Pb, making the correlations between Pb and Al spatially variable.



Fig. 8. The spatial distribution of local correlation coefficients (r_i) between Ti and Al.

In order to further explore the spatially varying relationships, scatter plots between Pb and Al, and Ti and Al were produced (Fig. 9). All samples and three groups of soil samples were arbitrarily selected based on the location from positive correlation, weak correlation and negative correlation areas between Pb and Al (Fig. S2). As expected, positive correlations between Ti and Al existed in all samples and all the three groups, implying that their relationships were generally spatially "invariable". In contrast, Pb exhibited the generally positive, negative and weak correlations with Al in the positive, negative, and weak correlation groups, respectively. Due to the complicated factors, the positive and negative relationships between Ti and Al on the scatter plots were still quite weak. This is in contrast to very good linear correlations between Ti and Al for all the samples and groups. The overall results confirm that anthropogenic factors had a great impact on the concentration of Pb in the highly urbanized central areas, causing varied correlations between Pb and the conservative element Al.

GWR provides a useful way to explore the spatially varying relationships among environmental parameters, providing a promising approach to investigate the complex relationships at the local level which are useful for improved soil management.



Fig. 9. Scatter plots between 1) Pb and Al, and 2) Ti and Al in a) all samples, b) positive correlation areas, c) weak correlation areas, d) negative correlation areas.

Conclusions

The relationships between Pb and Al in urban London soils were spatially varying, which have not been revealed before. The negative relationships between Pb and Al were found in the northeast and north areas and weak relationships were located in central areas, associated with the impact of strong anthropogenic activities on Pb concentration. Road traffic, industry activities and construction in the centre of London may be linked to the weakened or changed direction of relationship from positive to negative correlations. The positive relationships between Pb and Al were found in two areas of southeast and southwest and a small area in central London, which were associated with large parklands and greenspaces areas with less influences by anthropogenic activities and natural geochemical signature retained. Such new findings are important for a better understanding of the complicated relationships in urban geochemistry, especially with strong human activities which are strongly spatially variable. It should be noted that the GWR method has only revealed the spatially varying patterns of geochemistry elements in the urban area, implying the spatial associations with influences factors. The causal effects of heavy metals contamination still require more detailed investigations.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at



Fig. S1. Land use map of the London region



Fig. S2. The three areas were arbitrarily selected to produce the scatter plots between Pb and Al, and Ti and Al in the urban London to show their spatially varying relationships.

Bandwidth	AICc	\mathbb{R}^2
AIC	15111.38	0.52
1000 m	15180.01	0.57
3000 m	15508.88	0.38
5000 m	15826.08	0.33
10000 m	16247.50	0.28
20000 m	16462.22	0.26
50000 m	16533.77	0.25

Table S1. Comparison of R² and AIC_C between all the bandwidths of GWR models

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4.3 Simultaneous measurement of fifteen rare earth elements using diffusive gradients in thin films

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Simultaneous measurement of fifteen rare earth elements using diffusive gradients in thin films



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HIGHLIGHTS

- DGT is a feasible technique for simultaneous measurement of REEs in soils.
- REE elution efficiencies ranged from 86.5% to 93.8% using 2 M HCl.
- DGT uptake was independent of solution pH (3–9) and ionic strength (3 mM- 100 mM).
- Chelex[®]100 DGT had capacities of 5.39-6.75 μg cm⁻² for measurement of mixed REEs.

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GRAPHICAL ABSTRACT



ABSTRACT

A new method for simultaneous measurement of fifteen rare earth elements (REEs) [La (III), Ce (III), Pr (III), Nd (III), Sm (III), Eu (III), Gd (III), Tb (III), Dy (III), Ho (III), Er (III), Tm (III), Yb (III), Lu (III), and Y (III)] was established in this study using the diffusive gradients in thin films (DGT) technique with Chelex[®]100 binding gel. Five different types of ion exchange resins (Chelex®100, D418, D001-cc, 001 × 7, and HSTY®-SS) were selected for the initial investigation of their adsorption performance for REEs. The Chelex*100 binding gel had the greatest uptake efficiencies of >95% for the fifteen REE ions, which was used for all subsequent experiments. The binding gel exhibited rapid binding dynamics to REEs in mixed solution of the fifteen REE ions. Elution efficiencies ranging from 86.5% to 93.8% for these REEs were obtained based on extraction using 2.0 M HCl. The Chelex®100 DGT uptake of the fifteen REE ions increased linearly with the deployment time and found to be independent of pH(3-9) and ionic strength (3 mM-100 mM). The capacities of Chelex®100 DGT for measurement of the mixed elements were determined at a range of 5.39-6.75 µg cm⁻². Application of the DGT for soil analysis showed that Chelex[®]100 DGT was a useful tool in simultaneous measurement of the fifteen REE ions, even in a soil with high concentrations of REEs. This study demonstrated the advantage of Chelex*100 DGT in simultaneous measurement of the fifteen REE ions due to high uptake efficiencies and a wide tolerance to environmental interference. © 2018 Elsevier B.V. All rights reserved.

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1. Introduction

Rare earth elements (REEs), including the lanthanide group (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and yttrium (Y), are generally regarded as a group of trace metals with similar chemical features [1–3]. Practical application of REEs have been dramatically increasing especially with their usages in a large number of common commodities in our daily life since recent years [4]. Because of the unique physical and chemical properties of REEs, they become indispensable chemicals in modern industry such as new energy, new materials, environmental protection, aerospace, and electronic information industries [5-9]. Due to the growing demands for REEs and the excessive exploitation of rare earth minerals [10], more and more REEs enter the environment through anthropogenic inputs [11]. Recently, considerable concerns have been raised about the toxicological effects and related environmental risks of REEs, especially when they are accumulated in the environment [12-14]. The mining, processing and improper waste disposal are important pathways for exogenous REEs entering soil, water and air, causing increasing death rates of aquatic and terrestrial organisms [15,16]. Occupational exposure to dust containing REEs may cause pneumoconiosis according to previous studies [17,18]. It has been reported even at low levels in the environmental REEs may cause the generation of genetic toxicity in bone marrow cells and changes in the bone for long-term exposure [19–21]. Furthermore, long-term consumption of food contaminated with REEs can decrease the intelligence quotient of children and hinder the conduction of adult nervous system [22]. Due to the natural co-existence of REEs [1,23,24] and their potential environmental risks [25-27], simultaneous measurement of these REE ions in a single assay will greatly favor the evaluation of their environmental behavior.

Diffusive gradients in the films (DGT) is a dynamic passive sampling technique that has been developed for the measurement of labile chemicals, which was initially developed by Davison and co-workers in the early 1990s [28]. This technique is established based on a diffusion flux through a well-characterized diffusion layer, in which the concentration of a solute (C_{DGT}) at the outside surface of the diffusion layer over a span of time can be quantified according to Fick's First Law [29-31]. The traditional methods for evaluating REE bioavailability in soils include single-step chemical extractions such as neutral salts (CaCl₂) [32] and chelating agents such as ethylene-diamine-tetra-acetic acid (EDTA) [33] and sequential extraction methods [34]. In comparison, metals collected by DGT can mimic their uptake from soil to plants by lowering the concentration locally and inducing diffusive supply and release from the solid phase [35-38]. Previous studies have shown that the DGT measured metals in soils correlated strongly with their concentrations accumulated within plants [39,40]. DGT offers the advantage over traditional chemical extraction methods with the ability for oxidic materials to re-supply metals to soil solution [41]. Moreover, this technique has been applied in a wide range of research areas, such as water quality monitoring, chemical speciation in solution, sediment geochemistry, dynamic processes in waters and soils and bioavailability in waters and soils [42-47].

The first and most frequently used binding agent is an iminodiacetate chelating resin (Chelex[®]100), which has been developed for measurement of a large number of metal ions, e. g, Cu, Ni, Zn, Cd, Mn [28,29,48,49]. A similar layer using suspended particulate reagent-iminodiacetate (SPR-IDA) has been reported for measurement of trace metals (Co, Ni, Cu, Zn, Cd, Pb) with analysis using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [50]. Li et al. [51] developed a solution phase poly (4styrenesulfonate) (PSS) binding layer for measurement of Cu and Cd in synthetic water. Specific measurement of some cationic metals have been made using other binding agents [52–54]. Recently, due to the great DGT capacities, strong tolerance to competitive ions, and chemical stability, the Chelex[®] 100 gel has received increasing attention as a binding agent in DGT measurement [55–59].

To date, the sampling device for simultaneous measurement of fifteen REE ions using DGT is scarce. Studies related to the extraction of REE ions generally use various ion exchange resins such as strong acidic cation exchanger-sulfonic acid functionality (001×7 , D001-CC) [60–62] and chelate ion exchanger (D418) [63,64]. Wang et al. [65] studied the separation of heavy rare earths with extraction resin containing Cyanex272 and HEOPPA. Gupta et al. [66] investigated the adsorption of light REEs on Cyanex 923 from hydrochloric acid solutions. These extraction resins can be potentially used as binding agents for DGT measurement of REEs.

The aim of this study was to develop DGT for the simultaneous measurement of the fifteen REEs. Five different types of ion exchange resins (Chelex[®]100, D418, D001-cc, 001 × 7, and HSTY[®]-SS) were selected for the initial investigation of their adsorption performance for REEs, based on which the binding agent Chelex[®] 100 was chosen for DGT use. A series of validation experiments, including the binding kinetics of each element in mixed solutions and the tolerance of ionic strength and solution pH, were conducted to examine the DGT responses under laboratory conditions. In the meantime, the DGT capacities were measured and field application in soils were tested.

