The application of DGTs for assessing the effectiveness of in situ management of Hg and heavy metal contaminated sediment

Mark Xavier Bailon¹, Minoh Park¹, Young-Gyun Choi², Danny Reible³ and Yongseok Hong^{*1}

¹Department of Environmental Systems Engineering, Korea University, Sejong City, Republic of Korea ² Department of Environmental Engineering, Chungnam National University, Daejeon City, Republic of Korea ³ Department of Civil, Environmental, and Construction Engineering, Texas Tech University, Lubbock, Texas, USA

(Received August 27, 2019, Revised October 29, 2019, Accepted October 30, 2019)

Abstract. The effectiveness of in situ sediment capping as a technique for heavy metal risk mitigation in Hyeongsan River estuary, South Korea was studied. Sites in the estuary were found previously to show moderate to high levels of contamination of mercury, methylmercury and other heavy metals. A 400 m x 50 m section of the river was selected for a thin layer capping demonstration, where the total area was divided into 4 sections capped with different combinations of capping materials (zeolite, AC/zeolite, AC/sand, zeolite/sand). Pore water concentrations in the different sites were studied using diffusive gradient in thin film (DGT) probes. All capping amendments showed reduction in the pore water concentration of the different heavy metals with top 5 cm showing % reduction greater than 90% for some heavy metals. The relative maxima for the different metals were found to be translated to lower depths with addition of the caps. For two-layered cap with AC, order of placement should be considered since AC can easily be displaced due to its relatively low density. Investigation of methylmercury (MeHg) in the site showed that MeHg and %MeHg in pore water corresponds well with maxima for sulfide, Fe and Mn suggesting mercury methylation as probably coupled with sulfate, Fe and Mn reduction in sediments. Our results showed that thin-layer capping of active sorbents AC and zeolite, in combination with passive sand caps, are potential remediation strategy for sediments contaminated with heavy metals.

Keywords: Diffusive Gradient in Thin Film (DGT), sediment, mercury, heavy metal, capping

1. Introduction

In aquatic ecosystems, sediments serve as a main sink for heavy metals and eventually becomes a source of contamination because it plays a major role in the storage and transportation of potentially hazardous metals (Zhang et al. 2014b). Problems arise when metals deposited in the sediment surface are released from the sediments and become mobile and bioavailable due to benthic activity and changes in the environmental parameters of the water (Wang et al. 2017). One toxic heavy metal that is important to monitor and remediate in aquatic systems is mercury. Mercury, unlike other heavy metals, is persistent in the environment due to its long residence time in the atmosphere. It is also highly mobile and can bioaccumulate in organisms through the food chain (Tan et al. 2016). In anaerobic conditions, mercury can also be transformed to methylmercury, which is considered to be more toxic than inorganic mercury.

Hyeongsan River in Pohang City, South Korea was reported to have high contamination levels of mercury and methylmercury in its natural water and sediments. High levels of mercury were also observed in bivalves collected from the site in 2016. Levels of other heavy metals in the area were found to be classified as Contaminated Level II-

E-mail: yongseokhong@korea.ac.kr

Copyright © 2020 Techno-Press, Ltd. http://www.techno-press.org/?journal=mwt&subpage=7 IV (moderate to heavily contaminated) based on Korea sediment quality guidelines (Bailon *et al.* 2018). Due to high levels of Hg and other heavy metals, remedial approaches were investigated for the site. One strategy in remediation of contaminated rivers is immobilizing the heavy metals in the sediments by improving metal sorption, complexation, and precipitation capacity of sediments. In this strategy, the metal content of sediments is not lowered, but the mobility of metals is greatly reduced, which means less metals are released into the overlying water (Peng *et al.* 2009).

One of the most common approaches for sediment remediation involves applying the sorbents as a capping material. In situ capping involves placing a layer of clean material at the sediment-water interface. The three main mechanisms of inhibition of contaminant release from the sediment through a cap into the water column includes stabilization of the sediment by preventing resuspension of sediment particles, physical isolation of the sediment consequently shifting the active bioturbation from the contaminated sediments into the clean cap, preventing exposure of benthos to contaminants, and chemical isolation through the process of precipitation, sorption, or ionexchange depending on the capping material used (Jacobs and Förstner 1999, Jacobs and Förstner 2001). Sorbent materials useful as sediment amendment have a strong binding capacity for the target pollutant and thereby limiting the mobility of the pollutants (Yin and Zhu 2016). Two materials that can be used for in situ amendment of sediments for metal species are zeolite and activated carbon.

^{*}Corresponding author, Professor



Fig. 1 Experimental area (in yellow) in Hyeongsan river estuary, South Korea (Google, n.d.)

Zeolite is reported to be able to immobilize metals through three mechanisms which includes precipitation of insoluble metal phases, promotion of surface complexation of metals due to increased alkalinity of substrate, and cation exchange (Shi *et al.* 2009). Activated carbon is considered a universal adsorbent for contaminants and is of particular interest because of its high surface area and pore volume, and presence of acid groups in its structure that enables adsorption of heavy metals (Mohan and Pittman 2006). It has been found to be very effective in mercury removal (Silva *et al.* 2010).

Some studies have shown the effectiveness of capping as a sediment management technique. Addition of sediment caps was found to improve benthic habitat, allowed recolonization of benthic community, and help in isolating and stabilizing contaminants (Murphy et al. 2006, Kang et al. 2016, Xiong et al. 2018). This was confirmed by doing toxicity tests and measurement of chemical concentration of contaminants in the sediments which was found to be always below the effect threshold (Cecconi and Maffiotti 2000). Other means of measuring the effectiveness of sediment capping is by measuring the bioavailability of contaminants in the sediment pore water. Bioavailability is defined as the fraction of contaminants that is available for organismal uptake through all possible routes of exposure (Väänänen et al. 2018). For benthic organisms, one of the most potent exposure route is through the pore water and thus, investigating the concentrations of contaminants in pore water is important. Diffusive gradient in thin film (DGT) technique can be used to predict the bioavailability of heavy metal contaminants in sediment pore water.

DGT is a technique that involves accumulating the contaminant to a resin gel after diffusing through a

dispersion gel. The mass accumulated in the resin gel can then be used to compute for the labile concentration of the contaminants which can later be used to predict bioaccumulation tendencies of such contaminants (Bailon et al. 2019). Previous studies have shown the potential of DGT in measuring bioavailability of heavy metal contaminants in plants (Zhang et al. 2014a), earthworms (Bade et al. 2012), and microbes (Ndu et al. 2018). It has also been proven to reasonably predict MeHg uptake by clam thus providing the basis for DGT probes as substitute for sentinel organisms for monitoring bioavailable MeHg (Clarisse et al. 2012). Addition of active caps to contaminated sediments is expected to lower the mobile pore water concentrations of the contaminants in the sediments and further isolate the contaminants from the overlying water. This would be reflected in lower DGTmeasured concentrations and movement of the maximum pore water concentration deeper in the sediments.

