Influence of oxic/anoxic condition on sorption behavior of PFOS in sediment

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ABSTRACT: Sediment components and redox properties change with oxic/anoxic condition, which affect the environmental transport of perfluorooctane sulfonate (PFOS). Herein, the influence of oxic/anoxic condition on the variation of redox and residual components of sediments, where organic matter, iron and manganese oxides are separated from the original sediment collected from Lake Taihu, China, are investigated. Meanwhile, the distinguishing sorption behaviors of PFOS on various residual sediments under oxic and anoxic condition are studied. Sediment after extracting iron and manganese (S_{-FeMn}), which possessed the highest organic carbon (0.99%), had the highest affinity for PFOS under oxic condition. However, anoxic environment resulted in an increase of the pH, dissolving of organic carbon and de-protonation of S_{-FeMn}, which caused the lower sorption capacity of PFOS on S_{-FeMn}. Sediment after extracting manganese (S_{-Mn}) had the higher sorption ability in anoxic environment because the Fe^{2+} from S_{-Mn} provided more effective electrostatic sites for anionic PFOS. When the environment changed to oxic condition, the iron existed as trivalent form in S_{-Mn}, which resulted in a block of effective sorption site and reduced the sorption amounts of PFOS. The higher percentage of manganese oxides restrained the sorption of PFOS. Hence, whether or not oxic/anoxic condition promoted the PFOS sorption depended on both the percentage and form of various components in the sediment. The study generated further insight into the environmental transport of PFOS in the sediments with different properties and the wetland system, where oxic/anoxic subsurface flow was constructed.

Keywords: Sediment components, oxic condition, anoxic environemnt, PFOS, sorption

1. INTRODUCTION

Perfluorooctane sulfonate (PFOS, $C_8F_{17}O_3^-$) is an emerging pollutant which has drawn considerable scientific and public concerns and has been detected in water and sediment environment (Ahrens et al., 2010; Beskoski et al., 2013; Pan et al., 2014; Ahrens et al., 2015). In the aquatic environment, PFOS behaves in a hydrophobic fashion and binds with sediment, rather than remaining in the aqueous phase (Higgins and Luthy, 2006). Sorption of PFOS on sediment is a significant process because it affects the fate and environmental transport of PFOS.

Sediment particles consist of organic matter and minerals which include clay minerals, iron oxides and manganese oxides and so on. Each of these components plays different role in the sorption of organic contaminants (Li and Werth, 2001), and the scavenging capacities depends on their percentage in the sediment. Higgings and Luthy (2006) indicated that sorption of PFOS on sediments was correlated with the organic carbon content. However, other authors argued that the inorganic materials such as the metal oxides affected the fate and transport of PFOS (Johnson et al., 2007; Zhao et al., 2014). The minerals might indirectly reduce the sorption capability of organic pollutants by blocking sorption sites (Bonin and Simpson, 2007). However, these studies were undertaken under oxic condition which were different from the natural environment (anoxic ambient).

The redox potential (Eh) and pH of the system affect the sorption behavior of PFOS on sediment. Therefore, the sorption of PFOS under anoxic condition is very vital due to dynamic changes of redox conditions during the process of sedimentation. As a result, variations take place in the format of the chemical composition of sediments. Eventually, these variations in local conditions affect the processes of migration and precipitation of chemical substances in water body and sediment. For example, the iron exists in the form of the precipitation of the ferric hydroxide, which blocks the effective sorption sites to reduce the uptake amounts in the oxic environment. However, Fe^{2+} was an important factor to remove a variety of organic and inorganic pollutants in natural anoxic condition (Rugge et al., 1998; Strathmann and Stone, 2000). The existence of Fe^{2+} improved the electrostatic interactions between the anions and the free iron oxide (Fink et al., 1970).The two contradictory results derived from the unilateral research which neglected the influence of natural environmental condition (oxic and anoxic) on the composition with different formation, which consequently affected the sorption behavior of PFOS on sediment. To some degree, the resulting distribution parameters and mechanism is unilateral considering the fact that the environmental condition at the sediment-water interface is mostly anoxic. Therefore, a detailed understanding of the transport and fate of PFOS in sediment must include the interaction with iron oxides, manganese oxides and organic matter on actual anoxic condition.

To the best of our knowledge, little is known about the influence of oxic or anoxic condition on the sorption behavior of PFOS on sediments with different components. Therefore, the objectives of this study are (1) to generate further insight into the partitioning and fate of PFOS as it happens in natural ambient condition (oxic and anoxic environment) in the subsurface environment and (2) to understand the relative contributions of the various sediment components to PFOS sorption and the interactions between these components, which influence PFOS fate.

2. MATERIALS AND METHODS

2.1. Standards and Reagents

The potassium salt of perfluorooctane sulfonate (PFOS, 98%) and ammonium acetate (99%) were purchased from Fluka (Milwaukee, WI, USA). Sodium perfluoro-[1,2,3,4]-$^{13}C_4$-octanesulfonate (MPFOS, 99%, 50 μg/mL solution in methanol) was provided by Wellington Laboratories (Canada). HPLC-grade methanol was obtained from Fisher Scientific Chemical (USA). All the other reagents used in the experiment were of analytical grades.

