Due to “internal P-loading” for lake eutrophication, it is important to quantify the P-release intensity at SWI for the restoration of contaminated lake (Förstner et al. 1994). So, the environmental behavior and biogeochemistry of P, Fe, and S in sediments should be understood (Shaw et al. 1990). The chemical property in sediment porewater has been verified as the sensitive indicator of the biogeochemical reaction happening between water and sediment particle (Zhang et al. 2002; Fones et al. 2004; Wu et al. 2011, 2014, 2015a, b, c, d). The bioavailability and mobility for P or meals can be investigated by conventional methods, such as a linear distribution coefficient ($K_d$), a nonlinear adsorption isotherm (Freundlich or Langmuir), sequential extraction procedures, or other procedures and analytical methods (Hamilton-Taylor and Morris 1985; Cutter and Oatts 1987; Barbanti et al. 1994; Golterman 2004; Kopáček et al. 2005; Wilson et al. 2008; Lin et al. 2009; Shilla et al. 2009; Wang et al. 2009). Compared with “bulk” analysis methods, the diffusive gradients in thin films (DGT) technique (Davison et al. 1994, 2000) is an advanced method for DGT profile/image of trace elements in sediment porewater (Zhang et al. 2002; Fones et al. 2004; Wu et al. 2011, 2014, 2015a, b, c, d), geochemical process (Naylor et al. 2004; Ding et al. 2012), kinetic exchange at the DGT/sediment microzone (Harper et al. 1998; Ernstberger et al. 2002), and microniche research (Widerlund and Davison 2007). The root of aquatic plant is important for P-cycling, and the kinetic P-uptake at root/sediment interface plays a key role in lake restoration (Nuttall 1985). The mobility and bioavailability of P in the rhizosphere are influenced by the physicochemical properties of sediments (Christensen 1997; SØndergaard and Lægaard 1977; Farmer 1985). DGT test in root microenvironments can act as an indicator for element availability and the element taken up by root (Lehto et al. 2006; Mason et al. 2010).

In this chapter, we introduced the eutrophic problem in lake sediments (Dianchi and Erhai lakes), which should be revealed and assessed by DGT technique, and the layout of DGT and the related techniques has been discussed for the research of P-transfer across environmental interfaces, including DGT measurement for P, S(-II),
and Fe, the software and program for P-transfer in sediment microzone, the analytical method for element 2D-distribution in sediment microzone, and DGT’s function to research P-bioavailability and P-transfer across sediment/root interface. Moreover, the studying zones for DGT at SWI (Dianchi Lake) or sediment/root interface (Erhai Lake) were also introduced.

2.1 Problem Introduction

DGT is the analytical tool and research method for the profile character, the remobilization character, and the geochemical reaction mechanisms, and it has been widely used in all kinds of water bodies (lake, sea, and river). However, DGT has seldom been used for the geochemical character of P at SWI of lakes (Monbet et al. 2008; Ding et al. 2012), and the mechanism of “internal P-loading” should be revealed more thoroughly. Moreover, the previous researchers have never assessed “internal P-loading” in eutrophic lake comprehensively, and only one or two kinds of DGT probes have been investigated. Lake sediment is significant for the nutrient cycle, the reason of which is that it is the internal pool and source for plant root and benthic alga. The soluble nutrient released from sediment porewater can supply P. Under the anaerobic condition, the reduction of Fe(III) hydroxyoxide may lead to the release of soluble reactive P (SRP) associated with mineral phases (Palmer-Felgate et al. 2011). The anoxic condition promotes the reduction of insoluble Fe(III) hydroxyoxide to soluble Fe(II), resulting in the P-release from the sediments and into the surrounding water (Böstrom and Pettersson 1982; Christophoridis and Fytianos 2006). For example, Sundby et al. (1986) found that inorganic P (DIP, PO₄³⁻) and Fe²⁺ were released simultaneously in equivalent concentrations as oxygen concentrations approached near zero in a benthic chamber in the sediments of Gullmarnsfjorden, Sweden. The last reason and the decomposition of algae/organic matter may cause “internal P-loading” of lake (Cook et al. 2010). Roden and Edmonds (1997) suggested an indirect reduction pathway, attributing P-release from Fe(III) hydroxyoxide due to sulfate-reducing bacteria which enhance the formation of insoluble FeS.