The focus of this study is in situ capping using a combination of passive and active caps. This study specifically aims to assess the effectiveness of zeolite, coconut activated carbon and sand as capping material for contaminated sediment in Hyeongsan river estuary. Labile fractions of contaminants in pore water, as well as, some chemical species important in the study of metal remobilization and mercury methylation in sediment were measured using DGT technique.

2. Methods

2.1 Site description and placement of amendment

Hyeongsan river is a river in South Korea that stretches 62 km, flowing from Gyeongju City to Pohang City. Hyeongsan river estuary in Pohang City, South Korea. The river is located adjacent to an industrial complex that houses companies that specializes in steel manufacturing, and the production of electrical and electronic equipment. It has been the subject of environmental studies because of significant levels of both heavy metals (Bailon et al. 2018) and organic contaminants (Koh et al. 2004). A 400m x 50m experimental area between the Sianan Big bridge and Hyeongsan Big Bridge, near the Gumu Creek area was selected for an amended capping demonstration as this area was found to be moderately to heavily contaminated with Hg and other heavy metals. The experimental area was divided into 4 sections of dimensions 100 m x 50 m, with each section treated with a different type of amendment. Activated carbon and zeolite were selected as cap amendment in active cap areas and sand was used as capping material in passive cap areas. The first section, labeled HS1, was amended by placing a 24 kg zeolite per square meter. The second section, HS2, was amended by placing a first layer of zeolite (16 kg per square meter), and second layer of AC (2 kg per square meter). The third section, HS3, was amended by placing a first layer of AC layer (6 kg per square meter), and a second layer of sand (25 kg per square meter). The last section, HS4, was amended by placing a first layer of zeolite (24 kg per square meter), and a second layer of sand (25 kg per square meter). The estimated thickness of the cap added in each site are shown in Fig. 1.

2.2 Diffusive gradient in thin film probe fabrication

DGT probes were prepared according to the procedure described in previous studies (Hong *et al.* 2014) with some modification. Brief descriptions are provided below and in Table 2. Three types of gel solutions were used to prepare the diffusive gel and the resin gels for the study. Gel solution 1 (GS1) consists of 1% DATD cross-linker (Biorad, USA) and 26.5% acrylamide. Gel solution 2 (GS2) consists of 1.5% N,N'-methylene bisacrylamide (Bio-rad, USA) and 28.5% acrylamide (Bio-rad, USA). Gel solution 3 (GS3) was employed for the diffusive layer and prepared by dissolving 1.5 g of agarose (Fisher, USA) in 100 ml of water on a heating plate. Because GS3 solidifies as the solution cools, GS3 are used as hot solutions during gel preparation. All gel solutions are prepared using deionized (DI) water.

Total Hg (THg) and MeHg resin gels were prepared using 3-mercaptopropyl functionalized silica gel (3-MFSG, Sigma-Aldrich, USA). Heavy metal (HM) and sulfide resin gels were prepared using CHELEX (Bio-rad, USA) and AgI powder, respectively. Phosphate DGT resin gels were prepared using ferrihydrite as sorbent. Ferrihydrite was prepared by titrating slowly a 0.1 M Fe³⁺ solution with 0.1 M NaOH with continuous stirring until pH 7. The resulting ferrihydrite slurry was then centrifuged at 4000 rpm for 10 minutes, and the overlying water was discarded and exchanged with new DI water. Washing was done 3 times to remove any impurities from the ferrihydrite.

For resin gels using GS1 and GS2, 10% ammonium persulfate (APS, Bio-rad, USA) and tetramethylethylenediamine (TEMED, Bio-rad, USA) were

Table 1 Coordinates of deployment location and list of sampler deployed per location

Code	Latitude	Longitude	Pre-capping	Post-Capping
HS1	36° 00.305' N	129°22.087' E	THg, HM	THg, MeHg, HM, S ²⁻ , PO ₄ ³⁻
HS2	36° 00.338' N	129°22.136' E	THg, HM	THg, MeHg, HM, S ²⁻ , PO ₄ ³⁻
HS3	36° 00.374' N	129°22.187' E	THg	THg, MeHg, HM, S ²⁻ , PO ₄ ³⁻
HS4	36° 00.409' N	129°22.236' E	THg	THg, MeHg, HM, S ²⁻ , PO4 ³⁻

used as catalyst and initiator, respectively. All resin gels were casted between two glass plates separated by a 0.75 mm plastic spacer and allowed to sit at room temperature until complete gelation. For sulfide resin gels, processing was done as quickly as possible and in the dark to prevent AgI light exposure. Resin gels were stored in DI water for at least 24 hours to reach a stable thickness. Water is changed several times to remove non-associated sorbent powder from the gels.

Diffusive gels were prepared by casting hot GS3 solution in two glass plates separated by 0.75 mm plastic spacer. The gels were allowed to sit at room temperature for 1 hour. This diffusive gel was used for all DGT probes used in this study. The resin and diffusive gels were cut to fit into paddle-type DGT with exposed area of 2 cm x 15 cm. Resin gels were placed on top of the DGT holder and were covered completely by the larger diffusive gel. A 0.45 μ m polysulfone filter was then placed on top of the filter tightly sealed. Prepared DGT probes were stored in double zipper bags and stored in the refrigerator prior to use.

2.3 Field deployment of DGT probes

DGT probes were deployed twice on-site. First deployment was done in June 2018 to investigate the precapping conditions on site. A second deployment was done in November 2018 for evaluating the effectiveness of the cap. The deployment locations and the types of sampler deployed in each location are summarized in Table 1. To allow better contact between the sediment and the filter, the DGT probes were inserted at an angle into the sediments by professional divers. During insertion, some top parts of the gel are left above the sediment-water interfaces. The probes were left on site for 72 hours during every deployment. There were some differences in the depth of insertion of the DGT probes at different locations because of difficulty of inserting the probes further into the sediments.