2.2. Sediment and Water Sampling

Surface sediment (top 1 – 5 cm) was collected from Lake Taihu, China, with a column sediment sampler (Beeker) and was kept in polypropylene (PP) bags at 4 ± 2 °C for the succedent analysis. The sediment was freeze-dried and passed through 0.2 mm sieves before being used. Water sample was collected using a PP bucket pre-cleaned with methanol and Milli-Q water on the same spot of sediment collection, and stored at 4 ± 2 °C after filtration.

2.3. Sediment Sequential Extraction

Residual sediments were obtained by extracting organic matter, iron and manganese oxides, respectively. $NH_2OH \cdot HCl$ (0.1 M) and HNO_3 (0.01 M) were used to remove manganese oxides, and the product was denoted as S_{-Mn} (Li et al., 2006). Both iron and manganese oxides were extracted with 0.2 M of $(NH_4)_2C_2O_4$ buffered with $H_2C_2O_4$ at pH 3.0 and shaken in the dark for 4 h, and the product was marked as S_{-FeMn} (Pei et al., 2006). Both NaOCl (0.1M) and H_2O_2 (30 %) were employed to remove organic matter (OM) based on previous reports (Kaiser and Guggenberger, 2003; Mikutta et al., 2005), and the products were denoted as S_{-OM1} and S_{-OM2}, respectively. The samples were centrifuged at 3800 rpm for 30 min, and supernatant was filtered (0.45 μm) into 50 mL of PP tube for the determination of Fe and Mn. The residual sediments were washed 4 times with filtered lake water (FLW) and air-dried. The extraction efficiency (EE) was calculated by the following equation. Note that the sediment to reagent ratio is 1:10.

$$EE = (C_{pt} - C_p) / C_t \times 100\% \tag{1}$$

Where C_{pt} is pseudo-total content; C_p is particle content after extraction; C_t is total extractable amount. Pseudo-total amounts (C_{pt}) of Fe and Mn were obtained by a flame atomic absorption spectrometer (AA6300, Shimadzu, Japan). The total extractable amounts (C_t) of Fe and Mn were determined using the modified sequential extraction procedure (Tessier et al., 1979; Yu et al., 2001). Organic matter was quantified by measuring the total organic carbon (TOC) using a TOC-VCPH instrument (Shimadzu, Japan). The cation exchange capacity (CEC) of sediment samples was determined following the conventional methods (Tao et al., 2006).

Specific surface area (BET) of the sample was determined on a surface area and pore size analyzer (ASAP 2000, Micromeritics, USA). The Fourier transform infrared (FTIR) spectrum of the samples were obtained on a FTIR spectrophotometer (NEXUS 670, Nicolet, USA) by KBr disk (contained 1 mg of the sample and 300 mg of dried KBr) with the 400–4000 cm^{-1} range. The resolution of FTIR spectroscopy was 2.0 cm^{-1}.

2.4. Water Sample Preparation and Analysis

Water sample from Lake Taihu was filtered through 0.22 μm fiberglass membranes before extraction to remove suspended particles and biota. All the water samples were extracted by solid phase extraction (SPE) with Oasis WAX cartridges (Waters, 6cc, 150mg, 30μm). The extraction procedure followed those were described in previous publication (Ahrens et al., 2010). The SPE cartridges were first preconditioned by passing through 4 mL of ammonium hydroxide in methanol, 4 mL of methanol, and then 4 mL of Milli-Q water in turn. Before loading to the cartridge, the water samples were spiked with 100 μL of 1 ng of MPFOS. The cartridges were rinsed with 4 mL of 25 mM ammonium acetate buffer (pH 4) in Milli-Q water and dried by centrifugation at 3000 rpm for 20 min. The elution was carried out with 4 mL of methanol and 4 mL of 0.1% ammonium hydroxide, and then reduced to 1 mL under a nitrogen stream.

An ultra performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) was used to determine the concentration of PFOS. UPLC system (Waters Corp., USA) was equipped with a C18 column and MS system is a Quattro Premier XE tandem quadrupole mass spectrometer equipped with an electro-spray ionization source. The analytical procedures were reported previously (Zhou et al., 2010; 2013). Spike and recovery experiments were performed to determine the precision and accuracy of the extraction and the analytical procedure. Method recovery rate ranged from 104.6% to 110.7% across all experimental conditions. The instrument limit of determination (LOD, signal-to-noise ratio 3:1) was 2 ng/L, while the limit of quantification (LOQ, 10:1 signal-to-noise ratio) was 7 ng/L. The PFOS concentration in FLW was 2.82 ± 0.02 ng/L.