So, it is important to measure the concentration/flux of P/Fe/S involved in the geochemical process of P, which can be used for the mechanism of “internal P-loading.” When the lake environment permits P-release from sediment into water phase, total dissolved P (TDP) level in water can be elevated and “internal P-loading” appears, regardless of “external P-loading.” For example, Dianchi Lake is a lake with eutrophic status in southeast of China (Wu et al. 2015c, d). “Internal P-loading” is one important factor for P-cycle at SWI. So, it is important to research P-release mechanism and the mechanism of “internal P-loading.” Lake sediment, composed of complex minerals, porewater, as well as inorganic and organic compounds, can act as both a sink and a source of P (Christophoridis and Fytianos 2006). Temperature, pH, redox potential, nitrate, sulfate, bioturbation, algae bloom,
as well as the presence of Ca, Mn, Fe, Al, and Mg have been found to be able to control P-release (Kleeberg and Dudel 1997). The adsorption of P on Al(OH)₃ or the precipitation process of hydroxylapatite or fluorapatite (Ca₅(PO₄)₃(OH,F)) is the main reason for P-sequestration at SWI.

The sediment has been identified as the important pool for P in a lot of aquatic ecosystems (Lebo 1991; Conley et al. 1995; Paludan and Morris 1999; Zwolsman 1994; Zhang and Huang 2007). Thus, the P-release across the SWI through adsorption–desorption processes and coprecipitation–dissolution reactions plays a key role in controlling the dissolved phosphate concentrations in the overlying waters and porewaters (Froelich et al. 1982; Froelich 1988). Understanding the kinetic P-release between the sediment and porewater interface is significant for assessing the release risk and the P-mobility in lake sediments. Some researchers have focused on the linear distribution coefficient (Kd) or the nonlinear adsorption isotherm (Freundlich or Langmuir) to investigate the P distribution at SWI; other researchers have investigated the sequential extraction method for P-fractionation in sediments for assessing the bioavailable P in the sediment or potential P-release (Wilson et al. 2008; Shilla et al. 2009; Wang et al. 2009; Lin et al. 2009). Commonly, the adsorption–desorption studies are performed in dilute suspensions, whereas the sequential extraction procedures can systematically alter the chemical environment (Ernstberger et al. 2002).

The recently developed skill (Davison et al. 1994)—diffusive gradients in thin films (DGT) technique—has been used to measure in situ concentrations and fluxes of elements in the sediment/soil/water. It operates through introducing a localized sink that induces a diffusion flux to the DGT resin. The quantity measured directly is the mass of one element accumulated by the sink (the binding gel) during DGT deployment. These in situ DGT measurements depend on the element concentrations in sediment porewater and the resupply from the solid phases. Thus, the in situ evaluation for rate constants of the element release from the solid phase and capacities of element reservoir in the solid pool can be reached.