2.4 Post deployment processing of DGT

The probes were collected from the site and transported to the laboratory at Korea University – Sejong for postdeployment processing. Probes were washed with DI water to remove some sediments stuck in the outer cover of the probes. The sediment-water interface (SWI) was marked and the filter and the diffusive gel were removed. The resin gels were then sliced to 1 cm smaller gels starting from the

	Resin Gel Used					
Target species	Gel Solution	Resin	Amount 10% APS (µL)	Amount TEMED (µL)	Extractant	Analytical Procedure
THg	10 ml GS1	1 g 3-MFSG	50	15	5 ml of 50% HCl	US EPA 1631
MeHg	10 ml GS1	1 g 3-MFSG	50	15	50 ml of acidic thiourea (1.13 mM thiourea in 0.1 M HCl)	US EPA 1630
HM	10 ml GS1	1 g CHELEX	150	20	10 ml of 1.0 M HNO3	ICP-MS
PO4 ³⁻	10 ml GS2	6 g ferrihydrite	160	16	1.5 ml of 0.25 M H ₂ SO ₄	Molybdenum blue method: UV- Vis spectrophotometry
S ²⁻	10 ml GS3	1 g AgI	0	0	-	Densitometry

Table 2 Summary of DGT procedures for the different analytes

SWI. They were then soaked for 24 hours in appropriate extractant as summarized in Table 2.

THg analysis was done following the purge and trap method indicated in the US EPA method 1631. It involves converting dissolved Hg species to elemental mercury using SnCl₂. The solution is then purged with N₂ gas and the elemental mercury is contained in gold traps. The trapped Hg is then thermally desorbed and analyzed using CVAFS (USEPA 2002). MeHg analysis was done using US EPA method 1630. MeHg in the extractant is ethylated using tetraethylborate and is purged and trapped onto TENAX traps. The traps are then flash heated in nitrogen stream and the released Hg species are thermally separated in a GC column and quantified using CVAFS (USEPA 1998). The heavy metal concentrations from HM DGT extracts were analyzed using ICP-MS with Y internal standard.

Molybdenum blue method was used to determine phosphate concentration colorimetrically. Color reagent (CR) was prepared by mixing 500 ml of 2.5 M H_2SO_4 , 50 ml potassium antimonyl tartrate, 150 ml of ammonium molybdate and 300 ml of ascorbic acid solution. The resin gels were removed from the extractant, and color reagent (CR) was added to the extract in a 2:1 ratio (extract:CR). The samples were left for 10 minutes to allow the color change, and the absorbance of the sample at 880 nm was determined using a UV-Visible spectrophotometer.

Sulfide accumulated in the AgI gels were analyzed using densitometry. To prepare the calibration curve, resin gels were soaked in 10 ml of DI water spiked with S²⁻ to a final concentration range of 0.1-10 µM. After 24 hours for establishing equilibrium, the gels were collected and placed on a transparent OHP film with the binding site facing up. To protect the surface, the gels were fixed with transparent tape. The analysis was done based on previously described procedure. In summary, the OHP film with the gels was placed in a flat-bed scanner and the image recorded using the software (Samsung SL-J1660 App). Prior to greyscale intensity measurement for the calibration experiment, the brightness of the scanned images was manually optimized so that the unexposed gel was just discernible from the white background. The same brightness setting was used for the succeeding image scans. The images were then analyzed for their greyscale intensity (0-255) using imageJ software (ImageJ 1.52j). The scanned images of the gels from the field DGT deployment were analyzed for their greyscale intensities using the same procedure. The S²⁻ concentrations were determined using the calibration curve previously developed (Teasdale, Hayward and Davison 1999).

2.5 Calculation of the DGT-labile heavy metal concentration

The concentrations of labile metals measured via (C_{DGT}) were calculated using the following equation (Zhang and Davison 1995):

$$C_{DGT} = \frac{M \,\Delta g}{DAT} \tag{1}$$

Where M is the accumulated mass (ng) of metal over the deployment time, Δg is the thickness of the diffusive gel (0.085 cm), and D is the diffusion coefficient of heavy metals in the diffusion layer (cm²/s). A is the area of the exposed window (cm²) and t is the deployment time of DGT in the sediment.

3. Results and discussion

3.1 Total mercury

As can be seen in Fig. 2, pre-capping data for the THg levels in sediment pore water showed that there was a significant increase in the THg values deeper in the sediments. The THg levels in the overlying water are generally very low compared to the sediment pore water suggesting historical sediment contaminant. Different sites showed different sediment THg profiles. Relative maxima were typically observed at 3-4 cm below the SWI. THg levels in HS sites sediment pore water ranged from 400 to 1200 ng/L. Since previous bioaccumulation studies supported that labile concentrations of contaminants as measured by DGT correlates well with the amount bioaccumulated by benthic organisms, it is highly likely that the contaminant level measured at the relatively lower depths from the SWI poses an important concern for benthic organisms that normally burrow at these depths



Fig. 2 In situ sediment depth profiles of THg and MeHg levels measured using DGT in Hyeongsan River Estuary, South Korea

(Amirbahman *et al.* 2013, Pisanello *et al.* 2016). High resolution studies show that the sharp concentration maxima of metals observed near the SWI (top 1-3 cm) may drive the metal fluxes to the overlying water (Simpson *et al.* 2002). These results emphasized the need for capping in the area.

Sites of the confluence with Gumu Creek (HS3 and HS4) showed the highest levels of mercury. This was consistent with the data obtained in previous study where high levels of mercury were attributed to effluents/discharges coming from along Gumu Creek (Bailon *et al.* 2018).

Different sets of capping material were employed in the different sites. Results showed that all the capping amendments were able to significantly reduce the THg level in the pore water across depths in all sampling sites. HS1 showed Hg level reduction ranging from 45 to 87% with high reduction observed in the first 5 cm of the sediment. For HS2, reduction of THg levels was less prominent compared to other sites. HS2 showed a reduction from 3 to 41% with some points below the SWI showing an increase in the THg level. These observations may suggest significant upwelling from below at this location. It is also possible that the relatively low density AC was disturbed by a typhoon occurring prior to the DGT deployment. In the

case of HS2, the AC was placed atop of the zeolite layer and so it was easily displaced during high energy flow events. Results for HS3 showed reduction rates of 38 to 93% with maximum reduction observed at a depth of 3-4 cm. HS4 also showed very high THg reductions at 7 to 95%. The percent reduction in the first 4 cm beneath the SWI are above 92% in HS3 and HS4. In general, the very high reduction percentage in the layer directly below the SWI is expected since the first 3-4 cm, are composed mainly of the capping amendment intermixed by sediment due to sediment mixing and bioturbation. Since the amendments used are effective sorbents for heavy metals, the cap is expected to prevent the leaching out of contaminants into the overlying water preventing its eventual uptake by aquatic organisms. The high reduction in the THg for the surficial sediments in HS3 and HS4 show the potential of the capping amendment for use in remediation. The primary advantage of HS3 and HS4 is the thin layer of sand at the surface that help contain the active amendment.