2.5. Sorption Experiments

2.5.1. Oxic Sorption. In this study, oxic condition was achieved only by the spontaneous oxygen exchange between the overlaying water and the atmosphere at room temperature. Briefly, 0.5 g of dried sediment was added into each 50 mL of PP tube and mixed with 20 mL of 0.5 mM NaCl solution prepared with FLW. The initial concentrations of PFOS ranged from 400 – 1500 ng/L. A volume of 2 mL NaN_3 solution (200 mg/L) was added to each tube to inhibit any microbial activity. All tubes were shaken for 48 h at 25 ± 0.1°C in a 2D-shaker at 250 rpm at pH 7.0 ± 0.1. The tubes were centrifuged at 9000 rpm for 30 min. Supernatant was filtered through 0.22 µm PP membrane and analyzed by UPLC-MS/MS. Blank experiments were set up using the same solid-to-water ratios as the samples but without adding PFOS. One control sample with only the test substance in 0.5 mM NaCl solution (no sediment sample) was subjected to precisely the same steps as the test systems, in order to check the stability of the substance in NaCl solution and its possible sorption on the surfaces of the vessels. All the experiments, including controls and blanks, were carried out in duplicate. The amount of PFOS adsorbed on sediment (C_s, ng/g) was calculated as followed.

$$C_s = (C_0 - C_e) \times V_0 / M_s \qquad (2)$$

Where C_0 (ng/L) is the initial PFOS concentration; C_e (ng/L) is the equilibrium PFOS concentration; V_0 is the initial volume, and M_s is the mass (g) of sediment.

2.5.2. Anoxic Sorption. Two additional PP tubes containing the samples and NaCl solution were opened as surrogates for the other tubes to determine pH and oxidation-reduction potential (ORP) prior to the additions of PFOS. All of the tubes were purged continuously with high-purity N_2 gas inside the anoxic box to remove dissolved oxygen and then were capped and allowed to stand in darkness for several days. At different interval, the two surrogate tubes were opened inside the N_2 atmosphere to determine their pH and ORP. When the ORP in the surrogate tubes was negative, the other tubes were then injected with a volume of aqueous PFOS solution to obtain different initial concentrations (400 – 1500 ng/L). The other conditions were as same as the oxic sorption.

3. RESULTS AND DISCUSSION

3.1. Characterization of Original and Residual Sediments.

The basic characterizations of original and residual sediments were carried out under oxic condition. The treatment of the sediments exhibited highly variable CEC, Fe, Mn and organic matter amounts (Table 1). The trend in CEC was indicative of the extent to which the organic matter of each sediment had been removed. As expected, the lowest level of CEC was observed in sediment treated with NaOCl and H_2O_2, in which the products were recorded as S_{-OM1} and S_{-OM2}.

The TOC fraction and the ratio of Fe/Mn of the original sediment were approximately 1.13% and 8, respectively. The total amount of extractable Fe and Mn oxides from the original sediment was 240.34 μmol Fe/g and 37.28 μmol Mn/g, respectively. These extractable fractions corresponded to 65% and 80% of the pseudo-total Fe and Mn oxides, respectively. The sediment treated with $NH_2OH{\cdot}HCl$ reagent was recorded as S_{-Mn}, in which almost 80% of Mn but just only 28% of Fe oxides were effectively removed, respectively. Some authors had related the slight removal of Fe oxides by $NH_2OH{\cdot}HCl$ to be partly due to the binding form of Fe in the sediments and their existence in amorphous or carbonate form (Turner et al., 2004; Guo et al., 2006). Unlike $NH_2OH{\cdot}HCl$, treatment with $(NH_4)_2C_2O_2$ removed over 80% each of Fe and Mn oxides from the original sediment and only about 12% of organic matter was extracted simultaneously, in which the product was recorded as S_{-FeMn}.

The two approaches towards extracting the organic matter effectively removed more than 79% of the organic matter in each case. However, about 19% Fe and 24% Mn were simultaneously removed by H_2O_2 compared with about 11% each of Fe and Mn removed by NaOCl treatment. These treatments showed that it was impossible to completely isolate either of the minerals, Fe or Mn, without interference with each other.

3.2. Variation in pH, Redox Potential.

The pH values of all the samples system gradually increased while the oxidation-reduction potential (ORP) decreased after the three months of anoxic incubation (Table 2). Reduction reactions consume protons, which may increase the pH of the sediment solution (Stumm and Sulzberger, 1992). The Eh values of all the samples under anoxic condition were below the reported critical redox potential for the reduction of Fe (Eh = +300 to +100 at pH 6 – 7) (Gotoh and Patrick, 1974), suggesting that reduction of Fe^{3+} to Fe^{2+} should have occurred. The extent of reduction varied considerably due to the chemical nature of individual component. Thus, the redox potentials decreased from 271 to -75 mV in original sediment (UNTD), from 306 to -17 mV in S_{-Mn}, from 229 to -52 mV in S_{-FeMn}, from 244 to -39 mV in S_{-OM1}, and from 311 to -12 mV in S_{-OM2} (Table 2).