2. Experimental

2.1. Materials and solutions

Strong acidic cation exchanger-sulfonic acid functionality (D001-cc, 001×7) and Chelate ion exchanger (D418) were purchased from Chemical Plant of NanKai University, China. Cell® HSTY[®] Metal Scavenger Toolkit was purchased from XinAo Science and Technology Co., Ltd. Acrylamide (ultrapure grade), N,N'methylenebisacrylamide (ultrapure grade), ammonium persulfate (ACS grade), N,N, N,N'- tetramethylethylenediamine (TEMED, ACS grade) were purchased from AMRESCO for the preparation of the binding gel [55]. Agarose (low electroosmosis) and Chelex® 100 (200-400 mesh, sodium form) were obtained from Bio-Rad [55]. A new dual-mode DGT holder with a 10 mm depth and 20 mm diameter exposure window was provided by EasySensor Ltd [67]. The REE ion solutions were prepared by dissolving $La(NO_3)_3 \cdot 6H_2O_1$, Ce(NO₃)₃·6H₂O, Pr(NO₃)₃·6H₂O, Nd(NO₃)₃·6H₂O, Sm(NO₃)₃·6H₂O, Eu(NO3)3.5H2O, $Gd(NO_3)_3 \cdot 6H_2O_7$ $Tb(NO_3)_3 \cdot 5H_2O_1$ Dy(NO₃)₃·5H₂O, Ho(NO₃)₃·5H₂O, Er(NO₃)₃·5H₂O, Tm(NO₃)₃·5H₂O, $Yb(NO_3)_3 \cdot 5H_2O$, $Lu(NO_3)_3 \cdot 5H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ in deionized water (18.2 MΩ cm Milli-Q water, Millipore). The concentration of stock solution for each REE was $100 \,\mu g \,m L^{-1}$. The test solutions used for subsequent experiments were composed of the fifteen REE ions, diluted from the stock solution. The pH values of the solutions were adjusted within 4.5-5.5 to avoid competition and precipitation reactions among multiple elements. Standard solutions of each element were supplied from the National Standard Materials Network, China. Plastic containers and DGT subassemblies were acid-cleaned in 10% (v/v) HNO₃ for more than 24 h and then rinsed thoroughly with deionized water prior to use [31,55]. For the experiment on ionic strength effects, NaCl was added to each solution at 0.01 mol L^{-1} to minimize adsorptive losses from solution 31,55

2.2. Gel preparation, DGT deployment and retrieval

Agarose diffusive gel containing 1.5% agarose was prepared by dissolving agarose in an approximate volume of deionized water at

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80 °C following published procedures [55]. The binding gel (Chelex[®]100 gel) for simultaneous uptake of REE ions was prepared according to Wang et al. [31] A weight of 2.0 g Chelex-100 and 0.2 g half-dried Zr-oxide powder were added to 5 mL of gel solution composed of 28.5% acrylamide (w/v) and 1.5% methacrylamide (w/ v). Optimization for the addition of Chelex-100 was performed by increasing its added amounts from 1.0 g to 2.0 g in the gel solutions to increase the capacity of the Chelex®100 DGT to absorb as much REE ions as possible. A small amount of half-dried Zr-oxide powder was included to render the gel physically hard and Chelex-100 particles equally distributed in the gel [31]. The final amount of Chelex[®] 100 resin was $0.3 \pm 0.01 \, \text{g cm}^{-3}$ in the gel, which was higher than the commercialized Chelex 100 gel (DGT Research Ltd., UK). The agarose diffusive gel disc was prepared with a 0.8 mm thickness and 25 mm diameter, as reported in previous studies. It proved that the variations in the thickness of the agarose diffusive gel under different ionic strength (0-1 M), pH (2-11) and temperature $(4-40 \,^\circ\text{C})$ conditions were within $\pm 0.7\%$ of their initial values [31]. A 0.1 mm-thick PVDF membrane filter (Durapore, 0.45 mm pore size) was placed on the top of the diffusive gel for protection. The filter has been found to behave as consistent diffusion coefficients of the agarose diffusive gel, which showed a significant effect on the diffusion rates of anions and cations with the order of

agarose < agarose + PVDF < agarose + Polyethersulfone (PES) < agarose + Cellulose Nitrate (CN) [31]. The Chelex [®]100 binding gel was covered by an agarose diffusive gel and PVDF membrane (Durapore, 0.45 mm pore size, 0.1 mm thickness), which was used for deployment in test solutions and soils. Solution samples were taken before the retrieval of the DGT samplers, filtered (0.45 µm), acidified to 3% (v/v) HNO3, and then stored at 4 °C until analysis [31].

Four other binding gels including the D418, D001-cc, 001×7 and HSTY[®]-SS were also used for DGT measurement of REE ions. Preparation of those gels were similar to that of the Chelex[®] 100 gel reported previously [55]. A weight of 2.0 g of each D418, D001-cc, 001×7 and HSTY[®]-SS powder was added to a volume 5 mL gel solution. The amounts of D418, D001-cc, 001×7 and HSTY[®]-SS in the gel were 0.3 ± 0.01 g cm⁻³. The DGT devices were assembled using a new dual-mode DGT holder with a 2 cm diameter exposure window (EasySensor Ltd, Nanjing, China) [67].

2.3. Characteristics of DGT performance

2.3.1. Sample analysis and calculation

All the fifteen REEs were measured using an inductively coupled plasma-mass spectrometer (ICP-MS, Agilent Technologies 7700, USA). All ICP-MS samples and standards were prepared using 3% HNO₃. The solutions of 5 μ g L⁻¹ Rh and Ge were used as internal standards to account for instrumental drift [31]. Quality control of standards was performed for every 30 samples [31]. During the selection of isotopic determination, according to the appropriate abundance and the interference-free conditions. The isotopes for 15 REE ions ⁸⁹Y, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁴Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, and ¹⁷⁵Lu were investigated. The DGT measured concentration for each REE ion in solutions was calculated based on the well-established DGT equation [29]. The details are provided in the Supporting Information Experimental section.

2.3.2. Selection of binding gel for DGT use

To test the validity of DGT measurement for REEs, comparison experiments using five different types of binding gels were performed. The binding gel discs (2.5 cm diameter) were immersed in 20 mL of solutions containing 200 μ g L⁻¹ of each REE and

0.01 mol L⁻¹ NaCl at pH 5. The Chelex[®]100, D418, D001-cc, 001 \times 7 and HSTY[®]-SS binding gels were simultaneously investigated for comparison. The solutions were stand at room temperature for 24 h to ensure maximum uptake.

2.3.3. Binding kinetics

The binding dynamics of the fifteen REE ions to Chelex[®] 100 gel was tested by immersing the gel discs in 10 mL of solutions containing $25 \,\mu g \, L^{-1}$ of each REE with 0.01 mol L^{-1} NaCl at pH 5.5. The solutions were immediately shaken at room temperature for various time intervals ranging from 1 to 120 min. Respective concentrations of each REE ion in the solutions were measured before and after immersion of the gels to calculate the absorbed mass on the gel at each time interval.

2.3.4. Elution efficiencies

Mixed solutions used for the uptake of REE ions contained the fifteen REE ions at concentrations of $200 \ \mu g \ L^{-1}$ at pH 4.45. The Chelex®100 gel discs were immersed in 20 mL of mixed solution in well-sealed plastic tubes, followed by shaking for 24 h. The REE ions-loaded gel discs were retrieved and eluted with 1.8 mL of 1.0 M HNO₃ or HCl solutions with different concentrations (1.0–3.0 M HCl) at room temperature.

2.3.5. Effects of pH and ionic strength

Effects of solution pH and ionic strength on the Chelex[®]100 DGT measurement were examined by deploying the DGT units in a series of 21 well-stirred mixed solutions containing approximately $25 \ \mu g \ L^{-1}$ of each REE ions at 25.5 °C for 8 h. The pH values of the mixed solutions were adjusted to 3.04, 3.94, 4.96, 6.04, 6.85, 7.89 and 9.05 while the ionic strength was constant at 0.01 mol L^{-1} NaCl. The ionic strengths of the mixed solutions were tested by different concentrations of NaCl ranging from 0.01 to 1000 mM while the pH value was constant at 5.0.

2.3.6. Determination of diffusion coefficients

The diffusion coefficients of the REE ions were determined by DGT time-series deployment method. The Chelex[®]100 DGTs were deployed in 10 L mixed solutions containing 0.01 mol L⁻¹ NaCl and the fifteen REE ions (pH 5.5) at 24 °C. Concentration of each REE in the test solution was approximately $25 \,\mu g \, L^{-1}$. The DGT devices were retrieved at different time intervals from 4 h to 24 h. The measured coefficients at a given temperature were corrected for 25 °C according to Zhang et al. [29] The details are provided in the Supporting Information experimental section.

2.3.7. Capacity for DGT response

The capacity of the Chelex[®]100 DGT for measuring the fifteen REE ions was determined by time-series DGT accumulation experiments. The Chelex[®]100 DGT units were exposed to 10 L of well-stirred solutions containing 500 μ g L⁻¹ of each REE ion at pH 4.45 (0.01 mol L⁻¹ NaCl, 24 °C) for varying deployment time from 4 to 120 h.

