

Research Article

# Influences of Heavy Metals in Water Treatment Chemicals on Drinking Water Quality and Risk Management

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## Abstract

Water treatment chemicals (WTCs) are important raw materials during the drinking water production process. Occasionally unqualified WTCs with heavy metals were provided to Water Treatment Plant (WTP) by supplier during emergency situation, such as earthquake, typhoon and city block for epidemic disease, just because it cannot obtain the qualified WTCs. The harmful heavy metals in WTCs may expose a certain health risk to the quality of drinking water. In this paper, the influence of heavy metals in WTCs on the quality of drinking water was explored and the feasible management measures are proposed, taking the ILha Verda Water Plant (IVP) in Macao as an example. The study was based on the testing results of heavy metals in WTCs and treated water from 2017 to 2022 in IVP. A series of mathematical models were established to evaluate the content of heavy metals in water brought by WTCs. The removal rates of the water treatment process to the heavy metals were calculated at same time. The maximum allowable concentrations of heavy metals in WTCs were calculated and accessed. The results show that the drinking water is safety if the heavy metals in unqualified WTCs are under the maximum allowable concentrations. Then it is proposed for the classification of WTCs and risk management. The study will provide theoretical and technical support for water quality safety supervision and water supply management.

## Keywords

Water Treatment Chemicals, PACL, Arsenic, Drinking Water Quality, Risk Management

## 1. Introduction

During the water treatment process, the WTCs are applied for flocculation, disinfection, purification and pH adjustment. All these chemical materials are important for water treatment procedures and are key substances for reducing naturally occurring organic matter and anthropogenic contaminant [1, 2]. The main WTCs include polyaluminum chloride (PACl), ferric chloride ( $\text{FeCl}_3$ ), sodium hypochlorite ( $\text{NaClO}$ ), etc. in IVP. These chemicals may contain

a certain content of heavy metals, such as As, Pb, Cd, Hg and Cr, which may affect the quality of drinking water. In order to ensure the quality of portable water, different countries and organizations have formulated the regulations and specifications to limit the content of heavy metals in WTCs [3-5]. PACl is an important coagulant and widely used in water treatment plants, which may contain a little heavy metal and is monitored strictly generally. The updated version of national standard of PACL was promulgated in 2019

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and formally implemented in August 2021. The guideline values for heavy metal in PACl have been renewed. Compared with the expired standard, it is more stringent and the concentration of heavy metals (As, Pb and Cd) are about half lower than that in the previous version.

Generally, the heavy metals in WTCs are controlled strictly by production suppliers. All WTCs in IVP are analyzed weekly by the Lab to supervise the quality. It is safe for water quality when the concentration of heavy metals in WTCs are under the guideline values. The monitoring test results show that the content of heavy metals is around the critical value or exceeds the guideline value occasionally because the quality of each batch of WTCs is different. These unqualified WTCs will be discarded according to the management regulation of IVP, which will not only cause certain economic losses, but also take pollution to the environment.

However, there are some unavoidable emergencies in the real world, such as war, earthquake, tsunamis, epidemic, etc. Under these situations, transportation will be interrupted and even the different cities will be blocked from each other. It is difficult to obtain the qualified WTCs within a long period of time. Then, the water plant will confront dilemma that use or stop adding the unqualified WTCs in water treatment procedure. How to ensure the drinking water quality and how to deal with the unqualified WTCs in a scientific way? It is an interesting research topic to discuss the influence of the WTCs on drinking water quality [6-10]. The WTCs with the overmounts heavy metal may bring a hazard risk to the quality of portal water. The influence and health risk of heavy metal on drinking water were studied by many researchers [11-15] in the past. But the influence of heavy metals in WTCs on drinking water quality is seldom discussed and there is few detailed research about the risk assessment and management.

This article takes IVP in Macao as a case to study the influence of the heavy metals in WTCs on the drinking water quality. The content of heavy metals in WTCs, raw water and treated water were collected in the past 6 years, which were used in calculation for the mathematical models. At same time, the influence of water treatment process was explored, especially the removal rate of heavy metals in water. The study also proposes the classification of WTCs and risk management suggestions.

## 2. Material and Methodology

### 2.1. The Collection of Data and Heavy Metal Analysis in WTCs

The concentrations of heavy metal in WTCs, raw water and treated water from 20017 to 2022 were obtained from the Lab & Research Center of Macao Water Supply Company Limited. The dosage of WTCs was collected from the Supervisory Control and Data Acquisition System (SCADA) of

Operation Department (OP) in IVP. Generally, the WTCs used in the treatment process are polyaluminum chloride (PACl), Ferric chloride ( $\text{FeCl}_3$ ), Sodium hypochlorite ( $\text{NaClO}$ ), Hydrochloric acid ( $\text{HCl}$ ), Citric acid and Activated carbon in IVP. The heavy metals were analyzed by the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Thermal Fisher, iCap9000). The heavy metal elements analyzed in different WTCs were shown in table 1.