3.2 Methylmercury

Several studies show that methylmercury production in estuarine environment are higher than previously expected and bottom sediments were also found to be one of the primary source of MeHg within coastal zones (Mitchell and Gilmour 2008). The high MeHg production in these environments is attributed to in situ biogeochemical conditions including high sulfate and organic matter (Chen et al. 2008). It is also important to study MeHg because of its inherent toxicity and bioaccumulation risks (Zahir et al. 2005). Since the measured DGT-labile Hg is high in the experimental area, significant methylmercury production is expected. This is also supported by the previously reported data where significant amounts of MeHg that were higher compared to that from other rivers in the world were detected in the bottom sediments of Hyeongsan River estuary (Bailon et al. 2018). For both HS1 and HS2, there is relatively low organic matter prior to the confluence with the Gumu Creek. At HS3, MeHg is relatively low in the surficial layer suggesting some reduction of the bioavailable Hg in the AC layer. At HS4, MeHg was relatively high throughout the column suggesting little influence of the zeolite sorbent.

3.3 Heavy metal levels

Similar to the results for THg, significant reduction in the levels of other metals were observed in situ after sorbent capping. Comparison with pre-capping levels were only possible for sites HS1 and HS2 since HM DGT probes were not deployed to sites HS3 and HS4 prior to capping. Depth profiles for the different metals in HS1 and HS2 are shown in Fig. 3.

For HS1, pore water concentration reductions of 80-99% of Ni, Zn, As and Pb were observed across depth while Cu and Cd showed reductions only in the benthic boundary layer and in upper 1-2 cm of sediments. Cr showed no reduction at any depth. It should be noted that Cr, Cu and Cd were all present in HS1 at concentrations below 1 ng/L while the other metals were typically present at higher concentrations (up to 50 ng/L pre-capping for Zn).

HS2 showed little or no reductions for most metals consistent with the potential loss of AC as discussed with THg results. Cu and As showed substantial reductions but reductions were much less clear in other metals.

Fig. 4 shows the results for the heavy metal concentration in HS3 and HS4. No comparison may be done between pre-capped and post-capped conditions for these two sites. However, post-capping concentrations in HS3 and HS4 are similar to post-capping concentrations in HS1 and HS2. This corresponds well with the thickness of the capping layer as confirmed by visual inspection of the sediment cores obtained from the site after capping.

3.4 Factors affecting mercury, methylmercury and heavy metal distribution in sediments

Sulfide (S²⁻) and phosphate (PO₄³⁻) levels in the sediment pore water were also determined in situ. With exception of the S²⁻ level at the SWI for HS4, S²⁻ in all sites are generally low in the upper sediments and increase sharply at depths of 8-9 cm below the SWI. S²⁻ levels in all sites, except for HS3, are on similar range of values 0.2-1.2 μ M. For HS3, S²⁻ values in the upper 8 cm of sediments

were in similar range as that of the other sites. But the levels increased significantly at further depths reaching a maximum level of 5.7 μ M at depths of 11-12 cm from the SWI. Relative maxima for the other sites were also located at similar depths. Dark patches in the resin gel collected can be attributed to sulfide-producing microniches. These microniches introduce local redox gradients in sediments. Efficiency of pore water sulfide sinks controls the dynamics of dissolved sulfide and formation of these microniches. The main controlling factor of which are availability of dissolved Fe and precipitation of FeS (Widerlund and Davison 2007).

 PO_4^{3-} follows an increasing trend with sediment depth similar with S²⁻. PO_4^{3-} levels in the overlying water in all sites showed higher values compared to the top sediments suggesting that the slightly elevated levels of PO_4^{3-} in the water directly above the sediments may originate from other possible sources. The levels of PO_4^{3-} in all sites were in similar range of 0.05-1.8 μ M with relative maxima located in depths of 10-13 cm. Phosphate release was strongly correlated with Fe redox cycling in HS2-4. In more anoxic conditions, such as deeper depths in sediment, reduction of Fe (III) oxyhydroxide may result to subsequent release of soluble reactive phosphate initially associated with the mineral phase (Wu *et al.* 2015).

A potential consequence of capping amendments is the possibility of abrupt restructuring of biogeochemical processes within the underlying sediments. Changes in such processes can directly influence the fate and transport of contaminants. The addition of sediment caps produces new anaerobic zones resulting to an excess of H2S which can produce sulfide precipitates where metals can bind, which leads to subsequent reduction in metal contaminant bioavailability. The increased size of the anaerobic zone in capped sediments could also lead to increased opportunities for reductive transformation (Himmelheber et al. 2008). In addition, the associated flux and mobility of MeHg to overlying water can be affected by Fe redox cycling, vertical position of redox transition zones, and activity of demethylating bacteria (Hammerschmidt et al. 2004). To understand this, the dynamics of the concentration levels of the different species across sediment depths were compared. Depth profiles for the normalized concentration values of THg, MeHg, S²⁻, PO₄³⁻, Mn, Fe, and %MeHg in pore water are shown in Fig. 5.

Strong correlation between the methylmercury and mercury concentration in pore water was evident based on the depth at which relative maxima for both species were observed. Differences in pattern at some depths may be attributed to other geochemical controls that can affect Hg and MeHg bioavailability, as well as their partitioning in sediments. Bioavailable mercury is metabolized by sulfatereducing bacteria in sediments. Mercury methylation may occur simultaneously with reduction reactions of iron and manganese oxides. The general assumption for biogeochemical reactions is that they proceed from the most energy yielding to the lowest energy yielding electron acceptor (Hong et al. 2014). The common pattern for redoxdriven reduction associated with organic matter decomposition is Mn, followed by Fe, and then sulfate. In addition, sulfate reduction has been postulated to occur







Fig. 4 Sediment depth profiles for the Post-capping concentration levels (ng/L) of selected Heavy metals in HS3 and HS4

locally in zones of high Fe and Mn reduction, to account for high turnover of sulfur (Naylor *et al.* 2004). This was observed in the different sites studied where the Mn maxima occurred at shallower depths, followed by Fe, and then S^{2-} where maxima of Fe and S occurred at similar depths.