2.3.8. DGT blanks and method detection limits

DGT blanks of the fifteen ions were measured by deploying blank Chelex[®] 100 DGT in 2 L of 0.01 mol L⁻¹ NaCl solution for 24 h. The REE ions accumulated in the gels were eluted using 1.8 mL of 2 M HCl solution for 16 h. Six replicates were carried out. Method detection limits (MDL) were determined as three times of the standard deviations of the blanks. The MDLs were further converted to DGT concentrations using a deployment time of 24 h with a diffusion thickness of 0.09 cm and a gel area 3.14 cm^2 .

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2.3.9. Competing effects of cations

To examine the possible interferences of various cations (Pb, Cu, Zn and Cd) on the measurement of REE ions using the Chelex®100 DGT technique, the DGT devices were deployed in 2L solutions containing 0.01 mol L⁻¹ NaCl and 25 μ g L⁻¹ of each REE ions mixed with different concentrations of Pb (4–80 μ g L⁻¹), Cd (4–80 μ g L⁻¹), Cu (4–80 μ g L⁻¹), and Zn (4–80 μ g L⁻¹) at pH 5.5 (25.5 °C). The DGT devices for each concentration treatment were retrieved in triplicate after a deployment time of 8 h. The REE ions loaded in the binding gel were eluted using 2 M HCl for 16 h. The concentrations of REE ions in the eluents were detected using an ICP-MS. The Chelex[®] resin has shown a high selectivity of sorption of metallic cations, especially for multivalent ions [28,29,48,49]. Therefore, the uptake of REE ions by Chelex[®] 100 DGT may be affected by the presence cations and less by anions.

2.3.10. Application in soils

The eight soil samples were collected at a depth of 0-20 cm in Maoniuping, Sichuan Province, China, with four samples from a REE mining area, two from the roadside and the other two from an agricultural land nearby. The soils from the mining site contained high concentrations of REEs, which became a challenging medium for DGT measurement. The physical and chemical properties of the soil samples are listed in Table S1 of the Supporting Information. The soil samples were air-dried at room temperature, sieved using a 2 mm mesh sieve, and mixed homogeneously. One Chelex®100 DGT unit was sequentially composed of a Chelex[®]100 binding gel, agarose diffusive gel and the Durapore PVDF membrane [68,69]. These layers were fixed in the new dual-mode plastic holder [67]. The 30 g of soils are conditioned at approximately 70% of the maximum water holding capacity (MWHC) for 48 h (24 ± 1 °C) in order to be adequately moist for DGT deployment [69,70]. The soil pastes were then filled up in the open cavity of the assembled DGT devices. After 24 h, the soil was removed from the exposure surface of the DGT device using deionized water [69]. The gel disc was eluted with 1.8 mL of 2.0 M HCl for 16 h to extract REE ions bound in the gel and analyzed by ICP-MS. In this study, dry soils were used to test the DGT measurement for REEs. Further studies may be carried out for the profiles in wet soils and wet sediments.

3. Results and discussion

3.1. Selection of binding gel for DGT use

An investigation was performed to choose the suitable binding

gel for simultaneous measurement of the fifteen REE ions in solution, using five different types of binding gels in mixed solutions. Uptake efficiency of each REE ion was unaffected by the Chelex[®] 100 gel because they were consistently >95%, which had the greatest uptake efficiencies than the other four binding gels (see Table S2). As presented in Table 1, accumulation masses of the fifteen REE ions in Chelex[®] 100 gels were obviously higher than the other four binding gels, with the maximum and minimum masses of 3529.94 ± 0.44 and 3369.20 ± 0.08 ng for Er (III) and Gd (III), respectively. The Chelex[®] 100 gel was thus selected for further study.

3.2. Binding kinetics

The binding kinetics of the fifteen REEs were investigated by immersing the Chelex[®]100 gel discs in the mixed solutions which were shaken for different time intervals. As shown in Fig. 1, the uptake of each REE increased dramatically within the first 20 min, followed by a stable stage. The ions of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Er(III), Tm(III), Yb(III), and Y(III) had high binding rates, reaching 90% of their individual total amounts in solutions at 20 min. For Tb (III), Ho (III) and Lu (III), their binding rates were about 75% at 20 min. The binding rates for the first 20 min for all 15 REE ions are listed in Table S3. The values are much higher than the DGT fluxes calculated through a thickness of 0.09 cm diffusion layer (0.08 cm agarose gel plus a 0.01 cm PVDF filter membrane) in a solution with a concentration of 20 μ g L⁻¹ for each REE at 25 °C (Table S3). For the fifteen REE ions, the ratio of the binding rate to the DGT-measured flux varied in the range of 44-54. These results demonstrated that the absorptions of the Chelex[®]100 gel for all the REE ions tested were fast enough to satisfy DGT uptake.

3.3. Elution efficiency

The solution 1.0 M HNO₃ has been used for eluting ions in Chelex[®]100 gel in the literature [29,71]. We first tested the use of 1.0 M HNO₃, but low recovery rates of <50% for all REE ions were achieved (Table 2). Subsequently, we tried to use a series of solutions prepared from different concentrations of HCl (1.0–3.0 M) as the eluent at room temperature. The results showed that elution using 2.0 M HCl obtained stable efficiencies for REE ions (200 μ g L⁻¹) ranging from 86.5% to 93.8% (Table 2). Similar phenomena have been reported by Mason et al. that the use of 1 M HCl obtained higher efficiencies than 1 M HNO₃ for elution of Cd, Cu,

Table 1

Comparisons of elution accumulated masses of each REE ion in five different types of binding gels in solutions containing 200 μ g L⁻¹ of each REE and 0.01 mol L⁻¹ NaCl. Values are mean \pm SD of three replicates.

Elements	HSTY [®] -SS	D418	D001-CC	001 imes 7	Chelex [®] 100
La	1737.93 ± 2.24	430.94 ± 21.62	652.94 ± 22.32	46.37 ± 12.37	3452.08 ± 0.28
Ce	1849.87 ± 2.02	311.64 ± 25.90	726.25 ± 21.04	49.40 ± 7.19	3442.44 ± 0.23
Pr	1971.15 ± 1.85	313.77 ± 23.37	794.67 ± 19.51	54.44 ± 6.71	3518.71 ± 0.39
Nd	2050.76 ± 2.02	311.34 ± 23.21	851.15 ± 18.34	59.58 ± 5.49	3527.51 ± 0.15
Sm	2024.89 ± 1.58	249.52 ± 24.38	881.58 ± 17.95	64.10 ± 4.87	3481.63 ± 0.16
Eu	2059.61 ± 1.69	249.46 ± 24.90	910.81 ± 16.92	63.76 ± 5.76	3463.09 ± 0.34
Gd	2073.70 ± 1.07	261.36 ± 25.26	916.15 ± 15.56	52.79 ± 7.98	3369.20 ± 0.08
Tb	2220.21 ± 0.77	387.56 ± 15.37	1116.22 ± 11.58	232.28 ± 1.01	3395.38 ± 0.20
Dy	2319.90 ± 1.54	287.58 ± 24.31	1123.17 ± 12.02	73.04 ± 5.00	3507.67 ± 0.27
Но	2304.80 ± 0.98	326.62 ± 21.86	1167.09 ± 10.25	100.11 ± 3.81	3389.60 ± 0.56
Er	2442.19 ± 1.35	300.66 ± 23.55	1256.47 ± 9.61	78.02 ± 5.76	3529.94 ± 0.44
Tm	2382.23 ± 1.17	266.71 ± 22.37	1270.32 ± 8.69	103.79 ± 3.73	3385.07 ± 0.59
Yb	2470.82 ± 1.43	196.70 ± 25.84	1318.54 ± 8.09	77.17 ± 4.71	3502.92 ± 0.87
Lu	2515.56 ± 0.97	309.65 ± 13.90	1439.58 ± 7.02	250.78 ± 0.21	3473.69 ± 0.77
Y	2317.32 + 1.45	384.38 ± 21.52	1197.34 + 9.74	75.92 + 6.51	3501.91 ± 0.78

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Fig. 1. Dynamic binding rates of each REE ion to the Chelex®100 gel. Values are the mean ± SD of three replicate measurements.

Mn, Mo, P, and Zn from a mixed binding gel [72]. Miyazaki and Barnes reported that chelating resin for concentration of some REEs required digestion with strong mineral acids for elution [73,74].