**Table 1.** The heavy metal elements analyzed in different WTCs.

| Name of WTCs     | Metal Elements |    |    |    |    |
|------------------|----------------|----|----|----|----|
|                  | As             | Cd | Cr | Pb | Hg |
| PACl             | ✓              | ✓  | ✓  | ✓  | ✓  |
| $\text{FeCl}_3$  | ✓              | ✓  | ✓  | ✓  | ✓  |
| $\text{NaClO}$   | ✓              |    |    | ✓  |    |
| $\text{HCl}$     | ✓              |    |    | ✓  |    |
| Citric acid      | ✓              |    |    | ✓  |    |
| Activated carbon | ✓              | ✓  |    | ✓  |    |

### 2.2. Quality Control of the Experiment

During the analysis procedure, quality control measures are required to ensure the accuracy of the testing result. All the metal elements were determined with analyzing blank samples. The parallel and spiked samples were detected by the ICP. The recovery of spiked heavy metal samples ranged from 88-102%. The certified standard solutions of heavy metals (1000 mg/L) were obtained from Accustandard, USA. The deionized water produced by Millipore water purifier was used for dilution of the standard solutions and samples. Glassware used in the experiment was cleaned by immersing those in 20%  $\text{HNO}_3$  for overnight and then rinsing several times with distilled water.

### 2.3. The Selection of Influencing Parameters

According to the statistics of the testing results for heavy metals during the past 6 years in IVP, it is shown that the Arsenic (As) in PACl and  $\text{FeCl}_3$  can affect the concentration of heavy metals in treated water. Sometimes the concentration of As in PACl exceeds the guideline values, which also exposes a problem to OP. The values of lead (Pb), cadmium (Cd) and mercury (Hg) in WTCs are lower than that of the guideline value. Chromium (Cr) was not detected in WTCs. In this paper, we mainly discuss the influence of As in PACl and other heavy metals in WTCs will be calculated using different formulas.

## 2.4. The Calculation Method

### 2.4.1. Calculation of the Increasing Amount of Single Metal in WTCs

Only two chemicals, PACl and sodium hypochlorite were detected to contain a certain amount of As in all WTCs. The increasing amount of single metal in WTCs was computed by the following expression:

$$C = x_1 \times T_1 \times 1000 + x_2 \times T_2 \times 1000 \quad (1)$$

Where, C- the total increasing amount of single metal element,  $\mu\text{g/L}$ , such as As;  $x_1$ - detection result of selected heavy metal ion in PACl, %;  $T_1$ - dosage of PACl adding in raw source water, mg/kg;  $x_2$ -detection result of selected heavy metal ion in sodium hypochlorite, %;  $T_2$  –dosage of sodium hypochlorite adding in raw source water, mg/kg; 1000- conversion multiple from mg/kg to  $\mu\text{g/L}$ .

If the unit of the testing result of heavy metal is mg/kg, the above formula will be converted into the following equation:

$$C = x_1 \times T_1 \div 1000 + x_2 \times T_2 \div 1000 \quad (2)$$

Where,  $x_1$ - detection result of selected heavy metal ion in PACl, mg/kg;  $x_2$ -detection result of selected heavy metal ion in sodium hypochlorite, mg/kg;  $T_1$  and  $T_2$  are dosage of WTCs, mg/kg.

### 2.4.2. Calculation of Removal Rate of As

The traditional water treatment process is precipitation of PACl and disinfection with  $\text{NaClO}$  in IVP. The equation for calculating the removal rate of As through the water treatment process is shown as followed:

$$P = \left(1 - \frac{C_T}{C_R + C}\right) \times 100\% \quad (3)$$

Where, P- removal rate of heavy metal ions (E.g. As), %;  $C_T$ : detection result of heavy metal ions (E.g. As) in treated water in IVP,  $\mu\text{g/L}$ ; C: increasing amount of heavy metal ions (E.g. As) brought in by WTCs,  $\mu\text{g/L}$ ;  $C_R$ : concentration of heavy metal ions (E.g. As) in raw source water in IVP,  $\mu\text{g/L}$ .