Concentrations of Fe^{2+} and Mn^{2+} were simultaneously monitored in two replicates containing none of the samples but just the aqueous solution. The drop in redox under anoxic conditions seemed to favor Fe reduction more than Mn reduction at the sediment–water interface as shown by the time-dependent release of iron and manganese to solution (Figure 1). The increase in dissolved iron as the condition became anoxic represented the reductive dissolution of iron hydroxides that formed during the oxidation experiment. It was noted that the presence of anoxic conditions did not significantly alter the amount of extractable Mn oxides from these sediments.

A general increase in the specific surface area was observed in all the treated samples compared with the original sample, and the higher values being recorded in samples from which the organic matter had been removed significantly (S_{-OM1} and S_{-OM2}) under oxic experimental condition (Table 2). This may partly be due to the fact that organic matter destruction uncovered mineral surfaces and rendered them accessible to N_2 gas, and also allowed N_2 molecules to enter the micropores within the domains. However, S_{-Mn} recorded the largest BET area under anoxic condition in contrast to the least value recorded under oxic atmosphere. The least of BET area was found in S_{-FeMn} among the treated samples. This was not surprising because as organic matter rich sample, it contained pores of <0.5 nm diameter where the diffusion of N_2 at 77K was kinetically restricted (De Jonge & Mittelmeijer-Hazeleger, 1996). Generally, the decline in specific surface area after reduction was concomitant with the transformation of ferric oxides to soluble Fe^{2+}.

3.3. Sorption Behavior and Mechanism.

An interesting finding observed in this study was that oxic/anoxic conditions had an opposite influence on the sorption of PFOS on the various sediments containing different components. For example, the oxic ambient promoted the sorption of PFOS on S_{-FeMn}. However, the sorption capability of PFOS under anoxic condition was better than that under oxic condition on S_{-Mn} (Figure 2). The original sorption data of PFOS under oxic and anoxic conditions in different types of sediments were shown in Table S1.

The chemical treatments with ammonium oxalate induced a carboxyl group (COO-) into S_{-FeMn}, which was obviously observed at 1625 cm^{-1} in the FTIR (Figure 3). Thus, apart from removing the mineral component (Fe and Mn), the treatment also protonated the carboxylic groups leading to a split of the joint bands of asym with comparatively high intensity (Mikutta et al., 2005). The protonation was contributed to the higher sorption capacity of S_{-FeMn} in oxic condition. When the environment changed to anoxic condition, the pH values gradually increased (Figure 4). The high pH value had been proved to promote organic matter desorption (Olivie-Lauquet et al., 2001; Gruau et al., 2004). Though S_{-FeMn} had the highest organic carbon (0.99%) among all the sediments in the oxic environment (Table 1), we found that the organic matter could be mobilized in reductive condition in the S_{-FeMn} (Figure 4). At the same time, the increase of the pH values in anoxic condition caused de-protonation of the carboxyl groups at mineral surfaces and thus decreased the positive net surface charge. Consequently, anionic

PFOS became more electronegative coupled with repulsion between S_{-FeMn} and PFOS. On the whole, the sorption capacity of PFOS on S_{-FeMn} decreased with decreasing of the redox potential and increasing of DOC. The result indicated that the samples containing abundant organic matter could effectively scavenge PFOS under oxic condition.

On the contrary, anoxic environment promoted the sorption of PFOS on S_{-Mn}. Though S_{-Mn} had 0.92% organic carbon, it possessed the higher percentage of residual Mn and Fe (Table 1), respectively. Previous study indicated that high amounts of ferrous and manganous ions were rapidly oxidized in air and tended to precipitate, thereby blocking sorption sites (Toth and Ott, 1970). The decrease of effective sorption sites resulted in a poor sorption capability of PFOS on S_{-Mn} in oxic ambient. The aqueous Fe^{2+} amounts from oxic to anoxic conditions increased from 0 to 0.53 mg/L after 95 days with nitrogen (Figure 1). However, the anoxic condition did not significantly alter the amounts of extractable Mn oxides of the sediment components. In anoxic natural habitats, Mn^{4+} is the only relevant oxidant of Fe^{2+} (Moraghan and Buresh, 1977; Myers and Nealson, 1988). This residual Mn, in the form of Mn^{4+} may not be sufficient to significantly oxidize the pre-formed Fe^{2+} in S_{-Mn} under anoxic condition. Thus, the increase of Fe^{2+} under anoxic conditions was responsible for the significant increase in sorption of PFOS on S_{-Mn}, which implied the electrostatic attraction between PFOS and Fe^{2+}-species. The study indicated that the sediment containing large number of iron could become important sink for PFOS in anoxic environment.