In the case of HS1, THg and MeHg follow same general trend of increasing concentration with depth. It can be said that the degree of mercury methylation increases with depth as apparent in the maximum %MeHg in pore water observed at depths of 9-11 cm from the SWI. Both Mn and Fe species are low in the surficial sediments and also increased significantly with depth. The same trend was also observed for both PO43- and S2- where drastic increase on the levels of these two species occurred at depths of 9-10 cm, corresponding well with high %MeHg in pore water calculated. Fe and S maxima were both observed at depths of 14 cm, which corresponds incidentally with maximum depth for MeHg suggesting possible tight coupling between sulfate reduction and mercury methylation. Highest methylmercury levels are commonly found highest near the redoxcline. The generally low MeHg values in shallower depths may be due to high demethylation in these layers due to penetration of oxygen close to the SWI and sorption of MeHg to Fe-oxyhydroxides in the oxic and sub-oxic sediment (Chen et al. 2008). Several studies already discussed that mercury methylation by reducing bacteria occurs in anoxic conditions. It has been proposed before that the uptake of Hg(II) in anoxic sediments is primarily controlled by the concentration of inorganic Hg sulfide species in sediment pore water (Hines et al. 2006, Drott et al. 2007). Neutral Hg-S complexes in water, primarily Hg- S^0 , was proposed to be the major control of transfer of Hg into sulfate reducing bacteria (SRB) since these complexes are capable of readily passing through bacterial membranes. Formation of such complexes is affected significantly by the concentration of dissolved sulfide (Hammerschmidt et al. 2004, Heyes et al. 2006, Hines et al. 2006). Studies showed that methylmercury generally increase with high reduced sulfur concentrations, but very high sulfide concentrations can also impede mercury methylation (Davis et al. 1997). The results of the study also showed that the %MeHg observed in sediment pore water in more brackish sites decreases with increasing sulfide concentration. The levels observed for S²⁻ in the different sites are all lower than 10 μ M, which is suitable for the formation of neutral HgS species. In sulfide concentrations of less than 10 µM, the dissolved Hg speciation is



Fig. 5 The normalized vertical pore water levels (Post-capping) of THg, MeHg, PO4³⁻, S²⁻, Mn, Fe and %MeHg measured by DGT in Hyeongsan River estuary

dominated by HgS, while in higher concentration, speciation of Hg shifts to other complexed species like $HgSH_2^-$ where mercury methylation is expected to be lower (Benoit *et al.* 2001, Han *et al.* 2008).

Depth profiles for Mn, Fe, S^{2-} and PO_4^{3-} in HS3 and HS4 follows the same trend as that of HS2. It is observable that increase in concentration of MeHg are commonly observed in layers where localized reduction occurs. In the case of HS3 and HS4, this is prominent in the profiles observed for MeHg and Mn, although at times, might be hard to pick up using DGT.

For all sites, relative maxima for the different metals and metalloid studies seemed to coincide with maxima for Mn and Fe mobility. It is possible that with the increasing reducing condition induced by making the sediment more anoxic due to added caps, chemical species that are previously associated with Mn and Fe oxides were simultaneously released during reactive dissolution of these oxides (Naylor *et al.* 2004). Previous study on correlation between As and Fe showed that sediment capping resulted to release of As from hydrous Fe and Mn oxides or as iron arsenate. The arsenate released can then further be reduced and reacted with sulfide forming complexes that have higher solubility and mobility (Casado-Martinez *et al.* 2010).

3.5 General insights on capping amendment

Sand is commonly used as a passive cap because it simply serves to separate a contaminated layer from the overlying water. In addition, previous studies showed that sand as a capping material is able to suppress fluxes of Cd. Cu, Ni and Zn from contaminated sediments into the overlying water (Han et al. 2016) and insoluble phosphorus maintaining overall low P concentration in the overlying water (Kim and Jung 2010). Here, sand was primarily employed to help contain other sorbing amendments. Because of low adsorptive capacity of passive caps like sand, the efficiency of such materials is dependent heavily on physical retardation mechanisms than chemical retardation. As such, erosive forces can result to breakthrough of contaminants to the cap by time. A good passive cap is recommended to be approximately 50 cm thick (Zhang et al. 2016), which is not considered costeffective and practical because of difficulty of placement. Thinner caps can be used when active materials like AC and zeolite are added. Simulation studies showed that addition of sorbent materials to sand caps drastically improves cap performance by increasing the sorptive capacity of the cap (Go et al. 2009).

The ability of sand caps to stabilize the capping layer is important in preventing significant effects of oxidation events to sediment contaminant dynamics. Oxidation events, like flooding, causes disturbances and significant oxidation of sediments resulting to enhanced remobilization of metal contaminants in sediments (Zoumis *et al.* 2001). As shown in Fig. 6, the core samples collected form the sites showed that there was minimal mixing between the sediments and the capping layer even with disturbance events like rain and tidal fluctuations in the area. Except for HS2, all capped sites also showed minimal displacement of the added cap which shows the high stability of the cap especially in normal flow conditions of the river.

The results of the study showed the great potential of activated carbon and zeolite in mitigating heavy metal contaminants in sediments. All of the sites exhibited great reduction in the heavy metal levels after capping. The results of the study were in agreement with the study of Simpson et al (2002) where zeolite/sand mix cap were found to greatly reduce fluxes of metals (Simpson et al. 2002). Like in other studies, AC amendment in our setups showed effective reduction of pore water concentrations of MeHg. Activated carbon-based capping amendment has been proven previously to decrease pore water concentration of MeHg. In the study of Gilmour et al (2018), AC-based Sedimite[™] amendment effectively reduce pore water concentration of MeHg in soil by 90% in just one month of residence time. AC was also found to increase the MeHg partitioning in soil from Penobscot River salt marsh (Gilmour et al. 2018). Although determination of specific mechanism was not done in this study, our results showed great potential for mercury and heavy metal its immobilization in contaminated sediments.

Because of the low density of AC, proper planning of its placement as a capping amendment is important. This is highlighted in the results for HS2 and HS3. It is expected that since two active materials were used for capping the



Fig. 6 Sediment core samples collected from the capped and uncapped sites in Hyeongsan River estuary

contaminated sediments, it was expected to show greater efficiency for remediation. However, because the AC was placed atop of the heavier zeolite layer, it was easily displaced by natural disturbances that occurred in the area, resulting to lower % reduction in heavy metal levels in the pore water. AC was also used in HS3, but it was placed directly above the sediment, and was stabilized by placing sand on top. This resulted to higher remediation efficiency observed.

The thickness of capping material should be considered to minimize organisms burrowing to contaminated sediments. In the present situation, the thin layer of capping material would be intermixed into the surficial sediments giving rise to a condition closer to a sediment treatment rather than capping. Greater effectiveness and isolation could be achieved through capping with a thicker layer although at a cost of additional materials and complexity and potentially greater effects on the river. The capping/treatment layer should be as thin as possible to achieve the needed remedial goal.