### 2.4.3. Calculation of Maximum Allowable Content for Heavy Metals in PACl

The maximum allowable content of heavy metals in PACl was calculated using the following two formulas:

$$C = x_1 \times T_1 \times 1000 \quad (4)$$

$$x_{max1} = 0.2 \times C_{max} \div T_{max1} \div 1000 \quad (5)$$

Where, C- increasing content of single heavy metal ion in PACl,  $\mu\text{g/L}$ , such as As, Pb, Hg, Cr, Cd;  $x_1$  – single heavy

metal ion content in PACl, %;  $T_1$  –the dosage of PACl adding in raw water, mg/kg; 1000– conversion multiple from mg/kg to  $\mu\text{g/L}$ ;  $x_{max1}$  – the maximum content of heavy metal ion in PACl, %;  $C_{max}$  – the guideline value of single heavy metal ion in drinking water in Macao regulation,  $\mu\text{g/L}$ , including As, Pb, Hg, Cr, Cd;  $T_{max1}$  – the maximum dosage of PACl, calculated as 30 mg/kg; 0.2- coefficient.

It is hypothesized that the maximum increasing concentration of single heavy metal ion brought by one kind of WTC is about 20% of the guideline value of drinking water regulation in Macao, so the coefficient is 0.2. The dosage of PACl in raw water is 10-20 mg/kg general and the maximum is 30 mg/kg.

### 2.4.4. Calculation of Maximum Allowable Content for Heavy Metals in $\text{FeCl}_3$

The maximum allowable content of heavy metals in  $\text{FeCl}_3$  was calculated as the followed:

$$C = x_3 \times T_3 \times 1000 \quad (6)$$

$$x_{max2} = 0.2 \times C_{max} \div T_{max2} \div 1000 \quad (7)$$

Where, C- increasing content of single heavy metal ion in  $\text{FeCl}_3$ ,  $\mu\text{g/L}$ , such as As, Pb, Hg, Cr, Cd;  $x_3$  – single heavy metal ion content in  $\text{FeCl}_3$ , %;  $T_3$  –the dosage of  $\text{FeCl}_3$  adding in raw water, mg/kg; 1000– conversion multiple from mg/kg to  $\mu\text{g/L}$ ;  $x_{max2}$  – the maximum content of heavy metal ion in  $\text{FeCl}_3$ , %;  $C_{max}$  – the guideline value of single heavy metal ion in drinking water in Macao regulation,  $\mu\text{g/L}$ , including As, Pb, Hg, Cr, Cd;  $T_{max1}$  – the maximum dosage of  $\text{FeCl}_3$ , calculated as 20 mg/kg; 0.2- coefficient.

The calculated method is the same as the PACl. The dosage of  $\text{FeCl}_3$  in raw water is 10-20 mg/kg and the maximum dosage is 20 mg/kg.

