Construction of an Effective and Efficient Pesticide Examination System

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Abstract: Bureau of Waterworks, Tokyo Metropolitan Government (Tokyo Waterworks) established an effective and efficient selection method for pesticides to be examined in consideration of various circumstances including detection status. Also, we developed examination methods for those pesticides of which examination methods had not yet been established.

This study also presents the results of the occurrence survey for these pesticides in raw water and treated water at water purification plants

1. Background

In Japan, pesticides in tap water are set as "Complementary items ".These items are set as a complement of Drinking Water Quality Standards, and the Ministry of Health, Labour and Welfare (MHLW) encourages water utilities to monitor and achieve the target value. The target value is set as a detected index value (DI), and each water utility is required to ensure that this index value is not exceeded 1.[1] The DI is calculated using Formula (1) below, which is the summation of the quotients of concentrations of detected pesticides divided by the target values for each pesticide as set by MHLW.

$$DI = \Sigma i \frac{DVi}{GVi} \quad ...(1)$$

DI:Detected index value DVi : Detected value of pesticide i GVi : Target value of pesticide i

Pesticides to be examined are selected from the "Target Pesticide List (Notification of MHLW in March, 2013)" [2] by each water utility in consideration of the detection possibility independently.

As the number and types of pesticides to be examined increases, the burden increases on each water utility. Thus, we established a selection method for effectively and efficiently conducting such examinations.

2. Survey Method and Results

2.1 Selection Method of Pesticides to be Examined and Its Process

The selection methods which Tokyo waterworks adopted was referenced to the results of the “Study on Chemical Substances in Tap Water by the Revised World Health Organization's (WHO) Guidelines for Drinking-Water Quality, etc.” (FY 2001-2003, Health and Labour Science Research).

The methods has two steps. First, we classified each pesticide into 5 or 10 grades regarding the 5 items, numbered (1) to (5)(Table 1).

(1) Pesticide shipment volume in major water source areas;
(2) Acceptable daily intake as an indicator of hazard (toxicity) (ADI);
(3) Detection status of pesticide in raw water and treated water at water purification plants owned by Tokyo Waterworks and in their water resources for the past five years;
(4) Biodegradability indicating degradability of pesticides;
(5) Water solubility of pesticides based on octanol/water partition coefficients (log P_{ow}).

Table 1: Pesticide Evaluation Scores at Tokyo Waterworks

(1)Shipment volume scores

Shipment volume(t/yr)	Score	Shipment volume(t/yr)	Score	
Less than 1	1	40 to less than 50		6
1 to less than 10	2	50 to less than 60		7
10 to less than 20	3	60 to less than 70	5※	8
20 to less than 30	4	70 to less than 80		9
30 to less than 40	5	80 or more		10

*Shipment volume in screening criteria 1-C uses a 5-grade evaluation

(2)Toxicity scores

ADI	Score
1 or more	1
0.1 to less than 1	2
0.01 to less than 0.1	3
0.001 to less than 0.01	4
below 0.001	5

(3)Detection status scores

Detected concentration	Score
Below LOQ	0
Between LOQ and 1/10 of target value	3
1/10 of target value or above	5

(4)Degradability scores

Biodegradability	Score
4 or more	1
3 to less than 4	2
2 to less than 3	3
1 to less than 2	4
below 1	5

(5)Water solubility scores

log P_{ow}	Score
6 or more	1
4 to less than 6	2
2 to less than 4	3
0 to less than 2	4
-5 to less than 0	5

Subsequently, we conducted screenings to determine if each pesticide falls into the three cases shown in Table 2. Pesticides which felt into all three cases were recognized as the pesticides with high possibility of being detected and high toxicity, and those were judged as high risk, and were selected as pesticides to be examined.

