



Risk assessment of heavy metals in pipe scales and loose deposits formed in drinking water distribution systems

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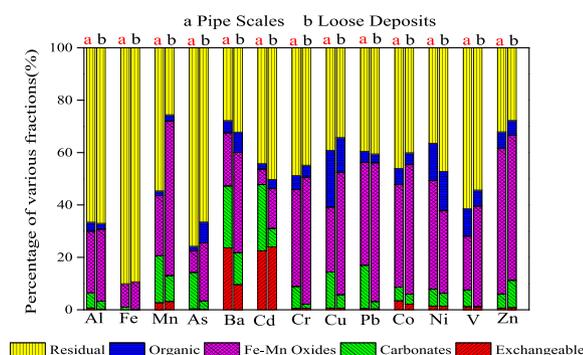
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HIGHLIGHTS

- Form and risks of heavy metals accumulated in drinking water pipes were studied.
- Ba, Cu and As were accumulated during the formation of Al and Mn commixtures.
- Thirteen inorganic contaminants were primarily bound with highly stable fractions.
- Heavy metals in loose deposits were more harmful.
- Cd and Ba had the highest risk among all heavy metals.

GRAPHICAL ABSTRACT



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ABSTRACT

The accumulation of inorganic contaminants in drinking water distribution systems (DWDS) can greatly threaten water quality and safety. This work mainly focused on the accumulation, speciation and risk assessment of inorganic contaminants found in pipe scales and loose deposits in DWDS. Global contamination factor (GCF), risk assessment code (RAC) and consensus-based sediment quality guidelines (CBSQGs) were adopted for the potential health risk assessment of inorganic contaminants. The Tessier sequential extraction method was used to study the speciation distribution of inorganic contaminants in fourteen samples (six pipe scale samples, eight loose deposit samples) collected from real DWDS. The significant correlation between Al and Mn showed there was a co-occurrence behavior of Al and Mn in pipe scales and loose deposits. In addition to the possible interactions between Al and Mn, Ba, Cu and As were possibly accumulated during the formation of Al and Mn commixtures. Mn, Cu, Pb, Zn, Ni, Co and Ba in the samples were mainly associated with the Fe-Mn oxides fraction, which indicated Fe-Mn oxides might play an important role in the accumulation and release of these inorganic contaminants. Fe, Al, As, Cr, V and Cd mainly existed in the residual fraction, which indicated their low mobility. The GCF results demonstrated that most of the sample sites had a certain environmental risk. The RAC results showed that high risk mainly resulted from Cd both in pipe scales and loose deposits. According to the CBSQGs evaluation, heavy metals in loose deposits were more harmful, and Ba exhibited the highest risk among all heavy metals.

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1. Introduction

The accumulation of inorganic contaminants in drinking water distribution systems (DWDS) has gained considerable attention over the past several years (Peng et al., 2010, 2012; Sun et al., 2017; Yang et al., 2017). These studies have demonstrated that while inorganic contaminants are typically present only at trace levels in treated water, inorganic contaminants can accumulate in DWDS pipe scales and loose deposits. For example, Lytle et al. reported that iron-based solids accumulated in DWDS, such as corrosion scales (e.g., α -FeOOH, Fe_3O_4 , CuO , PbO_2) and sediment (e.g., MnO_2 , $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$), could have a strong affinity to absorb and concentrate arsenic (Lytle et al., 2004).

Under normal circumstances, the trace-level contaminants accumulated in solid phases do not pose a health risk; however, accumulated inorganic contaminants could be potentially released back into the water supply, which may cause elevated levels at consumers' taps (Li et al., 2018). When the solid-liquid equilibrium between pipe scales and the water phase are destabilized, the release of contaminants into the water can occur via several mechanisms. The mechanisms include physical destabilization, chemical destabilization and microbiological destabilization (Sun et al., 2014; Yang et al., 2014). The chemical destabilization phenomenon can be attributed to the remobilization of contaminants via desorption and/or dissolution (Yang et al., 2012). For example, in United States, there was a sudden release of lead due to a switch in the water supply in Flint. This emergency led to the discoloration of tap water and the increase of blood lead levels in children (Liu et al., 2017). The potential ecological risk of inorganic contaminants is not only related to its total content, but more importantly is related to their existence forms. Inorganic contaminants are present in various forms in pipe scales and its different forms have different mobility and availability. For these reasons, it is necessary to identify and quantify the forms of inorganic contaminants in DWDS to gain a more precise understanding of the potential and actual impacts of elevated levels of inorganic contaminants in pipe scales.

Currently, to our knowledge, only Peng and Korshin (2011) had tried to study the speciation of inorganic contaminants accumulated in pipe scales that formed in DWDS. However, many sequential extraction procedures have been widely applied to estimate the speciation of inorganic contaminants in soils and natural water sediments. Therefore, the fractionation method employed to determine the speciation of heavy metals in natural water sediments and soils could be expected to be used for reference in a risk assessment of pipe solids. Peng and Korshin applied the sequential extraction methods to examine the speciation of several inorganic contaminants in samples of DWDS corrosion scales (Peng and Korshin, 2011). Commonly used selective sequential extraction procedures include the Tessier method and its modifications, as well as the three-step sequential extraction procedure proposed by the Community Bureau of Reference (BCR method) (Liang and Zhu, 2016; Okoro et al., 2014; Yin et al., 2016; Zhang et al., 2017). The first comprehensive and fundamental idea of sequential extractions to determine the chemical forms of inorganic contaminants in soils and sediments was developed by Tessier (Tessier et al., 1979). In this work, the five-stage procedure proposed by Tessier was attempted for the assessment of the speciation of trace inorganic contaminants in pipe scales and loose deposits formed in DWDS.