The mixing process is primarily due to bioturbation and hydrodynamic mixing. Much like normal surface sediment mixing, since one of the main functions of the added cap is to physically isolate the contaminants, sediment-cap mixing may affect the overall performance of the added cap. The long-term effectiveness of the added cap may be dependent on the original thickness of the cap. But even with natural mixing of the sediment and the added cap, reduction of metal fluxes and heavy metal immobilization were still observed in our study. In freshwater systems, the typical bioturbation depth is greater than 10 cm (Reible and Lampert 2014). Since the added cap is about 2 cm in thickness, if it is assumed that the top 10 cm of the sediment-cap layer will undergo natural mixing, the resulting mix would still contain about 20% of the added cap. A previous study on AC amendment in contaminated sediment showed significant reduction in pore water Hg even with addition of only 4.8-7.3% AC/gram dry weight of sediment (Gilmour et al. 2013).

DGT as a potential technique for evaluating remediation effectiveness is also highlighted in the study. The possibility

of doing analysis of resin gels from the DGT probes at spatial resolution of 1 cm or less enables depth profiling of contaminants. In addition, the use of other sorbent materials for the binding layers enabled studying different geochemical factors affecting mercury methylation. Its capability of providing high resolution measurement enables identification of redox zones as well as distribution of contaminants across depths. In addition, because of having a pre-concentration step, DGT is capable of measuring very low to high concentrations of contaminants. It is used to measure mobile interstitial metal concentrations which are likely to be bioavailable. Its capability to measure the bioavailable fraction of contaminants in the sediment pore water can be used as a predictor for contaminant bioaccumulation in benthic organisms. Several studies have also highlighted the potential of DGT measurements to model toxicity and bioaccumulation risks to benthic organisms (Jacobs 2003, Amirbahman et al. 2013, Amato et al. 2015, Bailon et al. 2019).

4. Conclusion

Sediment capping using combination of capping material was proven to be an effective in situ management method for immobilizing heavy metal contaminants in sediments. The use of zeolite and activated carbon, in combination with passive sand caps, have shown significant reduction in the labile concentrations of Hg, MeHg and other heavy metals in the sediment across depths. Application of 2-3 cm caps containing the active sorbents ensures that even with natural mixing of top sediments with the added cap, the cap-sediment mix would still contain significant amount of the capping material for heavy metal immobilization.

Results of the study showed that the depths where maximum MeHg levels were observed corresponded well with the depths for development of reducing conditions as has been observed previously. Further tests like sequential extraction of sediments and AVS-SEM determination, may be done to further understand the biogeochemistry of methylmercury in the capped sediments. The long term effectiveness of capping as a management system should also be studied by repeat deployment of DGT after a longer residence time of the added cap.

Acknowledgement

The research described in this paper was financially supported by the Basic Science Research Program through the National Research Foundation of Korea (2018R1D1A1B07049757) and by the Korea Environmental Industry and Technology Institute (2018002480002) in Ministry of Environment.

References

Amato, E. D., Simpson, S. L., Belzunce-Segarra, M. J., Jarolimek, C. V. and Jolley, D. F. (2015), "Metal fluxes from porewaters and labile sedimentphases for predicting metalexposure andbioaccumulationinbenthicinvertebrates",Environ.Technol.,**49**(24),14204-14212.https://doi.org/10.1021/acs.est.5b03655.

- Amirbahman, A., Massey, D. I., Lotufo, G., Steenhaut, N., Brown, L. E., Biedenbach, J. M. and Magar, V. S. (2013), "Assessment of mercury bioavailability to benthic macroinvertebrates using diffusive gradients in thin films (DGT)", *Environ. Sci. Process. Impacts*, 15(11), 2104-2114. https://doi.org/10.1039/C3EM00355H.
- Bade R., Oh S. and Shin W. S. (2012). "Diffusive gradients in thin films (DGT) for the prediction of bioavailability of heavy metals in contaminated soils to earthworm (Eisenia foetida) and oral bioavailable concentrations", *Sci. Total. Environ.*, **416**, 127-136. https://doi.org/10.1016/j.ecoenv.2012.03.019
- Bailon, M. X., David, A. S., Park, Y., Kim, E. and Hong, Y. (2018), "Total mercury, methyl mercury, and heavy metal concentrations in Hyeongsan River and its tributaries in Pohang city, South Korea", *Environ. Monitor. Assess.*, **190**(5), 274. https://doi.org/10.1007/s10661-018-6624-4.
- Bailon, M. X., Park, M.-o. and Hong, Y. (2019), "Passive sampling methods for assessing the bioaccumulation of heavy metals in sediments", *Current Pollution Reports*, **5**(3), 129-143. https://doi.org/10.1007/s40726-019-00111-w.
- Benoit, J. M., Gilmour, C. C. and Mason, R. P. (2001), "The influence of sulfide on solid-phase mercury bioavailability for methylation by pure cultures of Desulfobulbus propionicus (1pr3)", *Environ. Sci. Technol.*, **35**(1), 127-132. https://doi.org/10.1021/es001415n.
- Casado-Martinez, M. C., Smith, B. D., Luoma, S. N. and Rainbow, P. S. (2010), "Bioaccumulation of arsenic from water and sediment by a deposit-feeding polychaete (Arenicola marina): A biodynamic modelling approach", *Aquatic Toxicology*, **98**(1), 34-43. https://doi.org/ 10.1016/j.aquatox.2010.01.015.
- Cecconi, G. and Maffiotti, A. (2000), "An integrated approach to assess the benthic quality after sediment capping in Venice lagoon AU Bona, F.", *Aquatic Eco. Health. Manage*, **3**(3), 379-386. https://doi.org/10.1080/14634980008657035.
- Chen, C., Amirbahman, A., Fisher, N., Harding, G., Lamborg, C., Nacci, D. and Taylor, D. (2008), "Methylmercury in marine ecosystems: spatial patterns and processes of production, bioaccumulation, and biomagnification", *EcoHealth*, **5**(4), 399-408. https://doi.org/10.1007/s10393-008-0201-1.
- Clarisse O., Lotufo G. R., Hintelmann H. and Best E. P. H. (2012). "Biomonitoring and assessment of monomethylmercury exposure in aqueous systems using the DGT technique", *Sci. Total. Environ.*, **416**, 449-454. https://doi.org/10.1016/j.scitotenv.2011.11.077.
- Davis, A., Bloom, N. S. and Que Hee, S. S. (1997), "The environmental geochemistry and bioaccessibility of mercury in soils and sediments: A review", *Risk Analysis*, **17**(5), 557-569. https://doi.org/10.1111/j.1539-6924.1997.tb00897.x.
- Drott, A., Lambertsson, L., Björn, E. and Skyllberg, U. (2007), "Importance of dissolved neutral mercury sulfides for methylmercury production in contaminated sediments", *Environ. Sci. Technol.*, **41**(7), 2270-2276. https://doi.org/10.1021/es061724z.
- Gilmour, C., Bell, T., Soren, A., Riedel, G., Riedel, G., Kopec, D., Bodaly, D. and Ghosh, U. (2018), "Activated carbon thin-layer placement as an in situ mercury remediation tool in a Penobscot River salt marsh", *Sci. Total Environ.*, **621**, 839-848. https://doi.org/10.1016/j.scitotenv.2017.11.050.
- Gilmour, C. C., Riedel, G. S., Riedel, G., Kwon, S., Landis, R., Brown, S. S., Menzie, C. and Ghosh, U. (2013), "Activated carbon mitigates mercury and methylmercury bioavailability in contaminated sediments", *Environ. Sci. Technol.*, **47**(22), 13001-13010. https://doi.org/10.1021/es4021074.