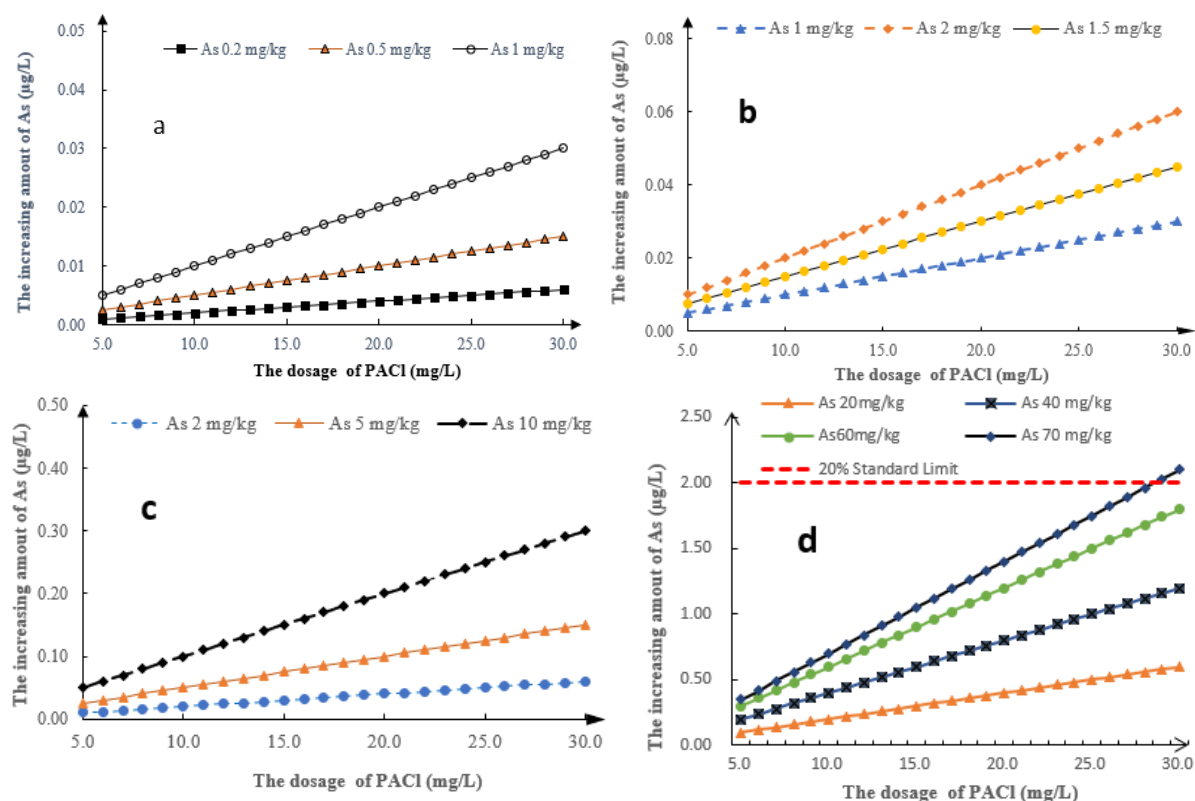
## 3. Result and Discussion

### 3.1. The Theoretical Increasing Amount of as in Raw Water

The concentration of As in raw water will increase when WTCs are added in water treatment procedure because these WTCs contain a certain amount of As ion. The theoretical increasing amount of As in raw water was calculated according to equation 1 & 2. The increasing amount of As in raw water was variety when the difference dosage of PACl was added to raw water with the different As content. The calculating results were shown in Figure 1. When As content in PACl was 0.2, 0.5, 1.0mg/kg respectively, and the dosage was between 8~30mg/kg, the theoretical increasing amount of As in raw water was shown in Figure 1(a). Even at the maximum dosage (30mg/L) and the highest As content (1.0mg/L), the increasing concentration was only 0.03  $\mu\text{g/L}$ . It indicated that there was little influence on raw water if the As content is

under the guideline value of new national standard ( $<1\text{mg/L}$ ). The use of qualified PACl can guarantee the safety and quality

of drinking water.



**Figure 1.** The theoretical increasing amount of As in raw water.

The guideline value of As in PACl decreased from 2 mg/kg to 1 mg/kg in the new version national standard. Figure 1(b) showed the changing value of As in raw water if the As content in PACl was between 1 and 2 mg/kg. The As concentration in raw water increased proportionally and the highest increment was  $0.06\text{ }\mu\text{g/L}$  that was still lower compared with the limit value ( $10\text{ }\mu\text{g/L}$ ) of As in drinking water, which indicated that it was still safe to use the PACl containing the As ion between 1 to 2 mg/kg. The aim of tightening the guideline value is to require the PACl manufacturers supply high qualified production and guarantee the safety of water supply further.

The theoretical increasing content of As in the raw water was calculated when the As content in PACl was above both expired and valid standard limit, such as 2, 5 and 10 mg/kg, and the results were shown in Figure 1(c). It is shown that the As content in the raw water increases significantly with the growth of the dosage when the As content in PACl is above the guideline value. The increase value of As in raw water was  $0.30\text{ }\mu\text{g/L}$  while the dosage in PACl was 30mg/kg with the higher As content (10mg/kg).

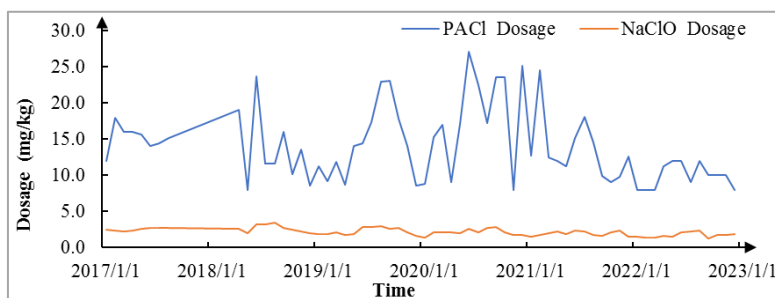
It is presumed that how will As content in water change if the As content in PACl constantly increasing and Figure 1 (d)

showed this change trend. It can be seen that the As content in raw water will be  $2\text{ }\mu\text{g/L}$  when the dosage is 30mg/kg and the content of As in raw water is 67 mg/kg, which is 20% of the guideline value of regulation ( $10\text{ }\mu\text{g/L}$ ) of drinking water in Macao and maybe take a potential risk to the drinking water.

The above results are theoretical calculation of As in raw water that induced by the adding of PACl. In the actual process of water treatment, raw water will be treated by several steps which can remove the heavy metals in raw water. It is necessary to discuss the removal rate of the water treatment process to heavy metals ions in IVP.