Among inorganic contaminants, metal contaminants are more harmful due to their toxicity, wide source, abundance, persistence and environmental non-degradability. Therefore, the application of some significant guidelines is urgently needed to assess the potential ecological risk of heavy metals in pipe scales and loose deposits. Many methodologies have been developed to assess the ecological risks of heavy metals, like the consensus-based sediment quality guidelines (CBSQGs), global contamination factor (GCF), the geo-accumulation index, contamination factor, degree of contamination and risk assessment code (RAC) (Barrio-Parra et al., 2018; Dabioch et al., 2013; Soliman et al., 2018). However, insufficient efforts in the risk assessment of heavy

metals in pipe scales and loose deposits via the aforementioned approaches have been reported.

In this work, we applied a five-stage procedure to analyze the speciation distribution of metal-type inorganic contaminants (Fe, Al, Mn, As, Cd, Cr, Pb, Ba, Cu, Zn, Co, Ni, and V) in 14 representative samples collected from a real DWDS of a northern city in China. To assess the potential risk, three indices, GCF, RAC and CBSQGs, were used. Through the research, it was possible to determine the levels, accumulation and speciation of the above inorganic contaminants in real DWDS samples and assess the potential mobility or toxicity of heavy metals. Meanwhile, we also assessed the potential health risks of inorganic contaminants in pipe scales and loose deposits.

2. Experimental procedure

2.1. Sampling and pretreatment of samples

Fourteen samples collected from different sites were named S1-S14, of which S1-S6 were pipe scales, and S7-S14 were loose deposits collected by hydrant flushing. The collected samples were dried in a freeze dryer and stored. Prior to all experimental procedures, the samples were crushed using an agate mortar, then passed through a 160-mesh sieve and homogenized.

2.2. Selective sequential extraction procedures

Speciation of the selected inorganic contaminants in pipe scales and loose deposits collected from DWDS were determined via the five-stage procedure proposed by Tessier (Tessier et al., 1979). The detailed steps of the sequential extraction are given in the supporting information.

2.3. Evaluation index

2.3.1. Global contamination factor (GCF)

To describe the potential bioavailability of heavy metals at different sampling sites, individual contamination factors (ICF) and global contamination factors (GCF) were calculated for all samples. In this study, the ICF for the various sampling sites were calculated by dividing the sum of the four extractions (exchangeable, carbonates, Fe-Mn oxides and the organic fraction) by the residual fraction for each site (Matong et al., 2016).

The GCF was calculated through the summation of the ICF for all the heavy metals obtained for each site. The ICF and GCF were classified as follows: $\text{ICF} < 1$ & $\text{GCF} < 6$ - indicates low risk, $1 < \text{ICF} < 3$ & $6 < \text{GCF} < 12$ - moderate risk, $3 < \text{ICF} < 6$ & $12 < \text{GCF} < 24$ - considerable risk and $\text{ICF} > 6$ & $\text{GCF} > 24$ - high contamination risk. The ICF and GCF were calculated by the following equations:

$$\text{ICF}_{\text{metal}} = \frac{C_{\text{nonresidual}}}{C_{\text{residual}}} \quad (1)$$

where $C_{\text{nonresidual}}$ is the sum of the nonresidual fractions ($\text{mg} \cdot \text{kg}^{-1}$) (which consist of exchangeable, carbonates, Fe-Mn oxides and the organic fraction). C_{residual} is the concentration of the residual fraction of each heavy metal ($\text{mg} \cdot \text{kg}^{-1}$).

$$\text{GCF} = \sum \text{ICF}_i \quad (2)$$

where $\sum \text{ICF}_i$ is the sum of the ICF value of the heavy metals for each site (As, Cd, Cr, Pb, Ba, Cu, Zn, Co, Ni, and V).

2.3.2. Risk assessment code (RAC)

Trace heavy metals associated with the first two fractions (exchangeable and carbonates fraction) were considered bioavailable, and because of their weak bonds with the solid phase, may equilibrate with the aqueous phase. The percentage of metals in exchangeable

and carbonates fractions was given an indication of the sediment reactivity and has been widely used to assess the potential risks associated with the presence of heavy metals (Pardo et al., 1990). The risk assessment of collected samples was carried out by assigning a risk assessment code (RAC, Table 1) based on the percentage of bioavailable metal in the samples. Table 1 shows the evaluation index of RAC (Nasr et al., 2018). The RAC were calculated by the following equations:

$$\text{RAC} = \frac{C_{\text{exchangeable}} + C_{\text{carbonates}}}{\sum C_i} \times 100\% \quad (3)$$

where $C_{\text{exchangeable}}$ and $C_{\text{carbonates}}$ are the concentrations of the exchangeable and carbonates fractions of each heavy metal ($\text{mg} \cdot \text{kg}^{-1}$). $\sum C_i$ is the sum of all the fractions of each heavy metal ($\text{mg} \cdot \text{kg}^{-1}$).

2.3.3. Consensus-based sediment quality guidelines (CBSQGs)

Consensus-based sediment quality guidelines (CBSQGs), a major evaluation tool for sediment quality assessment, were very useful in assessing the potential risk of heavy metals by comparing sediment contaminant concentrations with the corresponding quality guidelines (MacDonald et al., 2000). Generally, the CBSQGs included two thresholds, the threshold effect concentration (TEC) and the potential effect concentration (PEC). If the concentration of the heavy metal was smaller than the TEC values, it could be considered that the pollution intensity of the heavy metal was weak; once the concentration was larger than the PEC values, harmful biological effects deserved to be considered. The CBSQGs values of the eight toxic metals are listed in Table 2 (MacDonald and Ingersoll, 2010).