Table 2: Screening Criteria (3 cases)

Case 1: Focus on detection status and shipment volume

1-A	Detected in raw water, etc., in the last five years
1-B	No data, and has a shipment volume of at least 1 t/year
1-C	Does not fall into 1-A or 1-B, and has a total combined shipment volume and ADI score of at least 6
1-D	Decomposition products or oxons of pesticides selected in 1-A, 1-B, 1-C

Case 2: Evaluation of detection status, shipment volume, and ADI in parallel

2-A	Shipment volume of at least 1 t/year, and has a total combined shipment volume, ADI, and detection status score of at least 6
2-B	Decomposition products or oxons of pesticides selected in 2-A

Case 3: Consideration of the pesticide's properties

3-A	Shipment volume of at least 1 t/year, and has a total combined shipment volume, ADI, detection status, degradability, and water solubility score of at least 11
3-B	Decomposition products or oxons of pesticides selected in 3-A

From the 120 substances on the Target Pesticide List, approximately 80 substances were selected as a result of using this method as pesticides to be examined by Tokyo Waterworks.

2.2 Development of New Examination Methods

Among the 80 substances, 6 pesticides (Table 3) had not yet been established their examination methods. Therefore, we developed examination methods for these 6 pesticides.

Table 3:6 Pesticides Without Examination Methods

Pesticide name	Target value (mg/L)
Dithiocarbamate pesticide	0.005 (as CS_2)
Dazomet	0.006
Metam (carbam)	0.01
Glufosinate	0.02
Pyraclonil	0.01
Prothiofos	0.004

In the development of these examination methods, we focused on using methods such as Solid Phase Micro Extraction (SPME), Gas Chromatography - Mass Spectrometry (GC-MS), and Purge and Trap Gas Chromatography - Mass Spectrometry (P&T GC-MS), which are quick to use , which do not require complex pre-processing and large volumes of highly harmful organic solvents.

2.3 Examination methods for each pesticide

Table 4 lists the analytical instruments and measurement conditions used for each pesticide which we established examination method.

The limits of quantification (LOQ) and validity evaluation test results were determined based on the Guidelines[3)] established by MHLW.

Table 4: Analytical Instruments and Measurement Conditions for Each Pesticide

Pesticide name	Dithiocarbamate pesticide	Dazomet and Metam	Glufosinate		Pyraclonil	Prothiofos	
Measured substance	CS_2	MITC	Glufosinate	MPPA	Pyraclonil	Prothiofos	Prothiofos
Measuring tool	SPME GC-MS	P&T GC-MS	LC-MS/MS			GC-MS	
Column	CP-Volamine	InertCap AQUATIC	SM-18		ACQUITY UPLC	HP-5MS	
Other tool conditions	Fiber	Trap	Mobile phase A		Mobile phase A		
			Methanol		5 mM ammonium acetate methanol solution		
			Mobile phase B		Mobile phase B		
	DVB/CAR/PDMS	AQUA Trap-1	0.5% formic acid aqueous solution		5 mM ammonium acetate aqueous solution		
Ionization mode	EI	EI	ESI (−)		ESI (+)	EI	
Flow rate	(He gas)1.26 mL/min	(He gas)Constant pressure	(Mobile phase)0.5 mL/min		(Mobile phase)0.3 mL/min	(He gas)Constant pressure	
Injection volume		5 mL(P&T sample volume)	50 μL		50 μL	2 μL	
Temperature elevation or gradient conditions, B%	40 ℃(8 min)-40℃/min-265 ℃(0.5 min)	40 ℃(3.5 min)-4℃/min-80 ℃-8℃/min−160 ℃-20℃/min-200 ℃	5%(0 min)-50%(2 min)-5%(0 min)		90%(0 min)-1%(3-4 min)-90%(10 min)	70℃(2 min)-25℃/min-150℃-3℃/min-200℃-8℃/min-280℃(3 min)-20℃/min-	
Quantitative determination ions, m/z	Quantitative determination	Quantitative determination	Precursor ions		Precursor ions	Quantitative determination	
	76	73	180	151	315	309	162
	Qualifier ions	Qualifier ions	Product ions		Product ions	Qualifier ions	
	78, 44	45	85	133	169	267	139

(1) Dithiocarbamate Pesticide (Insect-fungicide)

Dithiocarbamate Pesticide is a generic term for 7 kinds of pesticides containing sulfur in their structures (Zineb, Ziram, Thiuram, Propineb, Polycarbamate, Manzeb [Mancozeb] and Maneb).