3.4. Effects of pH and ionic strength

The effects of pH on the Chelex[®]100 DGT measurement are shown in Table S4. Concentrations of REE ions measured by the DGT (C_{DGT}) agreed well with those in solutions (C_{SOL}) when the pH values in solutions increased from 3.04 to 9.05, with the C_{DGT}/C_{SOL} ratios varying between 0.80 and 1.11. The effects of ionic strength on the measurement of REE ions by the Chelex[®]100 DGT are shown in Table S5. The measurement were generally independent of ionic strength from 3 to 100 mM, with the $C_{\text{DGT}}/C_{\text{SOL}}$ ratio ranging from 0.82 to 1.14. When the ionic strength was 1000 mM there were slight decreases for the values of $C_{\text{DGT}}/C_{\text{SOL}}$. This deviation can be explained by a reduction of the diffusion coefficient due to the viscosity effect of agarose diffusive gel [75], leading to a lower accumulation of REE ions over the deployment period. When the ionic strengths were in the range of 0.01-2 mM, the $C_{\text{DGT}}/C_{\text{SOL}}$ ratios were higher than 1.1. This enrichment could be attributed to the electrostatic interactions between REE ions and the fixed negatively charged groups in the agarose gel [76,77]. Furthermore, Alfaro-de la Torre et al. also suggested that the free Na⁺ in the resin gel

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 70.8 ± 39.4

 71.1 ± 40.8

 74.9 ± 38.4

 69.5 ± 36.4

 91.1 ± 3.48

 91.8 ± 4.39

 92.4 ± 3.40

 89.4 ± 3.52

Table 2 Elution efficiencies of REE ions (200 $\mu g \, L^{-1})$ from the Chelex®100 gel using 1.8 mL of

 42.66 ± 5.8

 42.67 ± 4.9

 42.94 ± 1.7

 34.82 ± 17.2

Tm

Yb

Lu

Y

1.0 M HCl, 2.0 M HCl, and 3.0 M HCl and 1.0 M HNO ₃ , respectively.						
Elements	1.0 M HNO3	1.0 M HCl	2.0 M HCl	3.0 M HCl		
La	37.41 ± 15.4	94.1 ± 19.9	86.5 ± 3.69	66.5 ± 36.2		
Ce	38.88 ± 14.4	84.3 ± 10.37	87.2 ± 3.06	66.4 ± 39.5		
Pr	45.05 ± 5.3	84.3 ± 10.51	88.7 ± 3.07	66.8 ± 41.0		
Nd	42.53 ± 8.0	85.0 ± 10.33	90.2 ± 2.55	67.2 ± 41.0		
Sm	48.69 ± 2.1	83.5 ± 9.98	91.6 ± 2.88	65.2 ± 43.1		
Eu	48.76 ± 2.3	83.5 ± 10.10	90.0 ± 3.09	65.3 ± 42.7		
Gd	45.71 ± 3.7	87.7 ± 10.24	89.1 ± 2.97	67.5 ± 41.8		
Tb	49.31 ± 7.0	90.7 ± 10.68	93.8 ± 3.19	72.4 ± 40.55		
Dy	45.40 ± 2.0	87.2 ± 11.05	89.6 ± 3.89	68.8 ± 41.21		
Но	42.78 ± 6.0	88.5 ± 10.58	91.3 ± 3.79	70.7 ± 38.78		
Er	41.72 + 6.2	88.0 ± 11.08	91.6 + 3.28	71.2 + 39.4		

 90.4 ± 9.95

 89.1 ± 10.44

 92.6 ± 10.28

 87.3 ± 7.67

enhanced DGT measured metal concentrations at low ionic strength [78]. Overall, the pH and ionic strength results obtained in this study were in agreement with the measurement of metals reported by Zhang et al. [49] and Gimpel et al. [79].

3.5. Diffusion coefficients of REEs

The accumulated masses of all the REEs had linear correlations with the deployment time of DGT, with the significance level of p < 0.001 (Fig. 2). The slopes of the linear fitting equations were used for calculation of the effective diffusion coefficients which are summarized in Table S6, with a range of 4.72-5.40 ($\times E-6$ cm² s⁻¹, 25 °C). The measured D_{DGT} values for REE ions in this study were in agreement with transition elements reported by Panther et al. [80]. The D_{DGT} values for REE ions were about 80% of Mn, Co, Ni, Fe measured by ZrO-Chelex DGT (Table S7) [31]. Furthermore, the diffusion coefficients of metal ions in diffusive gels (agarose-derived cross-linker, APA) are ~85% of the diffusion coefficients of those in water, which have been found by Scally et al. [81] In this study, the ratios of diffusion coefficients of the fifteen REE ions in the agarose diffusive gel were 82%–90% of those measured values in water (Table S6).

3.6. Capacity for DGT response

The capacities of the Chelex[®] 100 DGT for measurement of the fifteen REE ions were investigated via time-series experiments



Deployment time of DGT (min)

Fig. 2. Determination of the effective diffusion coefficients (D_{DGT}) for each REE ions from time-dependent accumulations by DGT. Values are means ± SD of three replicates.
using the mixed REE solutions. The results are shown in Table S8 and Fig. S1. Linear and theoretically predicted responses were obtained with time up to 48 h for the fifteen REE ions, respectively. The uptake capacities of Chelex[®] 100 DGT for REEs in a mixed solution were in the range of $5.39-6.75 \,\mu g \, cm^{-2}$. The measured DGT capacities for the sum of the fifteen REE ions (89.65 $\mu g \, cm^{-2}$) was greater than 0.99 times of Fe (44.9 $\mu g \, cm^{-2}$) measured in a single element solution [58].

3.7. Competing effects of cations

The uptake of REE ions by the Chelex® 100 DGT may be affected

by the presence of cations (e.g., Pb, Cu, Zn and Cd), which compete for the same binding sites [28,48,52]. Such possible effects were investigated in this study (Fig. 3). The C_{DCT} values for the fifteen REE ions measured by the Chelex[®] 100 DGT agreed well with C_{SOL} values over different concentration ranges of the mixed cations, with most of the measured-to-predicted ratios varying around the expected values of 0.9–1.1, demonstrating that there was no significant competition between the other metals and REEs for the binding sites. A possible reason may be that the binding rates of all the REE ions were greater than 85% at first 10–20 min (Fig. 1), much higher than the binding rates of Pb, Cu, Zn and Cd ranging from 60% to 77% reported by Wang et al. [31] More than 90% of the REE ions were



Fig. 3. Competing effects of the mixed cations solution (Pb, Cd, Zn and Cu) on the uptake of REE ions by the Chelex*100 DGT. The vertical axis represents the ratio of DGT-measured concentration (C_{DGT}) to concentration in solution (C_{SOL}), with the dotted lines showing the values at 0.9 and 1.1. Values are means \pm SD of three replicates.

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Table 3
DGT blanks (ng cm^{-2}) and method detection limits (MDL, ng mL^{-1}) for the REEs.
Values given are the mean \pm SD of three replicate measurement.

Table 5

Spearman correlation coefficients between mea	asurements made by the Chelex [®] 100
DGT (µg L ⁻¹) and the total concentrations of R	EEs (mg kg), EDTA (mg kg) chemical
extraction in eight soil samples.	

Elements	Blanks	MDL	Elements	Blanks	MDL
La	0.79 ± 0.29	0.65	Tb	0.03 ± 0.61	0.61
Ce	0.13 ± 0.14	0.15	Dy	0.07 ± 0.47	0.47
Pr	0.03 ± 0.07	0.23	Но	0.02 ± 0.41	0.41
Nd	0.05 ± 0.17	0.51	Er	0.08 ± 0.18	0.18
Sm	0.02 ± 0.08	0.26	Tm	0.02 ± 0.34	0.34
Eu	0.03 ± 0.19	0.58	Yb	0.11 ± 0.11	0.11
Gd	0.04 ± 0.29	0.29	Lu	0.03 ± 0.29	0.29
			Y	0.62 ± 0.06	0.19
Conditions of	DGT deployment	$\therefore \Delta g = 0.$	09 cm. $t = 24$ h.	$A = 3.14 \text{ cm}^2$.	

extracted within 10 min of its interaction with the Chelex[®]100 gel. A similar behavior was observed for the fifteen REE ion. Interaction of the Chelex[®]100 gel with the REE ions were sufficiently rapid, permitted their separation from the latter [74]. Huynh et al. [57] found it was important for accurate DGT measurement to the fast kinetics of binding elements in the first few minutes. Furthermore, the $C_{\text{DGT}}/C_{\text{SOL}}$ ratios for all of 15 REE ions decreased only in the presence of metal cations (Pb, Cu, Zn and Cd) at the highest concentration tested (80 µg L⁻¹), which are unlikely to occur even in contaminated or over-fertilized environments [57,82]. This indicates that there is a great binding affinity of the Chelex[®] 100 gel for the fifteen REE ions.

3.8. DGT blanks and method detection limits

The blanks and MDLs for the Chelex[®] 100 DGT are listed in Table 3. The maximum and minimum blanks were found to be 0.02 and 0.79 (ng cm⁻²). The detected MDLs for the fifteen REE ions ranged from 0.11 to 0.65 ng mL⁻¹, with the minimum value for Tm (III), Ho (III), Sm (III) and the maximum value for La (III). The low DGT blanks and MDLs for all the REE ions indicate that the Chelex[®] 100 DGT used in this study allow simultaneous quantitative measurement of the tested elements in the test solution.

3.9. Deployment in soils

Triplicate Chelex[®] 100 DGT deployments were conducted in eight soil samples (two samples from each of a mining site, a tailing site, roadside and an agricultural land) to examine simultaneous

Element	C _{DGT} VS C _{Total} (mg kg)	C _{DGT} VS EDTA (mg kg)			
La	0.575	0.952 ^a			
Ce	0.690	0.976 ^a			
Pr	0.786 ^b	0.905 ^a			
Nd	0.714 ^b	0.952 ^a			
Sm	0.714 ^b	0.905 ^a			
Eu	0.881**	0.762 ^b			
Gd	0.690	0.929 ^a			
ть	0.786 ^b	0.833 ^b			
Dy	0.814 ^b	0.738 ^b			
Но	0.786 ^b	0.738 ^b			
Er	0.714 ^b	0.738 ^b			
Tm	0.667	0.571			
Yb	0.668	0.667			
Lu	0.405	0.262			
Y	0.755 ^b	0.810 ^b			

^a Correlation is significant at the 0.01 level (2-tailed).

