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Urban sediment contamination with heavy metals and organic matter in Southern China

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Review

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ABSTRACT

Urban sediments in Wenzhou City were found polluted with heavy metals (As, Hg, Cr, Pb, Cu, Cd, and Zn) and organic matter. Metal speciation also showed environmental risks of heavy metals in river sediments. Heat energy in the sediment can amount to 47% of that in standard coal. Investigations revealed 35 urban wetlands of 15 big cities in southern China were at ecological risks posed by heavy metals and excessive nutrients in sediments. Toxic metals and organic carbon must be taken into consideration when planning to project urban wetlands.The dredging of such sediments could possibly increase greenhouse gases emission that should be further investigated. It is also suggested to examine energy recycling from these wetland sediments.

Keywords: Urban sediment, Heavy metals, Organic carbon, South China, Greenhouse gas emission

1. INTRODUCTION

With rapid economic development for 4 decades, wetland sediments in most cities in China have been polluted at different levels by heavy metals [1,2]. Sediments are important storage sites of heavy metals and the potential sources of pollution. The Chinese tradition that sediments are dug from human impacted rivers and then used as fertilizers for farming can be traced back thousand years ago. Metals and metalloids accumulated in sediments pose environmental problems concerning metals being transferred from solid phases to the aquatic medium and thereby included in the food chain [3].

Urban wetlands play an important role in maintaining the environmental systems of cities in southeastern China where population is large, economy is active and rainfall is plentiful. These wetlands accept discharges from residential houses, factories, schools, offices, farms and rainwater which lixiviate and scour land surfaces, thus leading to the accumulation of organic and inorganic matters in the sediments. The fate of organic carbons in sediments has become a challenging issue, especially when they are exposed to air after dredging. The present study is then to investigate organic carbon in an urban wetland in Wenzhou City, southeastern China, while the implication on potential greenhouse gas emission from urban sediment is also discussed.

2. MATERIAL AND METHODS

We analyzed 31 sediment samples collected from 2 representative rivers (21 samples from R_A and 10 for R_B) in the urban area of Wenzhou, a prefecture city in southeastern China to assess contamination by heavy metals and organic matter. Total contents of heavy metals (As, Hg, Cr, Pb, Cu, Cd, and Zn) and their chemical forms were determined by using sequential extraction [6]. Ecological Risk Index (RI) [4] and Risk Assessment Code (RAC) [5]were employed to evaluate ecological and environmental risks of the rivers impacted by heavy metals. Ratio of second phase (the sum of exchangeable, oxidible, reducible fractions, labeled F1, F2 and F3)to primary phase (residual fraction, F4) (RSP) was adopted to describe metal speciation in sediment [3,7]. Total contents and chemical forms of organic carbon were analyzed by using potassium dichromate sulfuric acid spectrophotometry [8]) and ^{1}H NMR methods[9]. Organic index (calculated by the multiplication of carbon fraction and nitrogen fraction) [10] was employed to assess organic pollution level.

We also consulted literature published in Chinese on toxic metals in wetlands impacted by big cities in south China, giving a big picture of heavy metal and organic pollution in urban sediments. Potential greenhouse gas emission and recycling of organic - rich sediment in urban areas of representative big cities in China was also discussed.

3. RESULTS AND DISCUSSION

3.1 Heavy metals and risks of urban sediments in Wenzhou

3.1.1 Total contents and RI

The mean values of total contents of heavy metals (mg g-1) in the R_A was in the order of Zn (810.46, ±292.94) > Pb (228.73, ±57.67) > Cr (129.14, ±48.14) > Cu (102.66, ±46.71) > Cd (101.56, ±18.07) and R_B was Zn (1193.45, ±403.12) > Cu (332.40, ±180.34) > Cr (300.80, ±83.93) > Pb (97.25, ±21.06) > Cd (9.64, ±2.66). And the values of RI in R_A and R_B were (18208.53, ±3235.69) and (268.77, ±325.41), respectively. The contamination of heavy metals in the sediments of R_A (High risk) was more serious than that in the R_B (Considerable Risk).