2.4. Chemical analyses

The concentrations of the inorganic contaminants were determined by inductively coupled plasma atomic emission spectrometry (ICP-OES, OPTIMA 2000, PerkinElmer, USA) for high levels of metals, and inductively coupled plasma mass spectrometry (ICP-MS, NexION 300X, PerkinElmer, USA) for low levels of metals. Each measurement was carried out in triplicate to ensure the accuracy of the data. All samples were determined in duplicate, and the relative errors were approximately $\pm 5\%$. The quality control for the five-stage procedure was calculated from the difference between the total metal concentration and sum of the five fractions. In general, a recovery of 80–120% is common in a sequential extraction method.

2.5. Statistical analyses

SPSS 22.0 was used to perform the statistical description and correlation analyses. Pearson's correlation coefficients were used to calculate correlation relationships between the different inorganic contaminants in pipe scales and loose deposits. A p -value of <0.05 ($p < 0.05$) was considered a statistically significant correlation.

3. Results and discussion

3.1. Total content of inorganic contaminants in pipe scales and loose deposits

The total concentrations of inorganic contaminants in pipe scales and loose deposits are presented in Table 3. Among the inorganic contaminants found in pipe scales and loose deposits, Fe had the highest concentrations, followed by Al, Mn, Ba, Zn, Cu, Ni, Cr, V, Pb, As, Co, and Cd. Compared with the loose deposits, pipe scales tended to have higher concentrations of inorganic contaminants.

As indicated, certain amounts of inorganic pollutants have been accumulated in pipe scales and loose deposits. All samples contained some toxic heavy metals, such as Ba and Cd. Peng reported that the average Ba, Pb and As in scale samples, which were collected from 20 drinking water utilities across 12 states of the US, reached 228, 366 and 81 $\mu\text{g/g}$, respectively (Peng et al., 2012). The concentration of Pb in the US DWDS scale samples was much higher than that in the samples taken in this study. It could be because lead pipes had been used in the history of the United States (Świetlik et al., 2012; Triantafyllidou and Edwards, 2012; Wang et al., 2012a), and there is still a stock of lead pipes currently. In addition, copper pipes and lead copper pipes were commonly used for household tubing materials, and lead-containing solders had been applied for copper tubing installation. Even though the use of lead pipe in service lines or premise plumbing was prohibited in the US, older buildings might still be connected to lead service lines, lead goosenecks, and other pure lead components. Many studies have found that the release of lead into drinking water systems due to the corrosion of lead-bearing materials continued to be a major public health concern in the US (Masters and Edwards, 2015). However, lead pipes have never been used in China, and even copper tubing is rather rare. This study established the typical levels of inorganic contaminants, and the total content of inorganic contaminants was not a sufficient criterion for assessing the toxicity and harmfulness of pipe scales and loose deposits. It was necessary to obtain more comprehensive information on the elemental speciation.

3.2. Relationship between inorganic contaminants

The formation of scales that consist of tubercles has been primarily attributed to the corrosive phenomena of the electrochemical surface and the dissolution and precipitation of metal salts in the pipe networks. Porous deposits of iron oxide or oxyhydroxide phases and aluminosilicate and manganese deposits were the most commonly observed types of pipe solids composed of various pollutants, such as heavy metals and organic compounds (Makris et al., 2014).

Table 4 shows the correlation coefficients between Al, Fe, Mn and ten other heavy metals. In pipe scales and loose deposits, a significant positive correlation ($p < 0.01$) was found between Al & Mn, Al & Ba, Al & Cu, Al & As, Mn & Ba, Mn & Cu, and Mn & As, while a significant negative correlation was detected between Fe & Al. Additionally, a negative correlation ($p < 0.05$) could be identified between Fe & Cu. The high positive correlation between Al and Mn indicated that there was a co-occurrence phenomenon of Al and Mn in pipe scales. These findings were interesting, and the involved mechanisms deserved further investigation. Mn^{2+} could be doped into the internal structure of Al oxides by the adsorption process in the formation of amorphous $\text{Al}(\text{OH})_3$ in actual distribution systems (Wang et al., 2012b). On the other hand, Al-coagulant in treated water could destabilize the negatively charged Mn oxide particles and thus accelerate the formation and deposition of Mn oxide together with Al oxide (Posselt et al., 1968). These indicated that it could probably form hybrid structures with Al and Mn. Meanwhile, the high positive correlation between Al, Mn and heavy metals could indicate that Al-Mn commixtures served as scavengers, gathering up various metals into their internal structures in the formation of pipe scales. The significant negative correlation between Fe & Al and Fe & Cu

Table 1
Evaluation index of RAC.

Category	Risk	Metals in the carbonate and exchangeable fractions (%)
1	No risk	<1
2	Low risk	1–10
3	Medium risk	11–30
4	High risk	31–50
5	Very high risk	>50

Table 2
CBSQGs of eight toxic heavy metals.

CBSQG	As (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Ba (mg/kg)
TEC	9.79	0.99	31.6	35.80	43.40	22.7	121	60
PEC	33.00	4.98	149	128	111.00	48.6	459	60

Note: TEC means threshold effect concentration and PEC means the potential effect concentration.

indicated that Fe might mainly exist in the form of iron corrosion scales within cast iron pipes, in which the Fe content was high but the Al content was low; while for deposits collected from cement mortar lined pipes, the Fe content was low, and the Al content was relatively high, and the Al could be from residual coagulant and/or cement materials on the pipes. The source of Cu in the deposits is not clear, and further investigation is necessary.