- Go, J., Lampert, D. J., Stegemann, J. A. and Reible, D. D. (2009), "Predicting contaminant fate and transport in sediment caps: Mathematical modelling approaches", *Appl. Geochem.*, **24**(7), 1347-1353. https://doi.org/10.1016/j.apgeochem.2009.04.025.
- Google Maps. (n.d.), Hyeongsan River Pohang City, South Korea; <u>https://www.google.com/maps/place/Pohang-si,+Gyeongsangbuk-do.</u>
- Hammerschmidt, C. R., Fitzgerald, W. F., Lamborg, C. H., Balcom, P. H. and Visscher, P. T. (2004), "Biogeochemistry of methylmercury in sediments of Long Island Sound", *Marine Chemistry*, **90**(1), 31-52. https://doi.org/ 10.1016/j.marchem.2004.02.024.
- Han, J., Ro, H.-M., Cho, K. H. and Kim, K.-W. (2016), "Fluxes of nutrients and trace metals across the sediment-water interface controlled by sediment-capping agents: bentonite and sand", *Environ. Monitor: Assess.*, 188(10), 566. https://doi.org/10.1007/s10661-016-5583-x.
- Han, S., Obraztsova, A., Pretto, P., Deheyn, D. D., Gieskes, J. and Tebo, B. M. (2008), "Sulfide and iron control on mercury speciation in anoxic estuarine sediment slurries", *Marine Chemistry*, **111**(3), 214-220. https://doi.org/10.1016/j.marchem.2008.05.002.
- Heyes, A., Mason, R. P., Kim, E.-H. and Sunderland, E. (2006), "Mercury methylation in estuaries: Insights from using measuring rates using stable mercury isotopes" *Marine Chemistry*, **102**(1), 134-147. https://doi.org/ 10.1016/j.marchem.2005.09.018.
- Himmelheber, D. W., Taillefert, M., Pennell, K. D. and Hughes, J.
 B. (2008), "Spatial and temporal evolution of biogeochemical processes following In situ capping of contaminated sediments", *Environ.* Sci. Technol., 42(11), 4113-4120. https://doi.org/10.1021/es702626x.
- Hines, M. E., Faganeli, J., Adatto, I. and Horvat, M. (2006), "Microbial mercury transformations in marine, estuarine and freshwater sediment downstream of the Idrija Mercury Mine, Slovenia", *Appl. Geochem.*, **21**(11), 1924-1939. https://doi.org/10.1016/j.apgeochem.2006.08.008
- Hong, Y., Dan, N. P., Kim, E., Choi, H.-J. and Han, S. (2014), "Application of diffusive gel-type probes for assessing redox zonation and mercury methylation in the Mekong Delta sediment", *Environ. Sci. Process. Impacts*, **16**(7), 1799-1808. https://doi.org/10.1039/C3EM00728F.
- Jacobs, P. and Förstner, U. (2001), "Managing contaminated sediments", J. Soils Sediments, 1(4), 205. https://doi.org/10.1007/BF02987726.
- Jacobs, P. H. (2003), "Monitoring of subaqueous depots with active barrier systems for contaminated dredged material using dialysis samplers and DGT probes", *J. Soils Sediments*, **3**(2), 100-107. https://doi.org/10.1007/BF02991075.
- Jacobs P. H. and Förstner U. (1999). "Concept of subaqueous capping of contaminated sediments with active barrier systems (ABS) using natural and modified zeolites", *Water Research* **33**(9), 2083-7. https://doi.org/10.1016/S0043-1354(98)00432-1
- Kang, K., Lee, C.-G., Choi, J.-W., Kim, Y.-K. and Park, S.-J. (2016), "Evaluation of the Use of Sea Sand, Crushed Concrete, and Bentonite to Stabilize Trace Metals and to Interrupt Their Release from Contaminated Marine Sediments", *Water Air Soil Pollut.*, 227(9), 308. https://doi.org/10.1007/s11270-016-3028-3.
- Kim, G. and Jung, W. (2010), "Role of sand capping in phosphorus release from sediment", *KSCE J. Civil Eng.*, **14**(6), 815-821. https://doi.org/10.1007/s12205-010-0856-3.
- Koh, C. H., Khim, J. S., Kannan, K., Villeneuve, D. L., Senthilkumar, K. and Giesy, J. P. (2004), "Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) and 2,3,7,8-TCDD equivalents (TEQs) in sediment from the Hyeongsan River, Korea", *Environ. Pollut.*, **132**(3), 489-501. https://doi.org/10.1016/j.envpol.2004.05.001.