### 3.2. The Actual Increasing Amount of as Induced by WTC in Raw Water

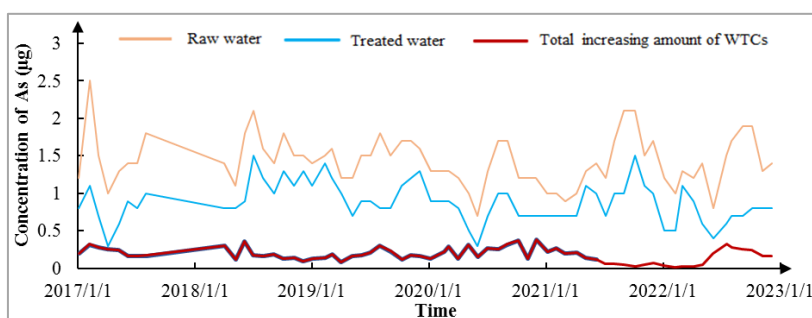
The dosage of WTCs for PACl and NaClO in the raw water in IVP were analyzed from 2017 to 2022 because As was detected mainly in these two materials. It was shown in Figure 2 that dosage of NaClO was between 1.4 and 3.4 mg/kg, and the dosage of PACl was between 8 and 30 mg/kg. The calculation of the content of heavy metal introduced by WTC based on this dosage.



**Figure 2.** The dosage of PACl and NaClO in IVP from 2017 to 2022.

Figure 3 showed the change trend of concentration of As ion in different water of IVP. It is shown that the concentration of As ion in the raw water is between 0.7 to 2.5  $\mu\text{g/L}$ . According to the statistical results of six years monitor, the As ion introduced by adding NaClO is very low and beyond 0.1  $\mu\text{g/L}$ , which almost has no impact on quality of raw water. So, the increment of the As concentration in raw water is mainly caused by adding PACl. The increased content of As in raw water by adding PACl is between 0.08  $\mu\text{g/L}$  and 0.38  $\mu\text{g/L}$ , which will have an influence on the content of As in raw water.

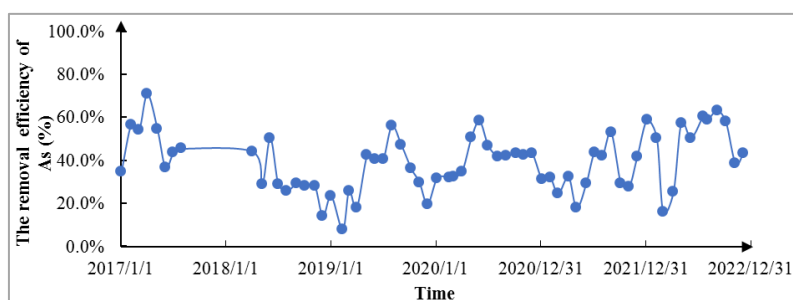
The total amount of As in the raw water after adding WTC is between 0.85 and 2.82  $\mu\text{g/L}$ . However, the heavy metal ions especially As will be removed effectively during the water treatment processes, such as flocculation, sedimentation, and filtration. This is the reason that the As in treated water has been significantly reduced just as shown in Figure 3.



**Figure 3.** The change trend of concentration of As ion in water of IVP (2017~2022).

### 3.3. The Removal Efficiency of Water Treatment Process to Metal Arsenic

There is a certain amount of heavy metals in the natural water resource and an increment introduced by adding WTCs. The water treatment processes can remove the heavy metal ions effectively. The main water treatment technology includes flocculation, precipitation, filtration and other processes in IVP. Figure 4 is the removal efficiency of As in the raw water by IVP water treatment process. It is shown that the removal efficiency has been significantly decreased, in which the highest removal efficiency is 76%.



**Figure 4.** The removal efficiency of As in the raw water in IVP (2017~2022).



Table 2 shows the removal efficiency of As in the raw water (including the content introduced by the WTC) of the IVP from 2017 to 2022. The highest removal efficiency was 71% and the lowest was 7.8% while the average efficiency was 39% in the past 6 years.