The relationships among thirteen inorganic contaminants are shown in Table S1. Table S1 shows that significant positive correlations ($p < 0.01$) were found between Ba & Cu, Ba & As, Pb & Cr, Pb & Zn, Cu & As, and Co & Ni. The significant positive correlations between these metals indicated there were co-occurrence relationships of these metals in pipe scales and loose deposits. The co-occurrence and accumulation of inorganic contaminants might include biochemical processes. It has been reported that some bacteria within a biofilm could result in the precipitation of iron minerals and thus influence the composition of corrosion scales (Konhauser, 1998). Research by Lytle et al. found that the sulfide produced by sulfate reducing bacteria (SRB) could affect the iron geochemistry of the corrosion scales in DWDS (Lytle et al., 2005). Wang et al. also indicated that the nitrate-reducing bacteria (NRB) *Acidovorax* and *Hydrogenophaga* promoted the formation of Fe_3O_4 (Wang et al., 2017). Alkaline or calcareous scales are the most commonly observed types of pipe scales composed of minerals, such as calcium carbonate, goethite, magnetite, green rust, and amorphous Fe phases. In addition, previous studies had reported that extracellular polymeric substances (EPS), organic constituents and these iron, aluminum and manganese minerals could sorb and concentrate inorganic contaminants by chemical adsorption and biological enrichment (Hitchcock et al., 2009; Oppenheimer-Shaanan et al., 2016; Simkiss, 1977).

3.3. Elemental speciation

The calculated percentages of the extracted elements in each fraction of 14 samples are shown in Fig. S1. Analyzing the results obtained by the sequential extraction procedure following the Tessier method, it was noted that the residual fraction had the highest contribution to most of the inorganic contaminants (Al, As, Cd, Cr, Fe, Pb, Ni, and V), and the residual fraction accounted for >40%. The residual solids were

composed mainly of primary and secondary minerals, and most inorganic contaminants can be fixed in their crystal structure. The residue state was stable and had low potential ecological risk.

3.3.1. Al, Fe and Mn

Al, Fe and Mn were the main metal constituents of pipe scales and loose deposits, and their oxides and deposits could concentrate metals via co-precipitation, adsorption and other processes. Al in the 14 samples was mainly present in the residual fraction. The second dominant fraction of Al was associated with Fe-Mn oxides (6.9–55.8%, with an average of 25.8%), followed by the carbonates fraction (1.1–13.9%, with an average of 4.2%). Al in S9 (loose deposits) was mainly present in the Fe-Mn oxides fraction.

Mn partitioning was dominated by the Fe-Mn oxides fraction (0.8–96.5%, with an average of 43.5%), the residual fraction (1.7–74.1%, with an average of 38.0%), the carbonates fraction (0.8–26.3%, with an average of 13.3%), indicating that majority of Mn was associated with the carbonates and the Fe-Mn oxides fractions in the nonresidual fraction.

The main speciation of Fe was in residual form (79.6–96.7%, with an average of 89.7%), which was deemed to have a very low mobility. This may represent crystalline Fe oxides and the Fe in primary silicate minerals (Li and Thornton, 2001). The remaining fraction was the Fe-Mn oxides fraction. For S2 and S3, 2.40% and 3.86% of Fe existed in the carbonates fraction.

Average percent distributions of Al, Fe and Mn in the 6 pipe scale samples and 8 loose deposit samples examined in this study are presented in Fig. 1. There was no obvious difference in the Al and Fe average fraction distributions between pipe scales and loose deposits. However, more than half of the Mn existed as Fe-Mn oxides in loose deposits (Li and Thornton, 2001). Combined with the correlation analysis results between Al, Fe, Mn and heavy metals, Al and Mn in the form of Fe-Mn oxides indicated that Al and Mn could have an important role in binding trace metals in pipe scales and loose deposits. A large proportion of Mn in the carbonates was most likely due to the similarity in ionic radii to the calcium element, which allowed Mn to substitute Ca in the carbonate phase (Sakan et al., 2013).

Table 3
Concentration of inorganic elements in pipe scales and loose deposits ($\mu\text{g/g}$).

Sample sites	Fe	Al	Mn	Ba	Pb	Cd	Cr	Cu	As	V	Co	Ni	Zn
S1	607,440	2071	596	39	8	3.60	14	7	4	14	4	1	9
S2	566,769	1638	575	66	3	1.89	35	7	5	20	3	2	34
S3	768,563	1588	850	176	17	1.40	33	62	17	6	1	2	7
S4	630,711	2309	4918	520	96	0.67	77	81	14	45	9	40	1864
S5	583,903	977	2622	141	5	0.14	35	19	6	22	2	5	305
S6	658,831	828	1679	71	3	0.08	18	10	6	19	3	5	121
S7	275,867	35,933	625	319	24	0.24	36	15	28	65	3	7	69
S8	666,992	4538	203	292	12	1.25	20	21	9	30	2	8	150
S9	568,624	3344	557	301	10	0.21	23	12	10	30	2	5	42
S10	455,769	10,385	3615	350	44	2.51	27	103	37	25	5	6	87
S11	70,475	180,728	17,535	1041	13	2.16	12	357	39	17	2	7	36
S12	62,190	111,500	12,600	440	22	2.53	15	454	26	17	2	7	32
S13	148,219	11,112	131	149	9	0.05	10	14	4	13	19	473	287
S14	76,470	14,779	184	145	10	0.04	13	8	3	12	16	398	194
Average	438,630	27,266	3335	289	20	1	26	84	15	24	5	69	231

Table 4
Correlation coefficients between Al, Fe, Mn and heavy metals.

