Measures to Sudden Water Quality Contamination Accident in Tokyo Waterworks

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INTRODUCTION

In May 2012, a tap water quality accident, caused by formaldehyde, occurred in water purification plants (WPPs) along the Tone River system, one of the substances of water quality standards. With this accident, as a countermeasure, 8 WPPs located in the Metropolitan area suspended water intakes/water supplies, and water supply was suspended for 360,000 households, or about 870,000 people (Figure 1). Hexamethylenetetramine (HMT) is not listed as an item for water quality standards based on Japan's Waterworks Law, however it reacts with chlorine used for purification process and generates formaldehyde.

In response to this incident, in March 2015 the Ministry of Health, Labour and Welfare stipulated 14 new substances similar to HMT which generate hazardous chemicals in the purification process and are difficult to be removed in normal purification treatment as "substances being difficult to dealt with by water treatment". However, the information on testing methods for these substances and removability in purification treatment were not presented at that time. For this reason, the we developed original testing methods and studied the detection status in water resource rivers. We also established removal methods in purification treatment process assuming case in which these substances flow into WPPs when a water quality accident happens in water resource rivers.

Figure 1: WPPs in which suspended water intake/water supply

Development of testing methods

Efficient testing methods were uniquely developed for 12 substances which we don't have knowledge of testing methods, out of the 14 substances which are difficult to removed in purification process.

Direct injection of liquid chromatography – tandem mass spectrometry (LC-MS/MS) (ESI/APCI): 10 substances
Simultaneous analysis by high performance liquid chromatography (HPLC) using DNPH: 2 substances

Table 1: List of substances which are difficult to be removed in the purification process and newly developed testing method

Classification	Substance name	Abbreviation	Testing method	Minimum Limit of Determination (μg/L)
Precursors of Chloroform	Acetonedicarboxylic Acid	ADC	DNPH Derivatization – HPLC Method	40
	Acetylacetone	ACA		40
	1, 3-Dihydroxybenzene	DHB	Direct injection of liquid chromatography – tandem mass spectrometry (LC-MS/MS) (APCI)	10
	1,3, 5-Trihydroxybenzene	THB		3
	2'-Aminoacetophenone	2'-AAP		2
	3'-Aminoacetophenone	3'-AAP		1
Precursors of Formaldehyde	1,1-Dimethylhydrazine	DMH	Direct injection of liquid chromatography – tandem mass spectrometry (LC-MS/MS) (ESI)	2
	N,N-Dimethylanaline	DMAN		1
	Trimethylamine	TMA		5
	Tetramethylenediamine	TMED		1
	N,N-Dimethylethylamine	DMEA		2
	Dimethylaminoethanol	DMAE		2
	Hexamethylenetetramine	HMT	*	–
Precursors of Bromate	Bromide (Potassium Bromate ... etc)	Br	*	–

*Testing method established (not included in subjects to study)

Investigation of detection status

We investigated the detection status of 14 substances by taking samples of major water resource points and WPP resource water (43 investigation points), using the newly developed testing methods.

- 13 substances were not detected, except for bromide
- Detected value of bromide was not affecting concentration of bromate in purified water in WPPs

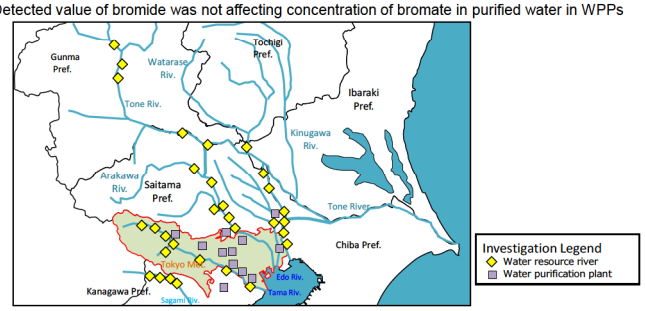

Figure 2: Investigation points of study on detection status in water resources

Finding factories consuming 14 substances and amounts consumed

We investigated factories that consume HMT, DMH and DMAN which are substances to Pollutant Release and Transfer Register (PRTR System), and the amounts consumed.