^b Correlation is significant at the 0.05 level (2-tailed).

measurement of 15 REE ions. As shown in Table 4, the total concentration of the REEs ranged from 17.44 to $30971.64 \text{ mg kg}^{-1}$ in the soil samples. With 95% of the total weight of REEs belonging to the group of light REEs, heavy REEs of the group such as Ho to Lu were relatively rare. The DGT-measured REE concentrations in the eight sampling sites were 0.03-29.53, 0.08-38.82, 0.02-1.98, $0.03-2.79 \,\mu g \, L^{-1}$ for mining soils, tailing soils, road soils and agricultural soils, respectively. The Spearman correlation coefficients were calculated to reveal the relationship between the total and DGT-measured concentrations in the soils (Table 5). A significantly positive correlation was found between them for 9 REEs, including Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er and Y (p < 0.05), demonstrating that the total concentrations may not be appropriate for bioavailability assessment. Furthermore, a comparison of the DGT results was made with a chemical extraction method (EDTA) for evaluation of REE bioavailability in the eight soil samples. As shown in Table 5, most REE ions exhibited a good correlation between the two methods (p < 0.01). It is worthwhile to note that the mechanisms of the two methods to measure the REE bioavailability were different, making it hard for a direct or simple comparison [83,84].

The present study provides an alternative approach to study REE bioavailability in soils. However, this approach is only at its starting

Table 4

The measured DGT concentrations (C_{DGT} , μ g L⁻¹) obtained with the Chelex*100 DGT and the total concentrations of REEs (C_{Total} , mg kg) in eight soil samples.

Elemen	nent Mining soil $(n = 2)$ Tailing soil $(n = 2)$			Road soil (n = 2)			Agricultural soil $(n = 2)$									
	C _{Total} (mg kg)	C_{DGT} (µg L ⁻¹)	C _{Total} (mg kg)	C_{DGT} (µg L ⁻¹)	C _{Total} (mg kg)	C_{DGT} (µg L^{-1})	C _{Total} (mg kg)	$C_{ m DGT}$ (µg L ⁻¹)	C _{Total} (mg kg)	C_{DGT} (µg L ⁻¹)	C _{Total} (mg kg)	C _{DGT} (μg L ⁻¹)	C _{Total} (mg kg)	C_{DGT} (µg L ⁻¹)	C _{Total} (mg kg)	$C_{ m DGT}$ (µg L ⁻¹)
La	10336.83	29.49	210.13	9.12	418.44	38.77	6559.85	28.48	1.44	0.24	440.16	1.1	3742.55	2.79	79.33	1.56
Ce	14368.16	5 29.53	1609.77	3.58	756.77	38.82	9178.44	32.55	11.24	0.26	620.22	1.21	5078.31	2.32	143.9	1.55
Pr	1290.09	3.37	24.71	0.64	77.5	4.08	798.39	3.01	0.3	0.02	51.53	0.12	426.86	0.65	13.62	0.59
Nd	3820.66	11.88	71.27	2.04	263.36	13.31	2352.04	9.77	1.01	0.07	151.67	0.44	1219.99	1.08	46.14	0.95
Sm	349.17	1.79	6.18	0.24	37.89	1.8	207.45	1.25	0.77	0.04	14.65	0.13	97.56	0.31	8.1	0.33
Eu	74.42	1.27	1.11	0.17	7.85	1.15	45.51	0.81	0.33	0.03	4.93	0.49	19.65	0.39	1.67	0.34
Gd	366.26	1.96	20.91	0.22	31.12	1.78	236.69	1.33	0.51	0.02	20.98	0.17	178.02	0.13	10.1	0.16
Tb	23.45	0.19	0.75	0.03	2.77	0.19	15.11	0.13	0.12	0.02	1.38	0.03	8.79	0.03	1.1	0.04
Dy	63.4	0.9	0.9	0.2	10.36	0.9	40.41	0.68	0.32	0.16	4.19	0.26	15.29	0.51	5.63	0.55
Но	9.55	0.17	0.16	0.05	1.61	0.18	6.25	0.14	0.08	0.05	0.61	0.07	2.06	1.15	1.03	0.08
Er	29.7	0.52	0.59	0.21	4.41	0.59	19.65	0.5	0.24	0.21	1.78	0.32	7.18	0.28	3.09	0.33
Tm	2.8	0.07	0.04	0.04	0.48	0.09	1.97	0.08	0.03	0.04	0.19	0.06	0.56	0.06	0.39	0.06
Yb	17.67	0.49	0.31	0.28	3.54	0.65	12.43	0.6	0.14	0.32	1.39	0.48	3.57	0.43	2.91	0.46
Lu	2.23	0.09	0.05	0.06	0.45	0.12	1.73	0.11	0.03	0.07	0.15	0.1	0.46	0.09	0.37	0.1
Y	217.25	4.2	3.87	1.77	40.7	4.78	159.3	3.61	0.88	1.31	16.64	1.98	53.74	1.85	30.8	2.14
Total REEs	30971.64	85.92	1950.74	18.65	1657.242	107.21	19635.24	83.05	17.44	2.87	1330.48	6.96	10854.57	12.08	348.19	9.25

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stage, thus more investigations are needed to reveal the DGT measured REEs in soils for a better understanding of the results as well as the performance DGT in comparison with the other bioavailability assessment methods.

4. Conclusions

This study validated the feasibility of using the Chelex[®] 100 DGT for the simultaneous measurement of fifteen REE ions in a single assay, based on a range of laboratory experiments as well as deployment in soils. The 2 M HCl (1.8 mL per gel) was found to be an effective eluent for Chelex[®] 100 gel with efficiencies of 86.5%– 93.8% for REE elements. Measurement of fifteen REE ions by Chelex[®] 100 DGT were consistent across a wide pH range (3–9) and ionic strengths (3 mM–100 mM). The Chelex[®] 100 DGT had capacities of 5.39–6.75 µg cm⁻² for measurement of mixed REEs. The developed DGT technique in this study is feasible for bioavailability assessment of REE ions in soils. The results in this study suggest that the Chelex[®] 100 DGT will be an effective tool for the simultaneous measurement of REE ions in the environment.

Notes

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.aca.2018.05.067.

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Chapter 5 Discussion

5.1 Overview of the Research Process

Human activities, including commercial, industrial, municipal and agricultural operations (Alloway, 1995; De Temmerman et al., 2003) release various potentially toxic trace metals into the urban soils (Aelion et al., 2009; Ballesta et al., 2010; Cai et al., 2010). During the past decades, heavy metals have been intensively investigated (Zhang, 2006), with less research being conducted on the REEs and their influencing factors at the regional scale (Zhang, 2006; Delbecque and Verdoodt, 2016; Wu et al., 2019). In addition, determination of the contamination level notably based on the total concentration of trace metal and past activities, is the first step in initial risk assessment (Brandt et al., 2008; Branco et al., 2013). Despite the total concentration of trace metal is not significantly reduced, several studies have now shown that it is possible to reduce the bioavailability and the ecological risk of trace metal associated with contaminated soils (Denys et al., 2009). There is increasing application of the bioavailability in site-specific risk assessment and management (Denys et al., 2009; Duruibe et al., 2007; Branco et al., 2013). Therefore, the primary objective of this thesis involved the investigation of the concentration, spatial distributions and influencing factors of Pb and REEs in urban soils of London at the regional scale for a better understanding of the dynamic interactions between human activities and urban geochemistry. To achieve these objectives the Local Moran's I and GWR techniques were applied to identify hotspots of 7 REEs concentrations and to reveal spatially varying relationships between Pb and Al in urban soils of London. The study of urban soils of London provides valuable information for policymakers not only from an environmental and health perspective, but also enables to improve the scientific and reasonable of hazard assessment and soil management. Meanwhile, the DGT technique was applied assess the potential bioavailability of REEs in soils which can be useful in estimating bioavailability in a risk assessment framework.

5.1.1 Mapping the contaminated areas exceeding a critical threshold

Having established the importance of studying the urban geochemistry in terms of the hazard imposed by potentially increasing concentration of trace metals with urbanization develop (Charlesworth et al., 2003; Pope et al., 2009), the question of managing the risk arises. In order to improve soil management strategies, it is crucial to be able to predict where 'hot spots' of contamination are likely to occur (Charlesworth et al., 2005). Mapping potentially contaminated hotspot allows immediate visualization of the change in the contaminant with space and identifies areas that may contain harmful concentrations (Duzgoren-Aydin, 2007). An example of the spatial outliers of soil Ce, La, Nd, Sc, Sm, Yb and Y in built-up areas of central of London are greater than local background values, which suggested that human activities such as vehicular emission, metal recycling and urbanization could also contribute to REE enrichment in urban areas. Information of the spatial outliers of contaminant is necessary for site assessment and any subsequent hazard assessment, which can help planners to request remediation best suited to commercial areas. Therefore, mapping the spatial clusters and spatial outliers of soil trace metals will not only improve accurate hazard assessment, but also to support of land-use planning decision for soil protection by understanding the spatial distribution of trace metals. This plays a crucial part in metropolitan region considering the heterogeneous, complex of urban soils and varieties of potential sources of contamination.