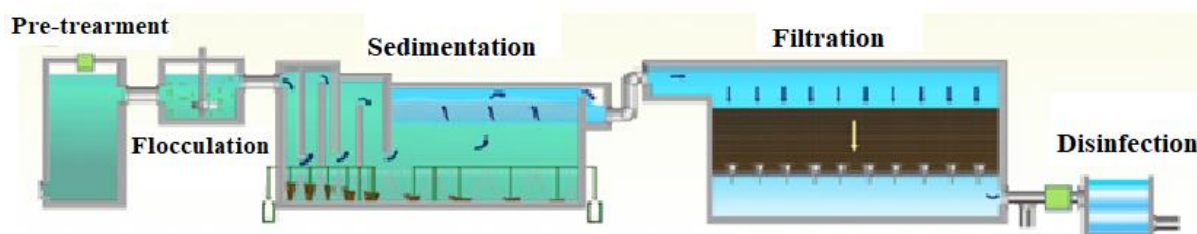
**Table 2.** The removal efficiency of As in the raw water.

| Concentration of As | Raw water<br>$\mu\text{g/L}$ | WTCs<br>$\mu\text{g/L}$ | Raw water +WTC<br>$\mu\text{g/L}$ | Treated water<br>$\mu\text{g/L}$ | Removal efficiency<br>% |
|---------------------|------------------------------|-------------------------|-----------------------------------|----------------------------------|-------------------------|
| Max                 | 2.50                         | 0.039                   | 2.53                              | 1.50                             | 71                      |
| Min                 | 0.70                         | 0.002                   | 0.72                              | 0.30                             | 7.8                     |
| Average             | 1.41                         | 0.018                   | 1.45                              | 0.88                             | 39                      |

### 3.4. The Influence of Water Treatment Process

The water treatment process has great influences on the quality of water, especially for As in water. For IVP, the main water treatment procedures include pre-treatment, flocculation, precipitation, filtration and disinfection. Figure 5 is the water treatment process diagram of IVP. During pre-treatment, the raw water goes through the pre-chlorination process and passes through the sieve in the water inlet to the treatment plant in order to remove the largest impurities of raw water such as leaves, twigs, fish and

other floating debris. After pre-treatment, the different WTCs are dosed in the water for coagulation, flocculation, pH adjustment and absorbing odors. The suspended solids in the water clump together after mixing with the chemicals, and form tiny sticky particles called "floc". After flocculation the water goes into the sedimentation tank to precipitate the solid particles. Then the water goes into several specially designed and filter for filtration. The disinfection is the final stage of water treatment. The treated water goes through post-chlorination in the water inlet and stays in tank for at least half an hour allowing the chlorine to take effect on the water for disinfection.



**Figure 5.** Diagram of water treatment process of IVP.

During the water treatment procedure, the key steps are flocculation and sedimentation for the removal of heavy metal ions. Heavy metal ions can be co-precipitated with alkali and the hydroxide precipitation of metal ions can be removed through the honeycomb inclined tubes at the bottom of the tank. After filtration, all the particles can be separated with the water leading to the clarification of water. The heavy metal As also can be co-precipitated with  $\text{Al}(\text{OH})_3$  or  $\text{Fe}(\text{OH})_3$ . Then  $\text{As}(\text{OH})_3$  precipitation is removed by filtration. The average removal efficiency of As in water is 44% in IVP, which can decrease the concentration of As. After treatment the physical and chemical indicators of the treated water have already met the European standards of drinking

water. The water treatment process is very important for the removal of As inducing by WTCs in water, thus to guarantee the drinking water quality.

### 3.5. The Hazard Risk Management of Heavy Metal in WTC

The main hazard heavy metals are As and Cr in WTCs through the statistical results in past 6 years in IVP. Pb is detected in  $\text{FeCl}_3$  sometimes while other hazard metals such as Cadmium (Cd), mercury (Hg) can be detected rarely in WTCs. From the chemical characteristics of Pb, Cd and Hg, they are easy to be co-precipitated with hydroxide and re-

moved by the water treatment process while the removal efficiency of As is just 44%. Therefore, the hazard risk to the water quality brought by heavy metal is mainly As and Cr.

The concentration of heavy in WTCs meets the guideline value of national standard for the qualified WTCs under the normal situation. But sometimes there are unqualified WTCs supplied to water treatment plants, especially in developing countries and economically backward regions. Then the content of hazard heavy metals will be high and exceed the national standard limit. It is necessary and helpful to reasonably evaluate the impact and recess the hazard risk of these heavy metals in WTCs on the water quality. The mathematical models were established to evaluate the maximum allowable values in the WTCs in this article based on the theoretical calculation, the test data and guideline value of WTCs and water quality in IVP.

### 3.5.1. The Maximum Allowable Values of Heavy Metals in PACl and FeCl<sub>3</sub>

The maximum allowable limit (MAL) of heavy metals in PACl was calculated according to the calculation equations 5 and 6. This method is based on the hypothesis that the content of heavy metal ions induced by PACl is not higher than 20% of the standard limit for drinking water. The dosage of PACl is 10~20mg/kg and the maximum dosage is 30mg/kg. The calculation results are shown in Table 3. The results show that the MALs of As and Pb in PACl are 70 mg/kg (0.007%) while they are 20mg/kg (0.002%) and 30 0mg/kg (0.03%) for Cd and Cr respectively. The permission concentration of Hg in PACL is very low, just 1 µg/L and the MAL is 7mg/kg (0.0007%).