3.1.2 RSP and RAC

Total metal content in polluted environmental samples is a poor indicator of bioavailability, mobility or toxicity and all of these depend on the different chemical forms of binding between trace metals and solid phases of the samples. The order of RSP in R_A was Zn (7.65, ±4.45) > Cd (2.93, ±0.84) > Cu (2.00, ±0.83) > Pb (1.46, ±0.47) > Cr (1.11, ±0.46), while the order of that in R_B was Cd (3.64, ±1.41) > Pb (0.63, ±0.13) > Cu (0.60, ±0.20) > Zn (0.37, ±0.10) > Cr (0.30, ±0.06). According to RAC, RA were assessed Zn, Cu, and Cr at low risk, Pb at medium risk and Cd at high risk, while R_B were assessed Cu and Cr at low risk and Zn, Pb, and Cd at Medium risk.

3.2 Heavy metal risks of urban sediments in south China

Thirty five urban wetlands in 15 big cities in southern China were contaminated by heavy metals according to RI assessments Urban rivers were closer to industrial and residential facilities than lakes, consequently being more impacted. Nineteen rivers were assessed 6 at High Risk, 9 at Considerable, 1 at Moderate and 3 at Low Risks, while lakes were 11 at Low and 5 at Moderate Risks (Table 1 and 2).

3.3 Organic carbon of urban sediment in Wenzhou

The contents of surface sediment organic carbon in Sanyang Wetland in Wenzhou ranged from 17.94 to 50.57mg/g, with an average value of 31.91mg/g and a standard deviation of ±17.50mg/g, and the heavy organic carbon fraction accounted for 97.44- 98.71% of the total organic carbon. The mean ratio of C/N was 13.64 with a standard deviation of ±0.78. The carbon fraction measured by 1H NMR was ranked as follows: Aliphatic group > Alkoxy group > Phenyl > Carboxyl > Acetal group, with a value of 38.38%, 21.79%, 18.08%, 18.03% and 3.4%, respectively. The high oxidation of organic carbon in sediments implied human impacts and anthropogenic sources from terrestrial areas.

The organic indexes of 9 urban wetland sediment samples ranged from 0.2413 to 1.769, with an average of 1.124, falling into the highest level Ⅳ. The results indicate that the sediments were highly impacted by anthropogenic activities.

3.4 Organic carbon in urban sediments of southeastern Chinese cities

3.4.1 Organic carbon contents

Total organic carbon of 17 selected urban wetlands in southern China was averaged at 39.77g/kg with a range from 2.68 to 129.0g/kg. These cities (including 9 provincial capitals) all have a population of over 2 million, and their wetlands have been polluted with organic matter. Fourteen of these selected urban wetlands had organic pollution level of III and IV, and other three had pollution at level II.

3.4.2 Global change issues related to ex situ disposal of polluted sediment

With increasing contamination of urban wetlands and heightening awareness of environmental protection, many cities in China have been or are planning dredging polluted sediments for better wetlands. In south China, urban wetlands are in big number and cover large areas of land, resulting in huge volume of polluted sediments. For example, Wenzhou is a coastal prefecture city with about 2 million of population and 910 km^2 of terrestrial land. Its three urban districts have 229 km^2 of water bodies (urban rivers, lakes and ponds), among which Sanyang Wetland has received increasing attention. Oure previous results indicated that there was 1.4 million m^3 of organic polluted sediments in 3.2 km^2 of rivers in this wetland[11]. The municipal government of Wenzhou has implemented the remediation and restoration of polluted rivers since 2005. However, the exposure of organic rich sediments to air after dredging led to various concerns because the oxidation of organic matter may increase the emission of carbon dioxide and other greenhouse gases.

3.4.3 Energy recycling

Organic polluted sediments contain valuable heat energy. The calorific values of sediments were 13010 - 18481 kJ/kg (i.e. about 47% of that of standard coal) for Sanyang Wetland and 7000 – 10000kJ/kg for Dianchi Lake [12]. It is thus possible to recycle heat energy from polluted sediment as a substitute of coal. The sediments can also be used for the production of brick or ceramics, honeycomb briquettes and so on.