- Mitchell, C. P. J. and Gilmour, C. C. (2008), "Methylmercury production in a Chesapeake Bay salt marsh", *J. Geophysical Res. Biogeosci.*, **113**(G2). https://doi.org/10.1029/2008JG000765.
- Mohan, D. and Pittman, C. U. (2006), "Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water", *J. Hazardous Mater.*, **137**(2), 762-811. https://doi.org/10.1016/j.jhazmat.2006.06.060.
- Murphy, P., Marquette, A., Reible, D. and Lowry Gregory, V. (2006), "Predicting the performance of activated carbon-, coke-, and soil-amended thin layer sediment caps", *J. Environ. Eng.*, **132**(7), 787-794. https://doi.org/10.1061/(ASCE)0733-9372(2006)132:7(787).
- Naylor, C., Davison, W., Motelica-Heino, M., Van Den Berg, G. A. and Van Der Heijdt, L. M. (2004), "Simultaneous release of sulfide with Fe, Mn, Ni and Zn in marine harbour sediment measured using a combined metal/sulfide DGT probe", *Sci. Total Environ.*, **328**(1), 275-286. https://doi.org/ 10.1016/j.scitotenv.2004.02.008.
- Ndu U., Christensen G. A., Rivera N. A., Gionfriddo C. M., Deshusses M. A., Elias D. A. and Hsu-Kim H. (2018).
 "Quantification of mercury bioavailability for methylation using Diffusive Gradient in Thin-Film samplers", *Environ. Sci. Technol.*, **52**(15), 8521-8529. https://doi.org/ 10.1021/acs.est.8b00647
- Peng, J. f., Song, Y. h., Yuan, P., Cui, X. y. and Qiu, G. l. (2009), "The remediation of heavy metals contaminated sediment", *J. Hazardous Mater.*, **161**(2-3), 633-640. https://doi.org/10.1016/j.jhazmat.2008.04.061.
- Pisanello, F., Marziali, L., Rosignoli, F., Poma, G., Roscioli, C., Pozzoni, F. and Guzzella, L. (2016), "In situ bioavailability of DDT and Hg in sediments of the Toce River (Lake Maggiore basin, Northern Italy): accumulation in benthic invertebrates and passive samplers", *Environ. Sci. Pollut. Res.*, 23(11), 10542-10555. https://doi.org/10.1007/s11356-015-5900-x.
- Reible, D. D. and Lampert, D. J. (2014), "Capping for Remediation of Contaminated Sediments. In D. D. Reible (Ed.)", *Processes, Assessment and Remediation of Contaminated Sediments*, Springer, New York, NY, USA. 325-363.
- Shi, W.-y., Shao, H.-b., Li, H., Shao, M.-a. and Du, S. (2009), "Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite", *J. Hazardous Mater.*, **170**(1), 1-6. https://doi.org/10.1016/j.jhazmat.2009.04.097.
- Silva, H. S., Ruiz, S. V., Granados, D. L. and Santángelo, J. M. (2010), "Adsorption of mercury (II) from liquid solutions using modified activated carbon", *Materials Research*, **13**(2), 129-134. https://doi.org/10.1590/S1516-14392010000200003.
- Simpson, S. L., Pryor, I. D., Mewburn, B. R., Batley, G. E. and Jolley, D. (2002), "Considerations for Capping Metal-Contaminated Sediments in Dynamic Estuarine Environments", *Environ. Sci. Technol.*, **36**(17), 3772-3778. https://doi.org/10.1021/es025632v.
- Tan, G., Sun, W., Xu, Y., Wang, H. and Xu, N. (2016), "Sorption of mercury (II) and atrazine by biochar, modified biochars and biochar based activated carbon in aqueous solution", *Bioresource Technology*, **211**, 727-735. https://doi.org/ 10.1016/j.biortech.2016.03.147.
- Teasdale, P. R., Hayward, S. and Davison, W. (1999), "In situ, high-resolution measurement of dissolved sulfide using diffusive gradients in thin films with Computer-Imaging Densitometry", *Analytical Chemistry*, **71**(11), 2186-2191. https://doi.org/10.1021/ac981329u.
- USEPA. (1998), Method 1630, Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold-Vapor Atomic Fluorescence Spectrometry, EPA-821-R-01-020; Office of Water and Office of Science and Technology: Washington, D.C., 1-55.
- USEPA (2002), Method 1631, revision E: mercury in water by

oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry, United States Environmental Protection Agency, 1-46

- Väänänen, K., Leppänen, M. T., Chen, X. and Akkanen, J. (2018), "Metal bioavailability in ecological risk assessment of freshwater ecosystems: From science to environmental management" Ecotoxicology Environ. Safety, 147, 430-446. https://doi.org/ 10.1016/j.ecoenv.2017.08.064.
- Wang, M., Zhu, Y., Cheng, L., Andserson, B., Zhao, X., Wang, D. and Ding, A. (2017), "Review on utilization of biochar for metalcontaminated soil and sediment remediation", J. Environ. Sci., 63, 156-173. https://doi.org/10.1016/j.jes.2017.08.004.
- Widerlund A. and Davison W. (2007). "Size and density distribution of sulfide-producing microniches in lake sediments", Environ. Sci. Technol., 41(23), 8044-8049. https://doi.org/ 10.1021/es071510x.
- Wu Z., Wang S., He M., Zhang L. and Jiao L. (2015). "Element remobilization, "internal P-loading," and sediment-P reactivity researched by DGT (diffusive gradients in thin films) technique" Environ. Sci. Pollut. Res. 22(20), 16173-16183. https://doi.org/ 10.1016/j.envpol.2011.02.015.
- Xiong C., Wang D., Tam N. F., Dai Y., Zhang X., Tang X. and Yang Y. (2018). "Enhancement of active thin-layer capping with natural zeolite to simultaneously inhibit nutrient and heavy metal release from sediments", Ecological Eng., 119, 64-72. https://doi.org/ 10.1016/j.ecoleng.2018.05.008.
- Yin H. and Zhu J. (2016). "In situ remediation of metal contaminated lake sediment using naturally occurring, calciumrich clay mineral-based low-cost amendment", Chem. Eng. J., 285, 112-120. https://doi.org/ 10.1016/j.cej.2015.09.108.
- Zahir F., Rizwi S. J., Haq S. K. and Khan R. H. (2005). "Low dose mercury toxicity and human health", Environ. Toxicology 351-360. Pharmacology, 20(2). https://doi.org/ 10.1016/j.etap.2005.03.007.
- Zhang C., Ding S., Xu D., Tang Y. and Wong M. H. (2014a). "Bioavailability assessment of phosphorus and metals in soils and sediments: A review of diffusive gradients in thin films (DGT)", Environ. Monitor. Assess., 186(11), 7367-7378. https://doi.org/ 10.1007/s10661-014-3933-0.
- Zhang C., Yu Z.-g., Zeng G.-m., Jiang M., Yang Z.-z., Cui F., Zhu M.-y., Shen L.-q. and Hu L. (2014b). "Effects of sediment geochemical properties on heavy metal bioavailability", Environ. International, 73, 270-281. https://doi.org/ 10.1016/j.envint.2014.08.010.
- Zhang C., Zhu M.-y., Zeng G.-m., Yu Z.-g., Cui F., Yang Z.-z. and Shen L.-q. (2016). "Active capping technology: A new environmental remediation of contaminated sediment", Environ. Res., **23**(5), Pollut. 4370-4386. Sci https://doi.org/ 10.1007/s11356-016-6076-8.
- Zhang H. and Davison W. (1995). "Performance characteristics of Diffusion Gradients in Thin Films for the in situ measurement of trace metals in aqueous solution", Analytical Chemistry, 67(19), 3391-3400. https://doi.org/ 10.1021/ac00115a005.
- Zoumis T., Schmidt A., Grigorova L. and Calmano W. (2001). "Contaminants in sediments: Remobilisation and demobilisation", Sci. Total. Environ., 266(1), 195-202. https://doi.org/ 10.1016/S0048-9697(00)00740-3.

CC