	Al	Fe	Mn
Al	1		
Fe	-0.679**	1	
Mn	0.935**	-0.519	1
Ba	0.836**	-0.434	0.859**
Pb	-0.051	0.107	0.163
Cd	0.337	0.004	0.395
Cr	-0.319	0.453	-0.112
Cu	0.882**	-0.557*	0.934**
As	0.685**	-0.36	0.691**
V	-0.076	0.054	-0.107
Co	-0.193	-0.453	-0.253
Ni	-0.118	-0.529	-0.246
Zn	-0.191	0.181	0.028

* $p < 0.05$, ** $p < 0.01$, the correlation of remaining is not significant.

3.3.2. As, Cr and V

Sequential extractions showed that As, Cr and V in the 14 samples were mainly present in the residual fraction. The relative content of the heavy metals in the residual fraction could be used as a measure of the contribution of natural water sources (Lytle et al., 2010). There were no obvious differences in the forms of As, Cr and V in pipe scales and loose deposits. These facts indicated the main mineralogical origins of As, Cr and V in pipe scales and loose deposits and their low mobility and low potential bioavailability under most conditions typical for drinking water systems. Therefore, it is unlikely for residual metals to be released into the water supply when the water quality parameter changes.

A significant amount of As was also present in the carbonate fraction for S1, S2, and S3, which were pipe scales. The difference was that part of the As in the loose deposits (S7-S12) was mainly in the Fe-Mn oxides fraction. The part of As in the carbonates fraction and Fe-Mn oxides fraction showed that As could adsorb onto pipe scales and loose deposits. Apart from Fe and Mn oxides, it was known that As may partially substitute for carbon in the carbonate of calcite (Lin et al., 2018). The carbonates fraction of As was a consequence of the alkaline reaction in DWDS. The speciation of As in the non-residual fraction (carbonates fraction and Fe-Mn oxides fraction) was in agreement with the results of other studies, in which As could be released by particulates physically dislodged by hydraulic events or via colloidal mobilization of iron-based corrosion solids caused by changes in water chemistry (Lytle et al., 2010).

The distribution of Cr in the 14 samples was dominated by the Fe-Mn oxides and residual fraction, thereby suggesting the importance of

the oxides and silicates for chromium binding, and the form of Cr^{3+} could enter the structure of minerals.

3.3.3. Cu, Pb, Zn, Ni, Co and Ba

Cu, Pb, Zn, Ni, Co and Ba were dominated by the Fe-Mn oxides fraction. Cu in the 14 samples was mainly associated with the Fe-Mn oxides fraction (3.7–63.0%, with an average of 37.4%) and the residual fraction (17.8–53.7%, with an average of 36.4%). The considerable amount of Cu associated with Fe-Mn oxides reflected the close affinity of Cu to be adsorbed and coprecipitated with poorly crystalline Fe and Mn hydroxides. A large proportion of Cu associated with the organic fraction was in agreement with the results of other studies (Iwegbue, 2013). Cu was commonly found strongly complexed with organic matter because of its high stability of Cu-organic complexes. Cu was preferentially retained on organic matter by complexation rather than ion exchange (Fuhrmann, 1994).

Large amounts of Pb occurred in the fraction associated with the Fe-Mn oxides fraction and the residual fraction, and the percentages of Pb these two fractions were 47.1% (3.7–61.4%) and 40.1% (17.9–59.4%), respectively. Fe-Mn oxides were considered important scavengers of Pb in the sediments, and Pb species could be strongly adsorbed to Fe-Mn oxides. Pb in S1-S3 was shown to be strongly associated with the carbonates fraction. Thus, CaCO_3 may act as a strong adsorbent for Pb and could complex Pb in the form of PbCO_3 (Zang et al., 2017).

In a word, the distributions of Cu, Pb, Zn, Ni, Co and Ba in the samples were mainly associated with the Fe-Mn oxides fraction. This was attributed to the adsorption, flocculation and coprecipitation of heavy metals with the colloids of Fe and Mn hydroxides. Gasparatos et al. concluded that the sorption of metals on Fe-Mn oxides was probably the most important mechanism for interpreting the behavior of this element in the environment (Gasparatos et al., 2015). The release of the metals in the Fe-Mn oxides fraction would most likely be affected by the redox potential and pH. These results might conclude that the release of the Cu, Pb, Zn, Ni, Co and Ba in pipe scales and loose deposits in DWDS might be governed by the components of Fe-Mn oxides, and the potential mobilization of these metals might increase with changes in water chemistry.

3.3.4. Cd

Cd in the pipe scale and loose deposit samples was predominantly associated with the residual fraction (7.2–62.6%, with an average of 66.8%), followed by the exchangeable fraction in loose deposits and the carbonates fraction in pipe scales. It was reported that Cd could be transformed from the more strongly bound oxidizable fractions to the exchangeable and carbonate fractions during the oxidation process of sediment (Cao et al., 2015). The carbonates fraction of Cd showed that alkaline changes in DWDS could cause changes in the Cd concentration. Quite a lot Cd existed in the form of the exchangeable fraction in the 14 sampling sites, which allowed Cd to get into the water systems most easily. The existence of Cd in the exchangeable fraction was expected to be susceptible to the water quality, and it might be released via desorption and/or dissolution.