The macrophytes such as Zizania caduciflora or Myriophyllum aquaticum are distributed widely in the lakes or rivers in China, such as Erhai Lake (the southeast of China). The technique for wetland treatment project to control “internal P-loading” has advantages for the ecological restoration of lake eutrophication. The water quality in lakes or rivers can be largely improved by macrophyte roots (Blindow et al. 1993; Barko et al. 1991; Gu et al. 2001; Brix and Schierup 1989; McNabb 1976; O’Dell et al. 1995; Canfield and Hoyer 1992; Leslie et al. 1983). Redox potential, pH, pCO₂, PO₂, and element concentrations in the proximity of macrophyte root determine the mobility and bioavailability of elements in rhizosphere (Hinsinger and Courchesne 2008). Aquatic plants in lake systems can effectively alter the chemistry of rhizosphere sediment by O₂ released from roots. The rhizosphere oxidation and the formation of Fe-plaque on roots of aquatic plants led to the accumulation of metals such as iron, zinc, and arsenic in rhizosphere (Otte et al. 1991; Kirk and Bajita 1995). Oxidation of ferrous iron to its ferric form would
lead to precipitation of Fe(III) hydroxyoxide in the rhizosphere (Otte et al. 1989), which in turn engenders a decreasing concentration gradient of dissolved iron toward the plant roots. These gradients would lead to the diffusion of iron, arsenic, and zinc in the direction of the roots. Assuming the uptake of the elements by roots is slower than supply through diffusion, an increase in the concentrations of all three elements would be expected to occur in the solid phase of the rhizosphere (Doyle and Otte 1997). Armstrong (1978) and Gambrell and Patrick (1978) suggested that the formation of Fe-plaque on roots served as a sink for elements and was consequently a hindrance to nutrient uptake by wetland plants. DGT technique for the measurement in the rhizosphere sediment can act as a predictor for the element taken up by plant root. The ferrihydrite-sorbent binding gel installed in DGT assembly is highly selective for labile P in sediment porewater. The diffusive gel layer in DGT assembly limits the largest flux of labile P from the sediment porewater into binding gel. This kind of induced flux of DGT is similar to that of P taken up by plant root. The Fick’s law calculation ensures the accurate DGT concentration. DGT concentration depends on the soluble P in sediment porewater, and the resupply rate of P desorbed from sediment solid into porewater.

At the SWI of eutrophic lakes, the eutrophic element, P, redox sensitive elements, Fe and S, undergo complex exchanges and cogochemical reactions, which control the eutrophic status and P-release risk. So, some questions should be answered, including: (1) What does the geochemical reaction determine the P-release and “internal P-loading” character in the vertical direction of sediment microzones? (2) How do kinetic parameters and sediment pools determine P-release/P-diffusion across the DGT/sediment interface? (3) How are S(-II)- or Fe-microniches analyzed and assessed at fine spatial scales in order to predict P-release risk? (4) Whether can the P-transfer and P-uptake in root of aquatic plant be assessed by DGT parameter? (5) Can DGT with multi-functions achieve the last measurement and assessment? The DGT techniques and the related methods with multi-functions for the two case studies (Dianchi and Erhai lakes) introduced in the next sections “Chap. 3” can solve the last questions.

### 2.2 The Research Idea and the General Design for DGT Research

DGT has been widely applied in the water body worldwide, as a powerful tool for the measurement of multi-elements and the research of environmental process at SWI. In this research, two problems should be answered: The first is the mechanism of P-release in sediment and the assessment for P-release intensity in eutrophic Dianchi Lake and the second is the P-uptake mechanism and P-transfer across sediment/root interface in Erhai Lake. DGT can be applied as a chemical sensor or a
passive sampler in the complex microenvironment (SWI) and the sediment/root microzone), and the other technique/method can be applied coupled with DGT technique in order to derive valuable data at fine spatial scales, environmental phenomenon, and the mechanism about P-transfer in sediment microzone or root/sediment interface. The schematic graph for the general design for DGT research is shown in Fig. 2.1. For the aim of the research for P-release mechanism and the related geochemical mechanism (Dianchi Lake), DGT probe with multilayer-binding gels and twin DGT probes have been developed for the simultaneous measurement of Fe/P/S elements in sediment porewater. The geochemical reactions were investigated, and the “internal P-loading” (Dianchi lake) was quantified. In order to quantify kinetic exchange of P and P-release/P-diffusion across DGT/sediment microzone, it is needed to develop numerical model to derive kinetic parameters and diagraph of P-exchange process as the functions of time/distance, and 1D-DIFS (DGT-induced fluxes in sediments) can be researched for input parameters, the operation of DIFS model, the discussion of output parameters and diagraphs, the mechanism for kinetic parameters controlling the