5.1.2 Use of spatial varying relationship to map contaminant distribution in urban soils

Previous studies on the hazard assessment of the contamination of soil heavy metals were usually based on a single heavy metal threshold (Juang et al., 2004; Zhao et al., 2008). Considering the potential sources of trace metals can be both natural and anthropogenic (Juang et al., 2004), there may also be more than one influencing factors for which risk is being

investigated and the possibility of interactions should be considered (Davis et al., 2009; Boon and Ramsey, 2010). In the case of Pb, the concentration of Pb was dominantly controlled by anthropogenic factors in urban soils of London, being elevated throughout the urban area, but relatively low value over some of the major parks in south west and south east of London. Results from the GWR models can be seen to correspond to the 'spatial variation' of urban geochemistry proposed in Chapter 1. The relationships between Pb and Al were spatially varying in urban soils, with different relationships in different areas. Such information enables different environmental situations to be considered and pollution levels that depend on local land use and environmental factors, which are more reasonable for assessing hazard to environment than a single value guideline (Zhao et al., 2008). Therefore, the spatial varying relationships of trace metals can be used to generate environmental factor maps for the urban soils, such as soil pH, rock type and land-use can help planners to design appropriate and scientific strategies for urban soils contaminated areas (Zeng et al., 2011). This is an important part of the hazard assessment process, especially considering the large cost involved with chemical analyses and site remediation (Zeng et al., 2011).

5.1.3 Bioavailability assessment of trace metals in urban soils

The concept of the bioavailable fraction means the concentration of a contaminant that is in a form able to be absorbed by the organism or is mobile. This value is important in health risk assessment and can be used to calculate the toxicity of specific contaminants (Lanno et al., 2004; Markus and McBratney, 2001). Although seldom addressed in risk assessment of trace metal in urban soils, bioavailability is one of the most important concepts in the evaluation and management of contaminated sites (Peijnenburg et al., 2007; Pauget et al., 2015). Currently, there is an increasing trend in adopting in risk assessment and management of contaminated sites the EU countries (Kumpiene et al., 2017). The present study provides an alternative approach to study REEs bioavailability in soils. The results of DGT measured REEs validated the feasibility of using the Chelex ® 100 DGT for the simultaneous measurements of fifteen REE ions in a single assay, based on a range of laboratory experiments and deployment in

soils. In comparison with a chemical extraction method (such as EDTA) for evaluation of REE bioavailability in soil samples, the DGT measured REE ions exhibited a good correlation between the two methods (p < 0.01). However, this approach is only at its starting stage, thus further investigations are needed to reveal the DGT measured REEs in soils for a better understanding of the results. DGT technique can be used as a promising tool to assess the release ability of trace metals in urban soils. Therefore, the results in this thesis suggest that the determination of DGT-measured from soil in combination with appropriate bioassays can be useful in estimating bioavailability in a risk assessment framework.

5.2 Contributions of Research

The main contribution of this research is to improve risk assessment and environment management of soils, through hotspot analysis of REEs, a better understanding of spatially varying relationships between Pb and Al and the development of a new measurement for the labile form of REEs.

The combination of urban environmental and health concern and the ever-growing population and market demand for REEs production requires the hazard assessment and soil management to take account of trace metal contamination in urban soils. In response, the hotspots and cool spots of 7 REEs were identified using the index of Local Moran's I. An important part of Local Moran's I, it the information about the spatial outliers of REEs in urban areas that may be affected by anthropogenic activities. The results can be provided as a tool for planners to identify potentially contamination areas and to develop appropriate strategies to remediate contaminated areas.

In addition, knowledge of the spatial varying relationships of trace metals is fundamental to an understanding of urban geochemistry and hence the achievement of suitable soil management strategies to protect vulnerable soil areas and reduce negative environmental impacts (Zhang, 2006; Delbecque and Verdoodt, 2016; Wu et al., 2019). In light of the 'average' or 'global' parameters to estimate the spatial relationships, a local spatial statistical technique named geographically weighted regression (GWR) was applied to reveal spatially varying

relationships between geochemical elements. It highlights the new finding of the spatially varying relationships between Pb and Al in urban soils of London, which have never been investigated before. Such a new finding is important for a better understanding of the complicated relationships in urban geochemistry, especially with intensive human activities.

Determination of total concentration and bioavailability of trace metals, especially based on used chemicals methods, is the first step in primitively risk assessment (Oberg and Bergbäck, 2005; Wragg et al., 2014). Previous research reported that the trace metal bioavailability is controlled by their release from the soil solid phases (Weitz et al., 2002; Ljung et al., 2006). Thus, the DGT technique are considered a useful tool to assess the bioavailability of trace metals, which substantially differs from the chemical extraction methods of soil analysis (Li and Ji, 2017; Han et al., 2018; Lin et al., 2018). In this regard, A few extraction methods for the evaluation of bioavailability of the REEs in soils have been reviewed (Das et al., 1995; Rauret, 1998). Results from DGT-measured experiments of 15 REE ions correlate well with other two traditional methods, reflected by the high binding rates, together with a wide tolerance toward environmental interferences. Comparison with conventional methods, the Chelex® 100 DGT, as a passive sampling method, has advantages in-situ measurement, high spatial resolution and dynamic process. Therefore, the DGT-measured as new method or improved information for bioavailability assessment of trace metals not only can be fed back into the scope of urban geochemical research with a specific application, but also may be incorporated into existing risk assessment methodologies.

5.3 Advancement in the Field of Soil Contamination

In the past, while spatial analysis of heavy metals assessment of urban soils has been well established based on multiple statistical methods and GIS techniques, the distribution of other trace metals in the urban area has received limited attention. Concerning the occurrence of REEs and other trace metals in the environment, their accumulations and potential human health effects have been reviewed. It is now evident that 7 REE concentrations in London

urban soils did not reach the environmental and health risk thresholds, while individual spatial outliers in the centre of London were identified by using Local Moran's I, which indicated that anthropogenic activities could contribute enrichment of REEs in urban soils. The results demonstrated that mapping potentially contaminated hotspots should be used as useful auxiliary information to evaluate the hazard assessment of trace metals in urban soils. Moreover, in order to better understand the relationship between trace metals, we have successfully revealed the "spatially varying relationship" between Pb and Al in soils of an urban area by using GWR. Such new finding provides in the other way to deal with urban environmental contamination: to reveal the spatially varying relationship, which is helpful for us to seek the links with the influencing factors. Thus, in the field of urban soils pollution, the concept of "spatial analysis of trace metals" deserves much more attention, and our study provides a good example for other researchers studying similar problems.

On the other hand, due to the natural co-existence of REEs and their potential environmental risks, simultaneous measurement of these REEs will greatly favour the evaluation of their risk assessment for environment and health. The new method presented here suggests that DGT will be an effective way for the assessment of labile REEs in soils, the values from DGT could be advanced in in-situ measurement, high spatial resolution and time averaged concentrations than traditional extraction methodologies. Furthermore, the most important part of DGT technique that the valuable DGT measurement not only could be useful in environmental monitoring and management, but also can offer a new connection to international engagement providing access to new knowledge or research production, due to the sampler itself has the significant advantages in low cost, high efficiency and easy operation.

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Chapter 6 Conclusions and Future work

6.1 Summary of Main Results

Trace metals contamination in urban soils remains a major environmental and health concern, especially the metropolitan city, as it has long history of industrialization and urbanization with high population. In the urban area, due to the complicated land-use and heterogeneity of urban soils, it is difficult to identify contaminated sources between geogenic and anthropogenic inputs. Thus, spatial analysis of trace metals in urban soils is essential to characterize their spatial variability for the hazard assessment and provide information on the relative contributions of different sources affecting accumulation. Furthermore, in order to enable development of appropriate environmental guidelines, it is essential to assess the current status of trace metal concentrations but also the bioavailable fraction in soils. Such information also assists in assessing potential risk to the environment or human health. Therefore, the development of a new method for assessment of labile REEs in soils are important to the assessment of the environmental risk.

The research developed in this thesis extended the existing knowledge base by investigating the spatial distribution of trace metals and their influencing factors from both nature and anthropogenic sources in urban areas in London and China (Mianning). Multiple methods were used to improve the hazard assessment and soil management of trace metals in urban soils. The first phase of the thesis was to identify potentially contaminated sources of REEs in urban soils of London and create hotspot maps for the spatial distribution of REEs to fully understand the geochemical behaviour of REEs and to determine potential contaminated areas at risk. Moreover, the model results show that the north and south of London areas are at low risk of REEs pollution, while the central of London is at relative high potential risk due to the influence of human activities. The second phase of the thesis was to explore spatially varying relationships between trace metals in urban soils. The study found that the relationships in different areas. The results show that the weak relationships were found in central areas, and the negative relationships between Pb and Al were located in the northeast

and north areas, indicated that the links with the influence of anthropogenic activities on Pb concentration may associated with road traffic, industry activities and construction in centre of London. The third goal of the work was to develop the sampling device for simultaneous measurements of 15 REE ions by using DGT. This method provides most important information in quantifying to what extent the trace metals contaminated soils tend to release trace metals when in contact with plant roots and other organisms. The key findings are summarized as follows:

6.1.1 The hotspots and cool spots of REEs were identified by Local Moran's I in urban London soils

Due to the complex land use and heterogeneous nature of urban soils, the concentrations and distribution of REEs vary over space. Based on GIS, the Local Moran's I is effective approaches to describe the spatial pattern of contamination and to explore possible contamination sources in urban soils.