In contrast to the results obtained from S_{-FeMn} and S_{-Mn}, the alteration of PFOS concentration seemed to affect the sorption trend on S_{-OM1}, S_{-OM2} and UNTD (Figure 2). Anoxic condition was beneficial to sorption of PFOS at the range of low concentration. However, oxic ambient promoted the sorption of PFOS with higher concentration on these three sediments. It was worthwhile to note that the PFOS concentration used in the current study was relatively low so that semi-micelle formation was unlikely. Hence, trace level PFOS existed as separate anion. The sorption mechanism discussed above indicated that the hydrophobic partition of PFOS into organic matter on sediments was the primary driving force in oxic ambient. In anoxic environment, the electrostatic attraction between PFOS and Fe^{2+} was the main driving force during the sorption process. The common feature of these three sediments was that they contained the higher iron and manganese (Table 1). Hence, it was easy to understand that the sorption capacities of PFOS on S_{-OM1}, S_{-OM2} and UNTD in anoxic ambient were higher than that in oxic condition because a large amount of Fe^{2+} in anoxic ambient promoted the sorption of PFOS by electrostatic attraction between Fe^{2+} and anionic PFOS. When the concentrations of PFOS increased, the sorption on the three types of sediments trended to be saturated. Was it attributed to their lower specific surface areas in anoxic ambient? According to the specific BET area of S_{-OM1} in anoxic condition (28.97 m^2/g) and the lateral area of PFOS molecular (0.25 nm^2/molecular), these sediments supplied enough sorption space for the PFOS within the range of concentration in this experiment. Were the effective sorption sites limited? As mentioned above, the Fe^{2+} contributed to the high sorption capacity in anoxic condition. A mass of 0.5 g S_{-OM1} possessed 169.99 μmol of the iron content. Though the effective Fe^{2+} from S_{-OM1} in the anoxic environment was only 3.4 μmol based on the Figure 1, the effective electrostatic sites supplied by Fe^{2+} were abundant for PFOS within the range of concentration in this experiment. Hence, what resulted in the gentle sorption of PFOS in the anoxic ambient? As shown in Table 1, the contents of Mn in S_{-OM1}, S_{-OM2} and UNTD were much higher than that in other sediments. Since the anoxic conditions did not significantly alter the amount of extractable Mn amounts. The manganese oxides, which had more negative surface charge, restrained the interaction of PFOS with sediment particles (Johnson et al., 2007; Becker et al., 2008). In other words, the lower concentration of PFOS was not interfered by manganese oxides, whereas, the manganese oxides to some extent interfered with the PFOS as its concentration increased. Though most organic matter were removed from S_{-OM1} and S_{-OM2}, there were still some fractions remained in these residual sediments. Hence, hydrophobic partition of PFOS into organic matter on these sediments happened in oxic environment.

4. CONCLUSIONS

The sorption system and process were complicated. The variation of oxic and anoxic condition changed the redox properties of system, affected the form of sediment components, and consequently influenced the sorption capacity of PFOS on residual sediment. Whether or not oxic/anoxic condition promoted the sorption of PFOS depended on the percentage of various components of the sediment. Inspecting various factors, the samples containing abundant organic matter but lower amount of Fe and Mn oxides could effectively scavenge PFOS under oxic condition. The sediment containing large number of iron but lower amount of Mn could become important sink for PFOS in anoxic environment. However, anoxic condition promoted the sorption of PFOS at the range of low concentration on the sediment containing large amount of both Fe and Mn oxides. When the concentration of PFOS increased, negative charges of Mn oxides restrained the interaction of more anionic PFOS and Fe^{2+}-species. In oxic environment, the sorption of PFOS was not interfered by Mn oxides because the hydrophobic partition of PFOS into organic matter was the main driving force.

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REFERENCE

Ahrens, L., Norstrom, K., Viktor, T., Palm Cousins, A., Josefsson, S., 2015. Stockholm Arlanda Airport as a source of per- and polyfluoroalkyl substances to water, sediment and fish. Chemosphere 129, 33-38.

Ahrens, L., Taniyasu, S., Yeung, L.W.Y., Yamashita, N., Lam, P.K.S., Ebinghaus, R., 2010. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. Chemosphere 79, 266-272.

Becker, A.M., Gerstmann, S., Frank, H., 2008. Perfluorooctanoic acid and perfluorooctane sulfonate in the sediment of the Roter Main river, Bayreuth, Germany. Environ. Pollut. 156, 818-820.

Beskoski, V.P., Takemine, S., Nakano, T., Beskoski, L.S., Gojgic-Cvijovic, G., Ilic, M., Miletic, S., Vrvic, M.M., 2013. Perfluorinated compounds in sediment samples from the wastewater canal of Pancevo (Serbia) industrial area. Chemosphere 91, 1408-1415.

Bonin, J.L., Simpson, M.J., 2007. Variation in phenanthrene sorption coefficients with soil organic matter fractionation: The result of structure or conformation? Environ. Sci. Technol. 41, 153-159.

De Jonge, H., Mittelmeijer-Hazeleger, M.C., 1996. Adsorption of CO_2 and N_2 on soil organic matter: nature of porosity, surface area, and diffusion mechanisms. Environ. Sci. Technol. 30, 408-413.

Fink, D.H., Thomas, G.W., Meyer, W.J., 1970. Adsorption of Anionic Detergents by Soils. J. Water Pollut. Control Fed. 42, 265-271.

Gruau, G., Dia, A., Olivie-Lauqueta, G., Davranche, M., Pinay, G., 2004. Controls on the distribution of rare earth elements in shallow groundwaters. Water Res. 38, 3576-3586.