Fig. 2.1 The schematic graph of the general design for DGT research
change character of DIFS curves, and P-release characters in sediment microzones. Due to the coupled biogeochemical process of Fe–S–P in sediment porewater, it is needed to research solubility of Fe-sulfide and Visual MINTEQ software can be used to achieve this aim; sulfide microniche determines the distribution of soluble inorganic sulfide in sediment porewater and influences the P-release from Fe-bound P; AgI-CID technique and ImageJ 1.38e software can be used to research sulfide microniche distribution character and the coupled Fe–S–P mechanism for P-release. Labile Fe-distribution in sediment microzone is the main factor for P-release from Fe-bound P, and LA-ICP-MS can be used for the analysis of labile Fe-bound by SPR-IDAggel in DGT probe. Based on chemical image of DGT-Fe in sediment microzone, Fe-distribution character and the prediction of P-release in “hot spots” in chemical image can be researched. The above-mentioned method/technique can be used to reveal P-release mechanism in sediment microzone and “internal P-loading,” thoroughly. Moreover, in order to research P-transfer and P-uptake at the interface of sediment and the rhizosphere of aquatic plants in Erhai Lake, DGT piston can be used for the tests in situ or in rhizobox to achieve the last aim; the derived $C_E$ value can be used to provide a major step forward in assessing hazards posed by P in eutrophic lake sediments. Finally, P-process at SWI or sediment/root interface and the release mechanism in microzone can be revealed, which is the base for the designation of the restoration of the eutrophic lake using in situ technology such as Al dose to prevent P-release or the ecological engineering technique of aquatic plants.

2.3 Studying Zones in Dianchi and Erhai Lakes

Dianchi Lake (102°37′59.76″–102°45′55.07″E, 24°40′38.89″–25°1′21.39″N) is the sixth largest freshwater lake of China at the foot of the Western Hills in southwest of Kunming city of Yunnan Province (southwest China). Dianchi Lake consists of two parts, which are the internal lake and the outer lake. The total area of Dianchi Lake is 306.3 km$^2$, with a length of 39 km (N–S), a width of 13 km (E–W), an average depth of about 5 m, and a total water capacity of 1.593 billion m$^3$. The different areas of Dianchi Lake are eutrophic in the various degrees. In 2009, the average total phosphorus (TP) concentrations in sediments are 2–3 g kg$^{-1}$ (0–5 cm), 1–2 g kg$^{-1}$ (5–10 cm), and 1–2 g kg$^{-1}$ (10–20 cm) in turn. The average contents of metal-bound P and organic P (OP) are about 17.57–48.82 % and 20–30 % of those of TP, respectively. The contents of OM in sediments are 8.24–677 g kg$^{-1}$ (0–5 cm), 4.5–590 g kg$^{-1}$ (5–10 cm), and 7.07–649.03 g kg$^{-1}$ (10–20 cm), respectively. The content of TN in sediments (0–20 cm) is 4.91 g kg$^{-1}$. Extensive blue algal blooms have happened frequently in recent years, and biomass of alga is $4.402 \times 10^6$–$1.102 \times 10^9$ cell l$^{-1}$ (Chinese Research Academy of Environmental Sciences 2014). Despite reduced “external P-loading,” Dianchi Lake has failed to recover from eutrophic status partially due to the P-release from
the sediment (“internal P-loading”). The sampling locations (Dianchi Lake) for DGT probe test are indicated in Fig. 2.2a (Wu et al. 2014, 2015d). The sampling locations for P-DIFS test (Dianchi Lake) are indicated in Fig. 2.2b. The longitudes and latitudes for all sampling sites are listed in Table 2.1 (Wu et al. 2014, 2015c, d).

Erhai Lake (100°5'E–100°17'E, 25°35'N–25°58'N) is situated at Dali Bai Autonomous Prefecture in Yunnan Province (China) and the second largest lake in Yunnan Plateau. The shape of this lake is like an ear with the length of 43 km and the width of 8.4 km. The lake has a surface area of 249 km² with the maximum water depth of 21.5 m. The storage capacity is $2.88 \times 10^9$ m³, and the water
residence time is 2.75 years. The nutrient level of Erhai Lake is changing from mesotrophication to eutrophication in recent years. The location for DGT test in situ and in rhizobox for P taken up by plant root is shown in Fig. 2.3.