- The spatial clusters and spatial outliers of Ce, La, Nd, Sc, Sm, Yb and Y in the urban topsoils of London city were analysed using the index of Local Moran's I, which is a powerful methodology for identifying the potential pollution hotspots of REEs.
- 2. The elevated REEs concentrations are associated with the Chalk and the predominant chalky deposits developed over carbonate rocks due to weathering, mineralization, and transportation processes. And the cool spatial patterns of REEs in the topsoil clearly show the influence of soil types and pH on REEs content.
- Relatively high concentration of Ce, La, Nd, Sc and Y hotspots are also found in parks, greenbelts, and agricultural lands especially in Brent, Harrow, Croydon, Bromley, Rainham, Redbridge and Barking, which indicates REEs could attribute to fertilizer application, industrial activities, and vehicular emission.

6.1.2 Relationship between Pb and Al in urban soils of London was spatially varying

Understanding the spatially varying relationships between chemical elements in urban soils and their influencing factors plays an important role in environmental monitoring and soil management, which deserves more attention. This study highlighted one of the most important issues in environmental pollution study: The relationships between various pollution related parameters are not globally constant but "spatially varying". While a positive relationship between two variables may exist in one area, their relationship can be negative in another area or seriously disturbed because of different influences of factors in different locations. Such "complicated" relationships often cause difficulties in scientific research. The way forward is to use "local" statistics to find out the relationships at the local level.

- 1. This study tackles this problem by using GWR and demonstrates how it works with Pb and Al in urban soils of London.
- 2. Relationship between Pb and Al in urban soils of London was spatially varying; positive correlation between Pb and Al was related to the existence of large parks in southeast and southwest, as well as a small central area of London where, due to less influences from human activities, the natural geochemical signatures were preserved; Anthropogenic factors weakened or even changed the relationship direction in northern London; GWR is effective in revealing spatially varying relationships in urban soils.
- 3. This study provides a new way of thinking and a good example for other researchers who are exploring spatial patterns of pollutants in the environment, especially in dealing with complicated distributions and relationships in environmental pollution studies.

6.1.3 Simultaneous measurement of fifteen REEs using diffusive gradients in thin films (DGT)

Due to the growing demands for REEs and the excessive exploitation of rare earth minerals, more and more REEs enter the environment through anthropogenic inputs. Recently, considerable concern has been raised about the toxicological effects and related environmental risks of REEs when their concentrations accumulate in the environment. To date, the sampling device for simultaneous measurements of fifteen REE ions using DGT is scarce. In contrast to the traditional chemical extractions, the DGT is an in-situ dynamic passive sampling technique, which becomes an increasingly important tool for risk assessment of chemicals in the environment.

- 1. In this study, we are exploring a new method for measurements of rare earth elements (REEs) in the environment.
- 2. We have developed a new technique, based on DGT for the simultaneous measurements of the fifteen REEs. Five different types of ion exchange resins (Chelex® 100, D418, D001-cc, 001×7, and HSTY®-SS) were selected for the initial investigation of their adsorption performance for REEs, based on which the binding agent Chelex® 100 was chosen for DGT use. A series of validation experiments were conducted to examine the DGT response under laboratory conditions. In the meantime, the DGT capacities were measured and field applications in soils were tested.
- 3. The results not only confirmed the feasibility and advantage of the DGT, but also suggested that the Chelex® 100 DGT would be an effective tool for the simultaneous measurement of REE ions in the environment.

6.2 Future Work

Based on the research results obtained in this study, several recommendations for future research directions are made as the following.

6.2.1 Spatially varying relationship between La and Al in urban soils of London

The GWR technique should be used to reveal the spatially varying relationships between La and Al in urban soils, so as to provide a series of results of GWR regression models such as local regression coefficient, the local residual and the local R^2 value for La and Al, and thus the results are helpful for the understanding of the influencing factors and sources of REEs in urban soils.

6.2.2 Comparison of the spatial patterns of La and Al with the spatial patterns of Pb and Al in urban soils of London

According to the results of GWR models for La and Pb, if there are both negative and weak correlations in the same local area, these spatial patterns do imply that both variables vary inconsistently and there should be some factors in common to influence both variables. Furthermore, it is well known that strong correlated relationship between the concentrations of REEs in soils and rocks (Lalor and Zhang, 2001), provides effective information for the relationship outlier investigation. Therefore, in terms of urban soil pollution studies, it is important to understand that the contaminated land assessment is local scale and the "potential" contaminated land indicated (Zhang et al., 2009) by outliers needs to be further investigated (Zhang et al., 2008). It will be useful for soil management and others in the risk assessment of metals in urban soils.

6.2.3 Using diffusive gradients in thin films (DGT) to study REEs bioavailability in Maoniuping-REEs mine tailings

Due to the large scale of mining and refining activities, large amounts of REEs have been released to the surrounding environment causing potentially harmful effects on local resident. Therefore, to determine the levels of soil contamination and to assess the potential bioavailability of REEs with different types of land use in REEs mining area, DGT was performed. In order to make a basic investigation of the soil quality in terms of REEs pollution at the Maoniuping area, it is necessary and useful for assessing the potential ecological risk in the study area.

6.2.4 Prediction of REEs uptake by plants using the diffusive gradient in thin films (DGT)

It is well-know that to assess the environmental risk of REEs in mining soils, the bioavailability of REEs to plants must be evaluated. Therefore, the relationship between the DGT-measured bioavailable flux of REE ions in soil and the flux of REE ions uptake by plants was examined. At the same time, the potential value of DGT predicting REE ions uptake into plants was also studied.

Appendix A

Appendix A The Figure of "Using Local Moran's I to identify pollution hotspots of rare earth elements in urban soils of London

A.1 "3.2 Spatial distribution of REEs"



Figure A. 1: Spatial distribution map of soil La concentrations in London soils.

Appendix A



Figure A. 1. 2: Spatial distribution maps of soil (a) Ce, (b) Nd, (c) Sc, (d) Sm, (e) Yb, (f) Y concentration in London soils.



A.2 "3.3 Spatial-cluster and spatial-outlier analysis"

Figure A. 2: The LISA maps of soil (a) Ce, (b) La, (c) Nd, (d) Sc, (e) Sm, (f) Yb, (g) Y (Distance Band = 1000 m).



A.3 "4.1 Geogenic factors"



Greater London Authority.



Figure A. 3.2: Hotspots of REEs overlaying on simplified soil parent material map of the Greater London Authority (GLA).



Figure A. 3.3: LISA map of soil La in London city (Highlighting 6 hotspots and 1 cool spot of La).

A.4 "4.1.1 Bedrock"



Figure A. 4: LISA maps for (a) Al2O3, (b) TiO2 (Distance Band = 1000 m).



A.5 "4.1.2 Influences of pH and soil type"

Figure A. 5: LISA maps for (c) SiO₂, (d) pH (Distance Band = 1000 m).



A.6 "4.2.1 Influences of fertilizer application"

Figure A. 6: LISA maps for (e) P_2O_5 , (f) Cu, (g) Pb, (h) Zn (Distance Band = 1000 m).



A.7 "4.2.2 Influences of industrial activities"

Figure A. 7: LISA maps for (e) P_2O_5 , (f) Cu, (g) Pb, (h) Zn (Distance Band = 1000 m).

Appendix B The Figure and Table of "Simultaneous measurem ent of fifteen Rees using diffusive gradients in thin films (DGT)"

Soil samples	pН	CEC ^a (cmol kg ⁻¹)	Organic matter (g/kg)	Total REEs (mg kg ⁻¹)
Mining soil	5.97	9.63	6.28	30971.64
winning som	7.00	9.61	6.61	1950.74
T-11 1	7.99	8.8	5.78	19635.24
Tannig son	7.32	39.2	4.03	1657.24
Dood soil	5.45	24.9	80.99	17.43
Road soil	4.63	45.4	130.43	1330.47
Agricultural soil	7.32	3.17	12.76	10854.57
	4.9	27.6	38.85	348.18

Table B-1: Selected physic-chemical properties of the soil samples used in this study

^a CEC, cation exchange capacity.

Table B-2: Comparison of uptake efficiencies for each REE ion in five different types of binding gels in solutions containing 200 μ g L⁻¹ of each REE and 0.01 mol L⁻¹ NaCl. Values are mean \pm SD of three replicates.