Guo, S.H., Wang, X.L., Li, Y., Chen, J.J., Yang, J.C., 2006. Investigation on Fe, Mn, Zn, Cu, Pb and Cd fractions in the natural surface coating samples and surficial sediments in the Songhua River, China. J. Environ. Sci.-China 18, 1193-1198.

Gotoh, S., Patrick, W.H., 1974. Transformation of iron in a waterlogged soil as influenced by redox potential and pH. Soil Sci. Soc. Am. J. 38, 66-71.

Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. Environ. Sci. Technol. 40, 7251-7256.

Johnson, R.L., Anschutz, A.J., Smolen, J.M., Simcik, M.F., Penn, R.L., 2007. The adsorption of perfluorooctane sulfonate onto sand, clay, and iron oxide surfaces. J. Chem. Eng. Data 52, 1165-1170.

Kaiser, K., Guggenberger, G., 2003. Mineral surfaces and soil organic matter. European J. Soil Sci. 54, 219–236.

Li, F.M., Wang, X.L., Li, Y., Guo, S.H., Zhong, A.P., 2006. Selective extraction and separation of Fe, Mn oxides and organic materials in river surficial sediments. J. Environ. Sci.-China 18, 1233-1240.

Li, J., Werth, C.J., 2001. Evaluating competitive sorption mechanisms of volatile organic compounds in soils and sediments using polymers and zeolites. Environ. Sci. Technol. 35, 568-574.

Mikutta, R., Kleber, M., Kaiser, K., Jahn, R., 2005. Review: Organic matter removal from soils using hydrogen peroxide, sodium hypochlorite, and disodium peroxodisulfate. Soil Sci. Soc. Am. J. 69, 120-135.

Moraghan, J.T., Buresh, R.J., 1977. Chemical Reduction of Nitrite and Nitrous-Oxide by Ferrous Iron. Soil Sci. Soc. Am. J. 41, 47-50.

Myers, C.R., Nealson, K.H., 1988. Microbial Reduction of Manganese Oxides - Interactions with Iron and Sulfur. Geochim. Cosmochim. Acta 52, 2727-2732.

Olivie-Lauquet, G., Gruau, G., Dia, A., Riou, C., Jaffrezic, A., Henin, O., 2001. Release of trace elements in wetlands: Role of seasonal variability. Water Res. 35, 943-952.

Pan, C.G., Ying, G.G., Liu, Y.S., Zhang, Q.Q., Chen, Z., Peng, F.J., Huang, G.Y., 2014. Contamination profiles of perfluoroalkyl substances in five typical rivers of the Pearl River Delta region, South China. Chemosphere 114, 16-25.

Pei, Z.G., Shan, X.Q., Wen, B., Zhang, S.Z., Yan, L.G., Khan, S.U., 2006. Effect of copper on the adsorption of p-nitrophenol onto soils. Environ. Pollut. 139, 541-549.

Rugge, K., Hofstetter, T.B., Haderlein, S.B., Bjerg, P.L., Knudsen, S., Zraunig, C., Mosbaek, H., Christensen, T.H., 1998. Characterization of predominant reductants in an anaerobic leachate-contaminated aquifer by nitroaromatic probe compounds. Environ. Sci. Technol. 32, 23-31.

Strathmann, T.J., Stone, A.T., 2000. Abiotic reduction of oxime carbamate pesticides by Fe(II): Catalytic role of mineral surfaces. Abstracts of Papers of the American Chemical Society 219, U620.

Stumm, W., Sulzberger, B., 1992. The Cycling of Iron in Natural Environments - Considerations Based on Laboratory Studies of Heterogeneous Redox Processes. Geochim. Cosmochim. Acta 56, 3233-3257.

Tao, Q.H., Wang, D.S., Tang, H.X., 2006. Effect of surfactants at low concentrations on the sorption of atrazine by natural sediment. Water Environ. Res. 78, 653-660.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace-Metals. Anal. Chem. 51, 844-851.

Toth, S.J., Ott, A.N., 1970. Characterization of Bottom Sediments - Cation Exchange Capacity and Exchangeable Cation Status. Environ. Sci. Technol. 4, 935-939.

Turner, A., Millward, G.E., Le Roux, S.M., 2004. Significance of oxides and particulate organic matter in controlling trace metal partitioning in a contaminated estuary. Mar. Chem. 88, 179-192.

Yu, K.C., Tsai, L.J., Chen, S.H., Ho, S.T., 2001. Chemical binding of heavy metals in anoxic river sediments. Water Res. 35, 4086-4094.

Zhao, L.X., Bian, J.N., Zhang, Y.H., Zhu, L.Y., Liu, Z.T., 2014. Comparison of the sorption behaviors and mechanisms of perfluorosulfonates and, perfluorocarboxylic acids on three kinds of clay minerals. Chemosphere 114, 51-58.

Zhou, Q., Deng, S.B., Fan, Q., Zhang, Q.Y., Yu, G., Huang, J., 2010. Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated sludge. Chemosphere 81, 453-458.