**Table 3.** Maximum allowable amount of heavy metal ions in PACl.

| Guideline value  | As     | Pb     | Cd     | Hg      | Cr     |
|--|--------|--------|--------|---------|--------|
| Regulations of Macao water supply and drainage ( $C_{max}$ , µg/L) | 10     | 10     | 3      | 1       | 50     |
| GB15892-2020 (%)   | 0.0001 | 0.0005 | 0.0001 | 0.00001 | 0.0005 |
| MAL $x_{max1}$ (%)   | 0.007  | 0.007  | 0.002  | 0.0007  | 0.03   |
| MAL $x_{max1}$ (mg/kg)   | 70     | 70     | 20     | 7       | 300    |

The maximum allowable values of heavy metals in FeCl<sub>3</sub> are calculated according to the calculation equation 7 and 8. The calculation model is set up as the As in PACl. The dosage of FeCl<sub>3</sub> in the water treatment process is generally 10-20 mg/kg and the maximum dosage is 20mg/kg. Calculated as the formulas and combined with the limits stipulated

in the regulations of Macao water supply and drainage, the maximum allowable amount of heavy metal ions in FeCl<sub>3</sub> are shown in Table 4. Among them,  $x_{max2}$  is calculated when the dosage is 20mg/kg, and 20% of the limit of heavy metal ions stipulated in the Macao Water Supply and Drainage Regulations is added.

**Table 4.** Maximum allowable amount of heavy metal ions in FeCl<sub>3</sub>.

| Guideline value  | As     | Pb     | Cd     | Hg      | Cr     |
|--|--------|--------|--------|---------|--------|
| Regulations of Macao water supply and drainage ( $C_{max}$ , µg/L) | 10     | 10     | 3      | 1       | 50     |
| GB/T 4482-2018(%)  | 0.0002 | 0.0005 | 0.0001 | 0.00001 | 0.0008 |
| MAL $x_{max2}$ (%)   | 0.01   | 0.01   | 0.003  | 0.001   | 0.05   |
| MAL $x_{max2}$ (mg/kg)   | 100    | 100    | 30     | 10      | 500    |

### 3.5.2. The Management of Heavy Metal in WTCs

During the production of tap water, qualified WTCs can be used directly. The management measures should be implemented immediately to prevent the risk to water quality.

It is an effective method to employ hierarchical management, which suggests setting up the emergency warning levels for WTCs. The content of different hazard heavy metal was calculated and the detailed classification list of heavy metal ions in WTCs is shown in tables 5 & 6 ac-

cording to different unit.

**Table 5.** Classification list of heavy metal ions in WTCs (Unit %).

| Classification                 | WTCs              | As    | Pb    | Cd    | Hg     | Cr    |
|--------------------------------|-------------------|-------|-------|-------|--------|-------|
| I: Safe level (Green) 10%      | PACl              | 0.003 | 0.003 | 0.001 | 0.0003 | 0.017 |
| II: Warning level (Yellow) 20% |                   | 0.007 | 0.007 | 0.002 | 0.001  | 0.033 |
| III: Crisis level (Red) 50%    |                   | 0.02  | 0.02  | 0.005 | 0.002  | 0.083 |
| I: Safe level (Green)          | FeCl <sub>3</sub> | 0.005 | 0.005 | 0.002 | 0.0005 | 0.025 |
| II: Warning level (Yellow )    |                   | 0.010 | 0.010 | 0.003 | 0.001  | 0.050 |
| III: Crisis level (Red )       |                   | 0.025 | 0.025 | 0.008 | 0.003  | 0.125 |

**Table 6.** Classification list of heavy metal ions in WTCs (Unit mg/kg).

| Classification             | WTCs              | As | Pb | Cd | Hg  | Cr  |
|----------------------------|-------------------|----|----|----|-----|-----|
| I: Safe level (Green)      | PACl              | 3  | 3  | 1  | 0.3 | 17  |
| II: Warning level (Yellow) |                   | 7  | 7  | 2  | 1   | 33  |
| III: Crisis level (Red)    |                   | 17 | 17 | 5  | 2   | 83  |
| I: Safe level ((Green)     | FeCl <sub>3</sub> | 5  | 5  | 2  | 0.5 | 25  |
| II: Warning level (Yellow) |                   | 10 | 10 | 3  | 1   | 50  |
| III: Crisis level (Red)    |                   | 25 | 25 | 8  | 3   | 125 |

There are three levels for the classification of WTCs. The first level is safe level marked with green, which means that the heavy metal content in the WTCs is lower than the guideline value of nation and the WTCs can be used in the water treatment procedure safely. There is no health risk for the WTCs in level I. However, the OP should pay attention to the WTCs and communicate with the WTCs supplier if the results are at the marginal value, for example, the content of As in PACl and FeCl<sub>3</sub> are 0.0001% (or 1 mg/kg) and 0.0002% (or 2 mg/kg) respectively.