Elements	HSTY®-SS	D418	D001-CC	001×7	Chelex® 100
La	91.31 ± 0.46	89.78 ± 0.30	90.48 ± 0.95	93.68 ± 0.68	97.23 ± 0.43
Ce	91.09 ± 0.45	89.92 ± 0.45	90.26 ± 0.92	93.57 ± 0.58	97.42 ± 0.36
Pr	90.93 ±0.42	89.58 ± 0.41	90.11 ± 0.94	93.52 ± 0.60	97.31 ± 0.38
Nd	90.71 ± 0.41	89.36 ± 0.43	89.84 ± 0.98	93.34 ± 0.61	97.11 ± 0.39
Sm	90.66 ±0.37	89.33 ± 0.50	89.78 ± 1.00	93.31 ± 0.61	97.04 ± 0.42
Eu	90.81 ±0.41	89.47 ± 0.45	89.94 ± 0.95	93.44 ± 0.62	97.18 ± 0.43
Gd	91.37 ±0.39	90.11 ± 0.34	90.54 ± 0.93	94.07 ± 0.58	97.82 ± 0.42
Tb	84.96 ± 0.35	83.90 ± 0.33	84.41 ± 0.94	88.18 ± 0.54	91.51 ± 0.84
Dy	90.90 ±0.34	89.70 ± 0.36	90.06 ± 0.85	93.63 ± 0.57	97.31 ± 0.41
Но	89.56 ± 0.35	88.40 ± 0.36	88.73 ± 0.86	92.32 ± 0.57	95.93 ± 0.43
Er	90.81 ± 0.33	89.64 ± 0.29	89.97 ± 0.87	93.66 ± 0.55	97.30 ± 0.42
Tm	89.48 ±0.34	88.41 ± 0.32	88.68 ± 0.85	92.28 ± 0.57	95.87 ± 0.45
Yb	90.89 ± 0.33	89.76 ± 0.36	90.04 ± 0.90	93.71 ± 0.57	97.35 ± 0.46
Lu	85.4 ± 0.22	84.54 ± 0.35	84.86 ± 0.96	88.46 ± 0.52	91.94 ± 0.81
Y	90.98 ± 0.37	89.69 ± 0.24	90.18 ± 0.79	93.74 ± 0.53	97.42 ± 0.38

Elements	Binding rate	DGT flux	Ratio	Elements	Binding rate	DGT flux	Ratio
La	1.57 ± 0.01	0.02	54	Tb	1.52 ± 0.01	0.03	44
Ce	1.59 ± 0.01	0.03	49	Dy	1.61 ± 0.01	0.03	50
Pr	1.61 ± 0.01	0.03	48	Но	1.52 ± 0.01	0.03	46
Nd	1.62 ± 0.01	0.03	48	Er	1.62 ± 0.01	0.03	51
Sm	1.63 ± 0.01	0.03	49	Tm	1.53 ± 0.01	0.02	53
Eu	1.62 ± 0.01	0.03	50	Yb	1.61 ± 0.01	0.03	51
Gd	1.56 ± 0.01	0.03	51	Lu	1.53 ± 0.01	0.03	46
				Y	1.58 ± 0.01	0.03	51

Table B-3: Comparison of the binding rate (ng cm⁻² min⁻¹) for each analyte over the first 20 min with the DGT-measured flux (ng cm⁻² min⁻¹). Values given are the mean \pm SD of three replicate measurements.

pН	La	Ce	Pr	Nd	Sm	Eu	Gd	
3.04	0.92	0.87	0.88	0.88	0.88	0.87	0.89	
3.94	1.08	1.00	1.03	1.03	1.01	1.02	1.05	
4.96	1.09	1.02	1.04	1.03	1.01	1.02	1.06	
6.04	1.10	1.00	0.99	0.96	1.04	1.04	1.03	
6.85	1.00	1.07	1.11	1.11	1.04	1.04	1.07	
7.89	1.07	0.92	0.96	0.96	0.92	0.90	0.91	
9.05	1.07	1.03	0.96	0.97	0.95	0.93	0.94	
pН	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
3.04	0.81	0.86	0.87	0.86	0.88	0.87	0.80	0.91
3.94	0.96	1.02	1.03	1.03	1.04	1.04	0.95	1.09
4.96	0.97	1.03	1.04	1.04	1.04	1.04	0.95	1.09
6.04	1.00	1.04	1.06	1.03	1.05	0.96	0.90	1.04
6.85	0.99	1.10	1.06	1.05	1.04	1.03	0.93	0.95
7.89	1.02	0.95	0.91	0.91	1.09	1.05	0.91	0.97
9.05	0.96	0.98	0.93	0.92	0.93	0.90	0.94	0.98

Table B-4: Values of C_{DGT}/C_{SOL} for the REE ions under different pH values.

Ionic strength	La	Ce	Р	Nd	Sm	Eu	Gd	
0.01	1.34	1.32	1.35	1.34	1.33	1.33	1.36	
0.1	1.37	1.34	1.39	1.36	1.37	1.36	1.39	
1	1.35	1.31	1.30	1.31	1.30	1.28	1.27	
2	1.39	1.28	1.27	1.28	1.27	1.26	1.27	
3	1.04	0.99	1.00	0.99	0.99	0.96	0.97	
4	1.15	1.05	1.06	1.07	1.05	1.04	1.05	
5	1.10	1.03	1.04	1.04	1.04	1.03	1.03	
10	1.04	1.02	1.04	1.05	1.06	1.06	1.11	
100	0.93	0.92	0.94	0.95	0.97	0.96	1.02	
1000	0.86	0.87	0.88	0.89	0.90	0.91	0.95	
Ionic strength	Tb	Dy	Но	Er	Tm	Yb	Lu	Y
0.01	1.4	1.34	1.41	1.36	1.43	1.35	1.43	1.37
0.1	1.42	1.37	1.44	1.37	1.44	1.36	1.43	1.35
1	1.30	1.29	1.29	1.27	1.27	1.27	1.25	1.29
2	1.27	1.28	1.26	1.25	1.26	1.25	1.22	1.26
3	0.98	0.98	0.98	0.97	0.98	0.97	0.95	0.98
4	1.05	1.05	1.03	1.03	1.04	1.03	1.01	1.04
5	1.03	1.03	1.02	1.02	1.02	1.01	1.00	1.03
10	1.02	1.06	1.09	1.07	1.14	1.09	1.06	1.04
100	0.82	0.95	0.98	0.96	1.04	0.99	0.84	0.94
1000	0.73	0.89	0.91	0.89	0.96	0.92	0.72	0.86

Table B-5: Values of C_{DGT}/C_{SOL} for the REE ions under different ionic strength conditions.

	$D\times E\text{-}6\ cm^2s^{\text{-}1}$	$D \times E$ -6 cm ² s ⁻¹
Element	This study	Water ^a
Y	5.11 ± 0.07	~
La	5.00 ± 0.20	6.16 - 6.18
Ce	5.35 ± 0.07	6.16 - 6.19
Pr	5.40 ± 0.06	6.15 - 6.17
Nd	5.40 ± 0.08	6.15 - 6.19
Sm	5.30 ± 0.05	6.07 - 6.09
Eu	5.23 ± 0.04	6.01
Gd	5.30 ± 0.05	5.95 - 5.99
Tb	5.00 ± 0.02	5.92 - 5.93
Dy	5.20 ± 0.05	5.88
Но	5.16 ± 0.05	5.87 - 5.89
Er	5.20 ± 0.06	5.81 - 5.85
Tm	5.20 ± 0.05	5.8
Yb	5.20 ± 0.05	5.77 - 5.85
Lu	4.72 ± 0.01	5.73

Table B-6: Diffusion coefficients ($D_{DGT} \pm$ standard deviations, 25 °C) of the REE ions through the agarose gel plus PVDF filter membrane. The diffusion coefficients of REE ions in water are listed for comparison.

^a from limiting ionic conductance measurements of Spedding et al.
Table B-7: Measured diffusion coefficients of Mn, Co and Ni (\times 10-6 cm²s⁻¹) using MBL-DGT and Chelex-DGT, and measured diffusion coefficients of Mn, Co, Ni and Fe (\times E-6 cm²s⁻¹) using ZrO-Chelex DGT, corrected to 25 ° C.

Element	Agarose-derived cross-linker (APA)		Agarose gel
	$D_{ m MBL}{}^{ m a}$	$D_{ m Chelex}{}^{ m b}$	$D_{ m Chelex}{}^{ m c}$
Mn	4.68	4.44	5.91
Co	5.29	5.38	6.53
Ni	5.13	5.29	6.54
Fe			6.40

^a Diffusion coefficient measured using MBL-DGT: pH 6.06; 0.01 mol L⁻¹ NaNO₃/0.004 mol L⁻¹ Mg(NO₃)₂.

 $^{b} \ Diffusion \ coefficient \ measured \ using \ Chelex-DGT: \ pH \ 6.06; \ 0.01 \ mol \ L^{-1} \ NaNO_{3}/0.004 \ mol \ L^{-1} \ Mg(NO_{3})_{2}.$

^c Diffusion coefficient measured using ZrO-Chelex DGT: pH 6.0; 10 mM NaNO.

Elements	M(µg cm ⁻²)	Elements	M(µg cm ⁻²)
La	5.39 ± 0.05	Tb	5.74 ± 0.06
Ce	6.27 ± 0.06	Dy	6.02 ± 0.06
Pr	6.31 ± 0.06	Но	5.96 ± 0.06
Nd	6.21 ± 0.06	Er	6.03 ± 0.06
Sm	6.20 ± 0.05	Tm	5.74 ± 0.06
Eu	6.21 ± 0.06	Yb	5.81 ± 0.06
Gd	5.45 ± 0.06	Lu	5.56 ± 0.06
		Y	6.75 ± 0.05

Table B-8: DGT capacities of the Chelex® 100 for measurements of REE ions in mixed solutions. Values given are the mean ± SD of three replicate measurements.

Appendix B



Figure B-1: DGT capacities of the Chelex® 100 for measurements of the fifteen REE ions in mixed solutions.