2.4 Summary

This chapter reported the environmental problem of Dianchi and Erhai lakes in the southwest of China. The “internal P-loading” in Dianchi Lake and two aquatic plants (Zizania caduciflora and Myriophyllum aquaticum) for the ecological restoration in Erhai Lake have been introduced. To reveal the mechanism of “internal P-loading” (Dianchi Lake) and P-uptake mechanism by plant roots (Erhai Lake), DGT and related techniques should be developed and applied. The DGT technique for lake sediment and rhizosphere should be designed to illustrate the environmental problem related to lake eutrophication. In order to lay out the DGT research program for the P-transfer across SWI or sediment/root interface, a series of DGT probes with new types, LA-ICP-MS, CID, 1D/2D-DIFS, Visual MINTEQ and ImageJ 1.38e softwares, and DGT test in rhizosphere have been arranged to achieve DGT profile/image at fine scale, DGT image of S(-II) or P, kinetic P-release at DGT/porewater/sediment interface, P-transfer across root/sediment interface for the quantification of “internal P-loading,” geochemical reactions for P-release, sulfide or Fe microniche for P-release, and the DGT function as a surrogate of plant

Table 2.1 Sampling locations of DGT tests in Dianchi Lake. (Seven sites (A–G) for DGT probe test; nine sites (1–9) for DGT–DIFS test)

<table>
<thead>
<tr>
<th>Site</th>
<th>Longitude</th>
<th>Latitude</th>
<th>Site</th>
<th>Longitude</th>
<th>Latitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>102°38′34″</td>
<td>24°59′30″</td>
<td>1</td>
<td>102.67</td>
<td>25.02</td>
</tr>
<tr>
<td>B</td>
<td>102°37′48″</td>
<td>24°46′24″</td>
<td>2</td>
<td>102.63</td>
<td>24.99</td>
</tr>
<tr>
<td>C</td>
<td>102°38′12.149″</td>
<td>24°41′22.542″</td>
<td>3</td>
<td>102.68</td>
<td>24.93</td>
</tr>
<tr>
<td>D</td>
<td>102°41′24.463″</td>
<td>24°47′52.517″</td>
<td>4</td>
<td>102.73</td>
<td>24.91</td>
</tr>
<tr>
<td>E</td>
<td>102°43′40.84″</td>
<td>24°52′27.39″</td>
<td>5</td>
<td>102.77</td>
<td>24.87</td>
</tr>
<tr>
<td>F</td>
<td>102°39′45.54″</td>
<td>24°57′1.01″</td>
<td>6</td>
<td>102.68</td>
<td>24.86</td>
</tr>
<tr>
<td>G</td>
<td>102°40′55.99″</td>
<td>24°52′27.39″</td>
<td>7</td>
<td>102.74</td>
<td>24.8</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>102.72</td>
<td>24.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>102.62</td>
<td>24.69</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2.3 The site for DGT test in rhizosphere of aquatic plants at Erhai Lake. *Open triangle* the site of the experimental base for aquatic plants in Erhai (Institute of Hydrobiology, Chinese Academy)

root for P-uptake. The logical stratification of the components (all sorts of DGT techniques) making up the general design for DGT research has been discussed. Moreover, DGT test locations for probe, piston, and DIFS in Dianchi Lake and DGT test in rhizosphere in Erhai Lake were also introduced.

References


Chinese Research Academy of Environmental Sciences (2014) The survey and the investigation of “internal loading character” of Dianchi Lake (Chinese)


DGT-based Measurement of Phosphorus in Sediment Microzones and Rhizospheres
Wang, S.; Wu, Z.
2016, XXVII, 170 p. 70 illus., 40 illus. in color., Hardcover
ISBN: 978-981-10-0720-0