Table 1. Heavy metal contents (mg g-1)and Potential Ecological Risk Index (RI) of 35 urban wetlands in 15 big cities, South China

Literature cited	City	Wetland	As	Hg	Pb	Cu	Cr	Cd	Zn	RI
Zhang et al.,2013	Hangzhou	Jiangcun River	-	-	31.0	53.3	-	2.7	212.7	Considerable risk
Zhang et al.,2013	Hangzhou	Yuhangtang River	-	-	25.2	51.8	-	2.5	239.6	Considerable risk
Zhang et al.,2013	Hangzhou	Grand Canal	-	-	37.7	35.6	-	2.4	287.5	Considerable risk
Zhang et al.,2013	Hangzhou	Xinkai River	-	-	22.9	131.6	-	2.1	311.9	Considerable risk
Zhang et al.,2013	Hangzhou	Shangtang River	-	-	26.9	61.8	-	2.2	365.0	Considerable risk
Shao et al.,2007	Hangzhou	Xixi Wetland(lake)	6.3	0.2	39.2	36.8	64.9	0.23	91.5	Low risk
Pan et al.,2014	Hangzhou	Hemu Wetland(lake)	-	-	41.6	85.6	86.6	-	383.0	Low risk
Tang et al.,2014	Ningbo	Huilong River	-	-	21.2	53.3	43.9	0.2	762.8	Low risk
Ma et al.,2011	Nanjing	Yueya Lake	-	-	54.3	65.3	63.2	4.1	439.2	Moderate risk
Ma et al.,2011	Nanjing	Zixia Lake	-	-	20.9	37.5	13.5	2.5	77.7	Moderate risk
Ma et al.,2011	Nanjing	Pipa Lake	-	-	21.0	13.2	18.7	1.2	62.0	Low risk
Ma et al.,2011	Nanjing	Qian Lake	-	-	45.5	33.1	22.1	2.5	153.5	Moderate risk
This study	Wenzhou	Sanyang River (RA)	-	-	216.3	92.8	123.0	106	871.0	High risk
This study	Wenzhou	Weisipu River (RB)			97.3	332.4	300.8	9.6	1193.5	Considerable risk
Zhou et al.,2008	Shanghai	Suzhou River	-	-	39.2	234.4	44.2	2.0	512.7	Considerable risk
Dai et al.,2010	Shenzheng	Shenzheng River	15.7	0.47	80.7	124.3	93.7	0.71	528.7	Considerable risk
Dai et al.,2010	Shenzheng	Buji River	10.5	0.41	63.2	204.0	218.1	1.26	742.4	High risk
Dai et al.,2010	Shenzheng	Longgang River	18.6	0.44	115.2	2243	2157	3.25	2756	High risk
Dai et al.,2010	Shenzheng	Maozhou River	11.2	0.20	42.7	145.0	117.0	0.33	289.0	Moderate risk
Qiu et al.,2016	Hengyang	Xiangjiang River	103.0	0.34	273.0	141.0	57.2	39.5	905.6	High risk
Zhao et al.,2012	Nanjing	Xuanwu Lake	-	-	41.5	35.5	68.9	0.5	145.4	Moderate risk
He et al.,2009	Chongqing	Qingshui stream	-	-	40.4	171.4	316.6	0.85	1023	Considerable risk
Zhang et al.,2012	Hefei	Nanfei River	-	-	22.6	41.2	55.2	0.34	129.4	Low risk
Zhang et al.,2007	Hengshui	Hengshuihu Lake	18.6	0.1	20.4	26.1	54.9	0.02	61.9	Low risk
Gong et al.,2006	Nanchang	Poyang Lake (east)	-	-	84.0	43.5	-	1.6	177.0	Low risk
Li et al.,2016	Fuzhou	Mingjiang River	-	-	79.1	42.3	66.6	0.9	195.6	High risk
Qiao et al.,2005	Wuhan	Moshui Lake	30.3	0.18	69.5	76.1	189.0	0.61	650.0	Low risk
Qiao et al.,2005	Wuhan	Jinyin Lake	16.6	0.18	40.7	80.9	178.0	0.61	195.0	Low risk
Qiao et al.,2005	Wuhan	Liangzi Lake	25.5	0.1	50.1	44.4	121.0	0.58	120.0	Low risk
Qiao et al.,2005	Wuhan	Lu Lake	15.1	0.1	44.0	44.6	116.0	0.46	127.0	Low risk
Qiao et al.,2005	Wuhan	Tangxun Lake	24.6	0.12	39.3	49.6	113.0	0.56	138.0	Low risk
Li et al.,2016	Wuhan	East Lake	-	-	51.8	35.9	85.7	0.3	166.8	Low risk
Wang et al.,2015	Dongguan	Danshui River	-	0.43	118.5	289.5	301.5	-	993.5	High risk
Wang et al.,2015	Dongguan	Xizhi River	-	0.08	53.4	14.0	32.5	-	114.4	Low risk
Wang et al.,2015	Dongguan	Dongjiang River	-	0.18	104.9	179.0	99.0	-	289.0	Considerable risk
Wei et al.,2010	Suzhou	Suzhou urban river	-	-	74.7	75.6	115.2	-	283.7	Low risk