Zhou, Q., Pan, G., Zhang, J., 2013. Effective sorption of perfluorooctane sulfonate (PFOS) on hexadecyltrimethylammonium bromide immobilized mesoporous SiO_2 hollow sphere. Chemosphere 90, 2461-2466.

Table 1. Characterization of sediment pretreated by different procedures.

			TOC (%)		Fe		Mn	
		CEC			Content		Content	
Pretreatments	Abbre.	(cmol/kg)	Content	EE (%)	(μmol/g)	EE (%)	(μmol/g)	EE (%)
Original	UNTD	16.87	1.13		367.72±2.94		46.74±1.75	
$NH_2OH \cdot HCl$	S_{-Mn}	11.23	0.92	18.58	299.58±0.28	28.35	17.11±0.28	79.48
$(NH_4)_2C_2O_4$	S_{-FeMn}	9.01	0.99	12.39	165.64±0.12	84.08	16.24±0.91	81.81
NaOCl	S_{-OM1}	8.48	0.18	84.07	339.98±2.41	11.54	42.79±0.41	10.59
H_2O_2	S_{-OM2}	7.71	0.24	79.76	321.71±1.22	19.14	37.82±0.05	23.93
C_t			1.13	100	240.34±9.43		37.28±4.36	

Table 2. Experiment condition of sorption under oxic and anoxic environment.

Samples	pH		Eh (mV)		BET (m^2/g)	
	oxic	anoxic	oxic	anoxic	oxic	anoxic
UNTD	6.7±0.3	7.4±0.2	271±30	-75±22	20.41	13.47
S_{-Mn}	4.0±0.2	5.2±0.9	306±49	-17±15	29.22	45.84
S_{-FeMn}	5.4±0.2	6.8±0.4	229±62	-52±25	34.72	10.26
S_{-OM1}	7.1±0.3	7.5±0.3	244±38	-39±16	47.29	28.97
S_{-OM2}	6.9±0.5	7.4±0.3	311±56	-12±23	42.02	21.62

List of figure captions

Figure 1. Aqueous Fe^{2+} (a) and Mn^{2+} (b) produced via the reduction of sediment components under N_2 atmosphere and NaN_3 as microbial inhibitor in anoxic experiment.

Figure 2. Comparative sorption of PFOS under oxic and anoxic conditions on different types of sediments (a) S_{-FeMn}, (b) S_{-Mn}, (c) S_{-OM1}, (d) S_{-OM2}, (e) UNTD.

Figure 3. FTIR spectra of the residual and original samples.

Figure 4. Nitrogen time-variation of pH, Eh and DOC of S_{-FeMn} under anoxic condition.

Figure 1

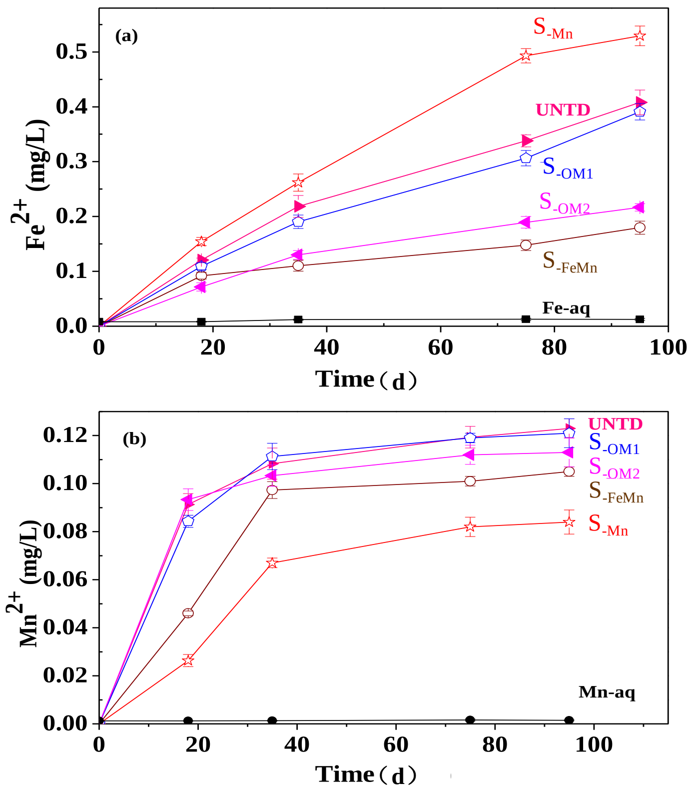

(a)
S-Mn
UNTD
S-OM1
S-OM2
S-FeMn
Fe-aq
Fe2+ (mg/L)
0.0
0.1
0.2
0.3
0.4
0.5
0
20
40
60
80
100
Time（d）
(b)
UNTD
S-OM1
S-OM2
S-FeMn
S-Mn
Mn-aq
Mn2+ (mg/L)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0
20
40
60
80
100
Time（d）