○There are15 factories in the Metropolitan area (12 of which use HMT)
2 factories in Saitama and Gunma consumed larger amount of HMT than the other factory.

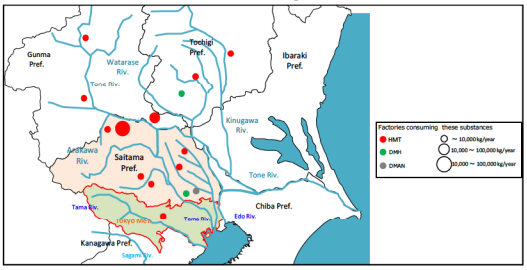

Figure 3: Amount of HMT, DMH and DMAN consumed by factory in the Tokyo Area

○Looking at the amount of HMT consumed by prefecture, a large amount is consumed in Saitama Prefecture adjacent to Tokyo, and the amount is increasing year by year.

It is highly likely HMT is detected in water resource rivers of our bureau.

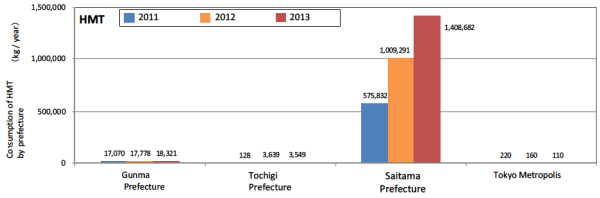

Figure 4: Consumption of HMT by Prefecture

Establishing methods for purification process

Regarding substances which are difficult to be removed in the purification process except, a study was conducted on removability by the powdered activated carbon and reactivity with chlorine.

○Treatment with powdered activated carbon
- Effective for removal of chloroform precursors
- Removed 50% or less of formaldehyde precursors , except DMH and DMAN

○Reactivity with chlorine
- All substances changed into chloroform or formaldehyde

○Formaldehyde precursors that cannot be removed with powdered activated carbon
①First, treat with chlorine and convert precursors into formaldehyde
②Next, formaldehyde can be absorbed by biological activated carbon (BAC)

Table 2 Powdered activated carbon removability and chlorine reactivity

Classification	Substance	Removal Rate by Powdered Activated Carbon (Reaction Time: 30 minutes)			Reactivity with chlorine		
	Injection Rate	10mg/L	50mg/L	100mg/L	0.5mg/L	1mg/L	2mg/L
Precursors of Chloroform	AcA	×	△	○	○	◎	◎
	DHB	×	○	◎	◎	◎	◎
	THR	△	◎	◎	◎	◎	◎
	2'-AAP	◎	◎	◎	◎	◎	◎
	3'-AAP	○	◎	◎	◎	◎	◎
Precursors of Formaldehyde	DMH	○	◎	◎	◎	◎	◎
	DMAN	○	◎	◎	◎	◎	◎
	TMA	×	×	×	△	○	◎
	TMED	×	×	△	◎	◎	◎
	DMEA	×	×	×	△	○	◎
	DMAE	×	×	×	×	△	○
	HMT	×	× (60mg/L)	–	–	◎	◎ (1.5mg/L)

Establishing methods for purification process methods

○Chloroform precursors
Can be removed if powdered activated carbon is injected before coagulation sedimentation

○Formaldehyde precursors
・DMH・DMAN
Can be removed if powdered activated carbon is injected before coagulation sedimentation

・TMA・TMED・DMEA・DMAE・HMT
①Inject chlorine before coagulation sedimentation to convert the precursor to formaldehyde
②The formaldehyde can be removed with BAC absorption

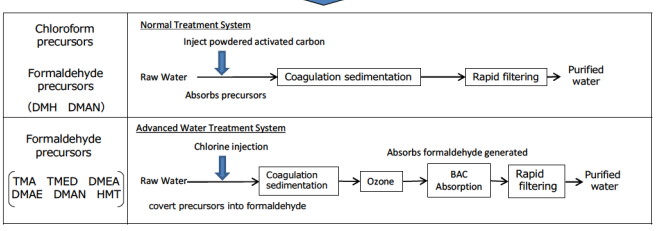

Figure 5: Removal method in purification process for substances which are difficult to remove in the purification process

References

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