Fig. 2 shows the average percent distributions of heavy metals in the 6 pipe scale samples and 8 loose deposit samples examined in this study. There were common fraction distribution characteristics of ten heavy metals between pipe scales and loose deposits. Ten heavy metals were primarily associated with the residual fraction and the Fe-Mn oxides fraction. Overall, the results of fractionation revealed the considerable association of nonresidual fractions. In this case, heavy metals in pipe scales and loose deposits can be potentially released back to the drinking water when the physical-chemical properties of water changed equilibration between solid and solution. Thus, some prevalent indices were needed to assess the natural impact and risk of the heavy metals based on the obtained fractionation results.

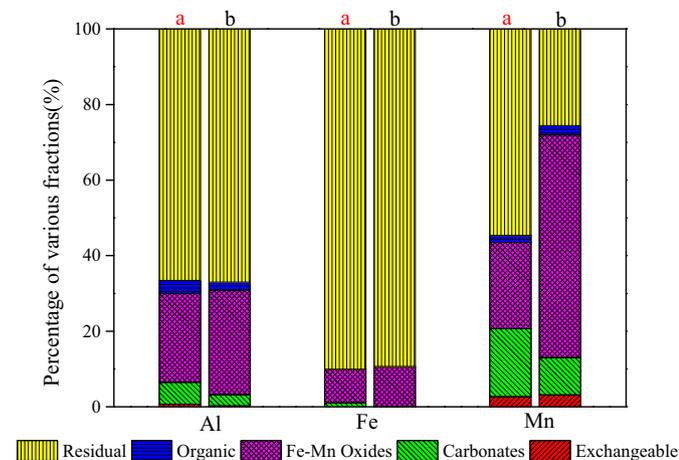


Fig. 1. Average percent distributions of Al, Fe and Mn in pipe scales (a) and loose deposits (b) examined by the five-stage procedure.

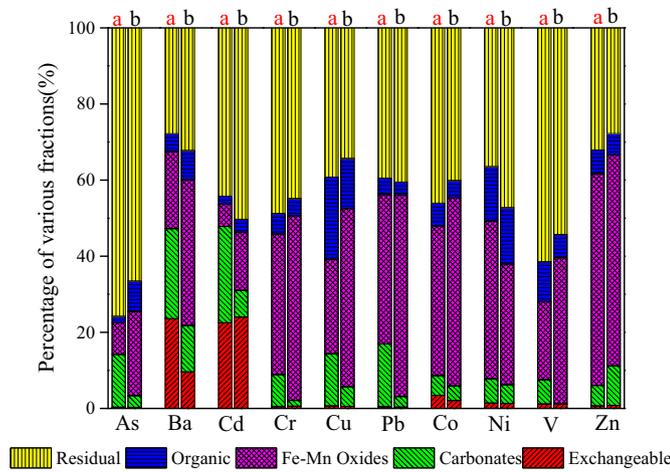


Fig. 2. Average percent distributions of heavy metals in pipe scales (a) and loose deposits (b) examined by the five-stage procedure.

3.4. Contamination and risk assessment

3.4.1. Global contamination factor (GCF)

The individual contamination factor (ICF) and global contamination factor (GCF) for the heavy metals obtained in pipe scales and loose deposits that formed in DWDS are shown in Table 5. The results showed the highest ICF and mobility of Cu, because it belonged to labile fractions, and it could be released from the loose deposits samples under water quality destabilization. As, V and Co showed low risk, while Cd, Cr, Pb, and Ni showed moderate risk in most samples.

The GCF demonstrated that almost all the sample sites (except S1–S2, S4) have a certain environmental risk. Sample sites S6 (pipe scales) and S12 (loose deposits) presented the highest environment risk compared to the other sample sites. It was shown that Cu, Ni and Zn contributed the largest part to S6, while Cu, Co, and Zn contributed the largest part to S12. At all the sample sites, Cu had the largest proportion, and As showed the lowest proportion. Overall, the risk from loose deposits was higher than that from pipe scales.

3.4.2. Risk assessment code (RAC)

Table S2 shows the results of RAC for ten heavy metals in all the sampling sites. The decreasing order of the average risk coefficient for each metal element was Cd > Ba > Cu > Pb > Zn > As > Co > Ni > Cr > V. The

Table 5
ICF and GCF of ten heavy metals in pipe scales and loose deposits.

Site	ICF										GCF
	As	Cd	Cr	Cu	Pb	Ba	Ni	V	Co	Zn	
S1	0.28	1.27	0.67	2.68	1.34	1.20	0.44	0.08	0.49	0.42	8.87
S2	1.15	0.65	2.19	5.89	3.39	3.35	0.71	1.15	0.72	1.81	21.01
S3	0.55	0.60	1.81	34.28	1.35	2.81	2.62	0.70	1.99	3.27	49.98
S4	0.19	1.59	0.33	2.08	0.23	4.35	3.08	0.35	0.90	2.26	15.36
S5	0.09	0.92	1.60	13.48	4.59	3.24	2.12	0.19	0.85	2.82	29.9
S6	0.11	12.74	0.92	38.53	2.39	2.36	14.64	6.90	8.23	14.98	101.8
S7	0.66	0.58	1.70	13.43	1.82	2.67	1.25	0.51	0.98	1.46	25.06
S8	0.31	0.99	4.15	19.65	0.69	0.36	0.95	1.02	1.00	8.92	38.04
S9	0.59	0.63	0.92	20.42	2.72	4.82	0.96	2.26	0.77	3.73	37.82
S10	0.15	0.82	1.70	18.70	1.26	7.15	1.15	0.28	0.77	1.32	33.3
S11	1.00	4.05	0.67	9.87	1.80	1.67	1.67	0.56	0.84	3.75	25.88
S12	0.32	0.84	1.39	19.70	1.10	4.72	2.21	0.66	10.08	25.80	66.82
S13	0.37	0.67	0.69	17.33	1.25	1.72	0.60	2.72	7.42	1.77	34.54
S14	1.13	1.62	0.91	19.08	2.29	1.82	0.87	0.73	2.14	1.17	31.76