Figure 2

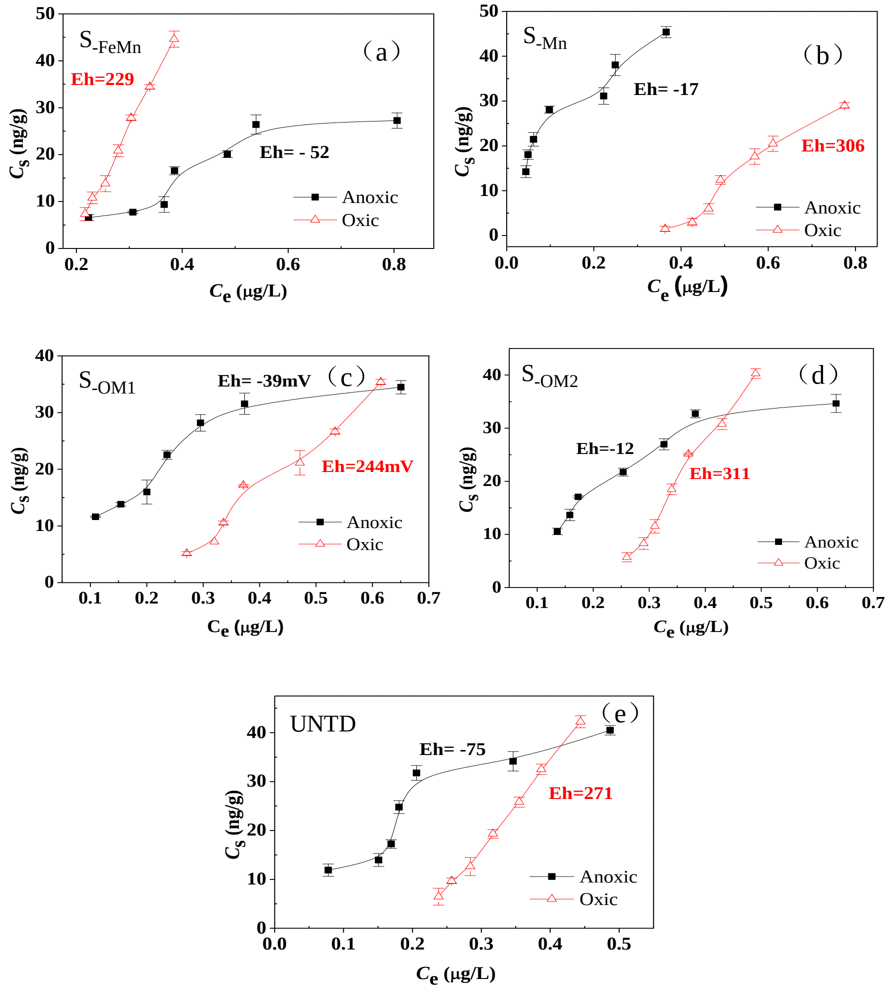
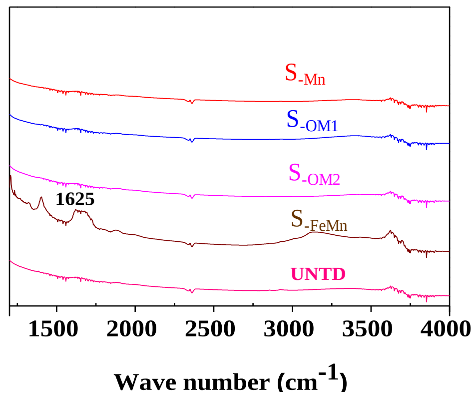
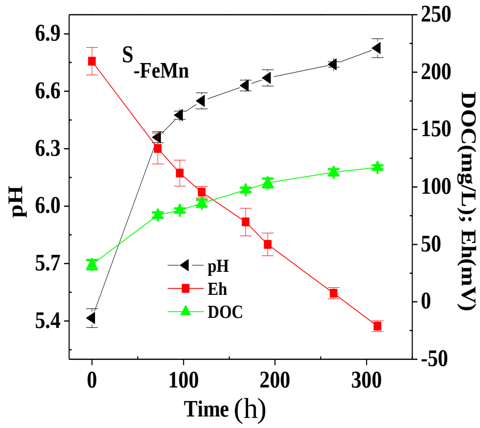

S-FeMn
(a)
Eh=229
Eh= - 52
Anoxic
Oxic
C_S (ng/g)
C_e (μg/L)
S-Mn
(b)
Eh= -17
Eh=306
Anoxic
Oxic
C_S (ng/g)
C_e (μg/L)
S-OM1
Eh= -39mV
(c)
Eh=244mV
Anoxic
Oxic
C_S (ng/g)
C_e (μg/L)
S-OM2
(d)
Eh=-12
Eh=311
Anoxic
Oxic
C_S (ng/g)
C_e (μg/L)
UNTD
(e)
Eh= -75
Eh=271
Anoxic
Oxic
C_S (ng/g)
C_e (μg/L)

Figure 3



S-Mn
S-OM1
S-OM2
1625
S-FeMn
UNTD
1500
2000
2500
3000
3500
4000
Wave number (cm-1)

413 **Figure 4**



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