The second level is warning level and the color is yellow. The range of set value is based on the MAL of WTCs and the limit values are not same for the different WTCs, such as the concentrations of As in PACl and FeCl<sub>3</sub> are 0.00010%<As<0.00067% (or 1<As<7 mg/kg) and 0.00020%<As<0.00140% (or 2<As<14 mg/kg) respectively. It shows that there is controlled health risk if the WTCs are used in the production of potable water. For the internal management procedure in the water treatment plant, the first action is to require the suppliers to replace the unqualified production or supply the qualified WTCs. Then OP will reassess the influence of the used WTCs and adjust dosage if necessary. At the same time Lab will re-check the unquali-

fied WTCs sample and strictly monitor the content of related heavy metal in treated water. It must report the incident to the executive group of water company if the heavy metal ion in treated water is higher 20% than that of the limit value in the Regulation of Macao water supply and drainage regulations.

The crisis level is the third level and the marked with red. The heavy metal contents in WTCs are high for the crisis level. For example, the content of As in PACl and FeCl<sub>3</sub> are 0.00067%<As<0.00170% (or 7<As<17mg/kg) and 0.00140%<As<0.00350% (or 14<As<35 mg/kg) respectively. The concentration of heavy metal ions in treated water will be higher than that of standard limit if adding the WTC at the level III with the maximum dosage, which may bring high health risk for the drinking water. In case the test results of WTCs in the III level, some emergency measures will be carried out immediately. The OP will stop using the unqualified WTCs production and notify the suppliers. The Lab will analysis the treated water and pipe water continuously to monitor the water quality. Once the heavy metal ions in the treated water is half higher than that of the guideline value of Macao, the water producing procedure will be stopped and reported the accident to the government department immediately.



## 4. Conclusion

The paper studies the impact of heavy metal content in WTCs on drinking water, focusing on the heavy metals (As) in PACL exceeding the guideline value. The risk of heavy metals in WTCs is assessed and classified, then some management suggestions are proposed. The qualified WTCs (first level) can be used safely and will not affect water quality. The unqualified WTCs in warning level (second level) can be applied in water treatment under some emergency circumstances, such as wars, tsunamis, epidemic closures, and earthquakes, which has a little influence on the water quality and can ensure the safety of drinking water. But the WTCs in the crisis level (third level) cannot be used in the production of tap water. This study not only provides basic research for water manufacturers, but also provides reference ideas for effective management of WTCs with different quality, which has certain environmental protection significance and social benefits.

## Highlights

- 1) Establish mathematical models to access theoretically the relationship between the dosage of water treatment chemicals (WTCs) and the content of heavy metals in water.
- 2) Study and analyze the influence of Arsenic (As) in polyaluminum chloride (PACl) on water quality during water treatment procedure, such as dosage, the content of heavy metals and removal efficiency of water treatment process.
- 3) Calculate the maximum allowable amount of heavy metal ions in different WTCs.
- 4) Set the risk and management classification of heavy metals in WTCs and propose the management suggestions.

## Abbreviations

WTCs: Water Treatment Chemicals  
 As: Arsenic  
 PACl: Polyaluminum Chloride  
 IVP: ILha Verda Water Plant  
 WTP: Water Treatment Plant  
 FeCl<sub>3</sub>: Ferric Chloride  
 NaClO: Sodium Hypochlorite  
 SCADA: Supervisory Control and Data Acquisition System  
 OP: Operation Department  
 HCl: Hydrochloric Acid  
 ICP: Inductively Coupled Plasma Optical Emission Spectrometry  
 Pb: Lead  
 Cd: Cadmium  
 Hg: Mercury  
 Cr: Chromium  
 MAL: Maximum Allowable Limit

## Author Contributions

Conceptualization, methodology, and writing were carried out by Li Z. X., Zhan S. X. and Gao T. I. Lei C. T. and Zhao Q. N. reviewed and edited previous draft versions and provided supervision. All authors have read and agreed to the published version of the manuscript.

## Conflicts of Interest

The authors declare no conflicts of interest.

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