Note: ICF means the individual contamination factors and GCF means global contamination factor.

samples showed low risk for As (except at S1–S3), Cr (except at S1), Cu (except at S1, S2, and S8), Pb (except at S1–S3), Co (except at S1, S2, and S4), Ni (except at S8, S13–S14), and Zn (except at S4, S5, S8, S9, S13, and S14), with RAC values <10%. Medium risk was indicated for Ba (except at S1–S3, S8–S10). Very high risk was indicated for Cd (at S1–S3, S11) and Ba (at S2), which should be noticed.

Fig. 3 shows the results of the comparison of average RAC for heavy metals in pipe scales and loose deposits. The mean RAC values of As, Cd, Cr, Cu, Pb, Ba, Co, Ni, V and Zn in pipe scales were 15.04, 34.18, 8.30, 9.85, 18.08, 29.29, 10.80, 4.59, 7.18 and 6.62%, respectively; however, the corresponding RAC values in loose deposits were 2.85, 41.31, 2.61, 9.16, 2.36, 35.29, 4.33, 8.77, 1.59 and 10.83%, respectively. The pipe scales and loose deposits showed the low risk for Cr, Cu, Co, Ni, V and Zn, with RAC values of <11%. Hence, there was no significant mobility for the above heavy metals. As and Pb showed medium risk in pipe scales but low risk in loose deposits. The high risk was corroborated for Cd both in pipe scales and loose deposits. The high proportion of Cd in the exchangeable and carbonates fraction at almost all the sites indicated the toxicity and availability of Cd, and it could pose serious problems to the ecosystem when abruptly released into the water supply. Ba showed medium risk in pipe scales but high risk in loose deposits.

3.4.3. CBSQGs

The CBSQGs method was mainly based on the concentration of heavy metals, while the evaluation factors of GCF and RAC were mainly based on the form of existence of heavy metals. GCF can be competent for evaluating the comprehensive impact of sampling sites, while RAC is mainly suitable for evaluating the impact of a single inorganic substance. The concentrations of heavy metals in pipe scales and loose deposits were compared to TEC and PEC values, as displayed in Fig. 4.

The concentrations of Cr, Pb and Cd were below their PEC at all sites, indicating that their toxic effects may be minimal. Although CBSQGs results showed that the risk of Cd was small, the RAC evaluation results suggested that Cd had high risk. The results of the five-stage procedure showed that Cd mainly existed in the exchangeable and carbonates form, which was vulnerable to the fluctuation of water quality conditions and could be released into the water again, thus affecting the water quality. Based on the aforementioned analyses, therefore, the risk of heavy metals was not only related to the concentration, but also related to the speciation. Although the content of some metals was very low, they could continually accumulate in pipe scales and loose deposits and their existence forms determined their harmfulness.

Cu and Zn concentrations in most sites were below their TEC; however, Cu concentrations at S11 and S12 (loose deposits) were above the PEC of Cu, and Zn concentration at S4 (pipe scales) was higher than the PEC of Zn. As had high risk at S7, S8 and S11, and these three sampling sites were loose deposits. According to the comprehensive evaluation,

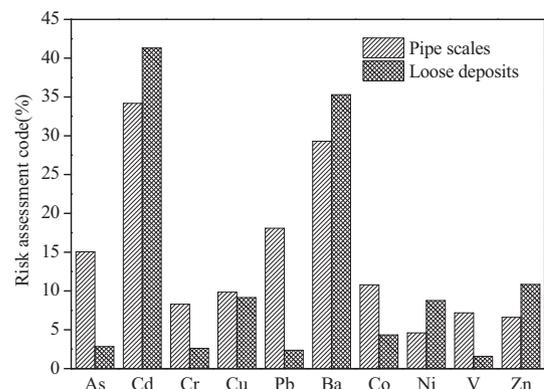


Fig. 3. Average RAC for heavy metals in pipe scales and loose deposits.