*Fifteen cities : 2 Province level (Chongqing' Shanghai); 6 Provincial capitals (Changsha, Hangzhou, Hefei, Nanchang, Nanjing,Wuhan); and 7 Prefecture cities (Dongguan, Hengyang, Hengshui, Ningbo, Shenzhen, Suzhou, Wenzhou)

Table 3. Organic carbon contents and organic indexes of urban wetland sediments in 17 cities, southeastern China

City	Urban Wetland	Urban population (million)	Literature	TOC (g/kg)	organic index	Organic pollution level	Remarks
Shanghai	Huangpu river	20.69	Peng et al., 2008	10.03	0.2192	III	Municipality directly under the Central Government
Nanjing	Qinhuai river	6.78	Ye et al.，2011	12.92	0.1568	II	The capital of Jiangsu Province
Suzhou	Miaojia river	8.02	Feng et al.，2010	46.00	1.921	IV	
Wuxi	Wuxi section of Jinhang canal	4.94	Shan, 2001	20.20	0.3832	III	
Hangzhou	West lake	4.95	Li et al.,2015	129.0	6.784	IV	The capital of Zhejiang Province
Ningbo	Dongqian Lake	5.20	Ran et al.,2007	24.59	0.4438	III	
Wenzhou	Sanyang wetland	6.20	This study	31.91	1.124	IV	
Wuhan	South Lake	8.59	Wei，2010	65.69	2.010	IV	The capital of Hubei Province
Nanchang	Aixi Lake	3.31	Zhang，2007	128.4	4.118	IV	The capital of Jiangxi Province
Hefei	Nanfei river	5.67	Li et al.，2013	49.25	1.248	IV	The capital of Anhui Province
Wuhu	Jing Lake	2.32	Wang，2007	12.02	0.2386	III	
Changsha	Tiane Lake	3.04	Wang，2010	31.91	0.4032	III	The capital of Hunan Province
Nantong	Tongjia river	4.70	Tang，2016	26.10	0.7389	IV	
Fuzhou	Youxizhou wetland	5.19	Jia，2009	14.72	0.1105	II	The capital of Fujian Province
Xiamen	Yundang Lake	3.49	Zheng et al.，2013	2.683	0.07011	II	
Guangzhou	Guangzhou section of Pearl River	12.08	Li，2014	30.58	0.6465	IV	The capital of Guangdong Province
Changzhou	Chaizhibang river	3.34	Tang，2014	40.03	1.360	IV	

4. CONCLUSIONS

Two representative rivers (RA and RB) in the urban area of Wenzhou City were found contaminated by heavy metals. RA and RB were assessed High Risk and Considerable Risk respectively by RI. And RSP and RAC indicated contamination of urban sediments in Wenzhou with high risk of Cd in the RB and low and medium risks of other metals in both RA and RB. Thirty five urban wetlands in 15 big cities in southern China were assessed 15 at High and Considerable and 20 at Moderate and Low risks. Urban sediments can no more be used as fertilizers or soil amendments applied to croplands and any other soils.

Sediments of Sanyang Wetland in Wenzhou have been polluted by organic matter with organic carbon content up to 50 mg/g. Aliphatic group accounted for 38% of the total organic carbon, presenting high oxidation level. Seventeen urban wetlands in the big cities in southern China were evaluated for their pollution with organic matter, and the results indicated that urban sediments were rich with organic carbon. Improper disposal of such polluted sediments can accelerate organic matter oxidation and consequently increase the emission of greenhouse gases. It is suggested to further research into polluted sediments as a carbon sink and a greenhouse gas source. Furthermore, the high caloric value of urban sediments could lead to great potential for energy recycling, and the feasibility to utilize these organic rich sediments as a potential energy needs further investigation and validation.

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