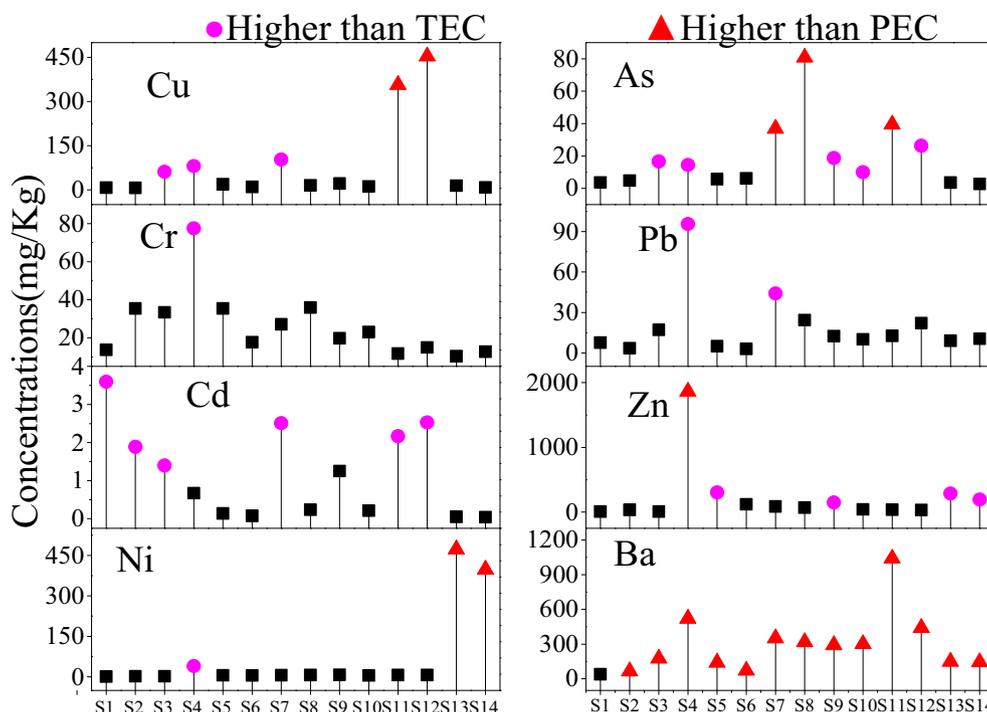


Fig. 4. Comparison between heavy metal concentrations and TEC, PEC.

Ba had the highest risk of all heavy metals, and the concentrations of Ba in all sampling sites (except at S1) were higher than the PEC.

Some measures can be taken to control the risks. It is suggested that water plants should strengthen the maintenance of the water supply pipe network and improve the frequency of the pipe network flushing (such as high water flow flushing, air scouring, or pigging) to reduce the accumulation of loose deposits. Meanwhile, the water treatment plants should upgrade water treatment processes to improve the removal efficiency of some trace contaminants (such as heavy metals, pharmaceuticals, endocrine disruptors, perfluorinated compounds, flame retardants or biocides), to reduce the residual coagulant concentrations in finished water (such as aluminum, iron metals), to increase the finished water chemical and biological stability, and thus inhibit pipe corrosion and biofilm growth in distribution systems.

Although this study provided a potentially available method for assessing the risks of typical heavy metals in loose deposits and pipe scales formed in DWDS, the involved heavy metal release mechanisms and the potential health risk of loose deposits and pipe scales in DWDS still need further study.

4. Conclusions

In this study, thirteen inorganic contaminants (Fe, Al, Mn, Ba, Zn, Cu, Ni, Cr, V, Pb, As, Co, and Cd) were determined in pipe scales and loose deposits. Among them, Fe had the highest concentrations, followed by Al, Mn, Ba, Zn, Cu, Ni, Cr, V, Pb, As, Co, and Cd. Pipe scales tended to have higher concentrations of inorganic contaminants. Significant positive correlations ($p < 0.01$) were validated between Al & Mn, Al & Ba, Al & Cu, Al & As, Mn & Ba, Mn & Cu, and Mn & As. The significant positive correlations between Al, Mn and other metals demonstrated that Al, Mn and their oxides could have the capacity to concentration metals via absorption and co-precipitation processes.

The results of the five-stage procedure indicated that high percentages of Al, As, Cd, Cr, Fe, Ni and V were associated with the residual fraction. The highest contributions of Cu, Mn, Pb, Zn, Co and Ba were present in the Fe-Mn oxides fraction. There were common fraction distribution

characteristics of thirteen inorganic contaminants between pipe scales and loose deposits. Al and Mn in the form of Fe-Mn oxides suggested that Al and Mn could have an important role in binding trace metals in pipe scales and loose deposits, which could significantly influence the water quality.

The highest ICF of Cu indicated its great possibility to be released from all the loose deposit samples. As, V and Co showed low risk, while Cd, Cr, Pb, and Ni exhibited moderate risk in most samples. The GCF results demonstrated that most of the sample sites (except S1, S2 and S4) had a certain environmental risk. S6 (pipe scales) and S12 (loose deposits) showed the highest environment risk compared to the other sample sites. The RAC results showed that high risk was correlated with Cd for both pipe scales and loose deposits, and Ba showed medium risk in pipe scales but high risk in loose deposits. According to the comprehensive CBSQGs evaluation, heavy metals in loose deposits were more harmful than heavy metals in pipe scales; among all heavy metals, Ba had the highest risk.

Novelty statement

Frequent occurrence of drinking water pollution incidents caused by heavy metals accumulated in drinking water distribution systems (DWDS) has gradually attracted international attention. This work comprehensively assessed the speciation, mobility and risks associated with inorganic contaminants accumulated in pipe scales and loose deposits in drinking water distribution systems (DWDS). The results obtained in this work could improve the understanding of the accumulation and potential health risks of inorganic contaminants in the pipe scales and loose deposits. The speciation analysis results indicated that most of the existing forms of inorganic contaminants in DWDS were stable, but the inorganic contaminants with relatively large exchangeable fractions were expected to be susceptible to water quality changes, and they might be more easily released under certain circumstances. The correlation analysis results showed that there were co-occurrence behaviors for Al and Mn oxides, and they might also have the ability to combine metals into their internal structures; therefore, we could reduce the

heavy metal-related risks by controlling the deposition of Mn and Al in DWDS. The risk assessment showed that the inorganic contaminants found in the pipe scales and loose deposits had a certain risk, thus, some measures should be taken to control the risks. Water industry should upgrade the treatment technology to reduce the source of contaminants and improve the frequency of the pipe network flushing to reduce the deposition of loose deposits.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.10.347>.

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