According to MHLW notification, these pesticides are needed to be evaluated by their value converted to the carbon disulfide (CS_2) they generate. [2)]

These pesticides are difficult to examine independently due to autolysis (decompose by themselves) gradually. For this reason, we decided to adopt the simpler method to examine CS_2 after decomposing with a reducting agent by using SPME-GC-MS (Fig. 1), based on the study by Katsura, et al.[5)].

The LOQ was determined to be 0.0005 mg/L ,which was 1/10th of the target value.

Sample:10 mL

↓ ←Sodium chloride 4g

↓ ←3 mol/L Sulfuric acid 0.1 mL

↓ ← 10% Ascorbic acid aqueous solution 0.2 mL

↓ ← Methanol 0.1 mL

Measured with SPME-GC-MS

(LOQ: 0.0005 mg/L)

Fig. 1: Analytical Flow Chart for Dithiocarbamate Pesticide

SPME-GC-MS is a method that uses a fiber coated in adsorbent (extracting phase) to extract a target substance from gas phase or liquid phase in a vial, and then measure it using GC-MS. For CS_2 measurements, a GC-MS equipped with a multifunctional auto-sampler was used to study the development of an examination method, and this can extract CS_2 automatically after adding the reducing agent, so many samples can be measured continuously. As for the reducing agent, we used ascorbic acid.

Then, we investigated the conversion ratio of the six types of Dithiocarbamate pesticides to CS_2.As a result , the conversion ratios were not uniform. The conversion ratios of Maneb was the lowest at 12%, on the other hand, Ziram's one was the highest at over 100%. For this reason, when CS_2 was detected, it was evaluated by multiplying by a coefficient of 100/12 to avoid underestimating the actual concentration.

(2) Dazomet and Metam (Insect-fungicide and soil fumigant)

Dazomet and Metam are hydrolyzed in environmental water and quickly decompose into volatile methyl isocyanate (MITC).[6] Therefore, we adopted a method of examining them by measuring MITC (Fig. 2) using a GC-MS equipped with a P&T. The LOQ for MITC was determined to be 0.00002 mg/L.

Sample:10mL

↓

Measured with P&T-GC-MS (as MITC)

(LOQ: 0.00002 mg/L)

Fig. 2: Analytical Flow Chart for Dazomet and Metam

The LOQ for Dazomet was determined to be 0.00005 mg/L (conversion coefficient of 2.22), and the LOQ for Metam was determined to be 0.00003 mg/L (conversion coefficient of 1.47). When MITC was detected during actual examination, it was evaluated by converting to Dazomet, which has the lower target value between Dazomet and Metam.

(3) Glufosinate (Amino acid herbicide)

Glufosinate is a substance with high hydrophilicity that is difficult to extract using a solid phase extraction method or a reverse polarity column with low polarity, both of which are widely used for pesticide measurement. Moreover, it is also known that Glufosinate easily decomposes in environmental water to produce 3-methylphosphinicopropionic acid (MPPA).[8] Therefore, we chose a liquid chromatography tandem mass spectrometer (LC-MS/MS) with which Glufosinate and MPPA were analyzed at the same time using an ion exchange column suitable for measurement of highly polar substances (Figure 3).

Sample:1mL

↓

Measured with LC-MS/MS

(LOQ: 0.005mg/L)

Fig. 3: Analytical Flow Chart for Glufosinate and MPPA

Although the LOQ of this method was 1/4 of the target value of Glufosinate, we could develop the rapid method that does not require any time-consuming pre-process such as drying or concentration.

(4) Pyraclonil (Herbicide)

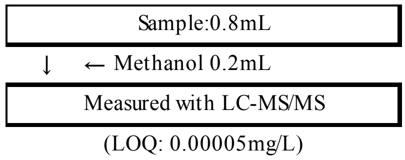

Fig. 4: Analytical Flow Chart for Pyraclonil

Pyraclonil has a hydrophobic nature (log P_{ow} = 2.18)[9] It is difficult to perform analysis using an ion exchange column or octadecyl-bonded C-18 column due to residue (remain) inside the column and other problems. Therefore, we adopted an LC-MS/MS examination method (Fig. 4) using an octyl-bonded C-8 column with low retention performance for hydrophobic substances. The LOQ was determined to be 0.00005 mg/L, which is less than 1/100th of the target value.

5) Prothiofos (Organophosphorus insecticide)

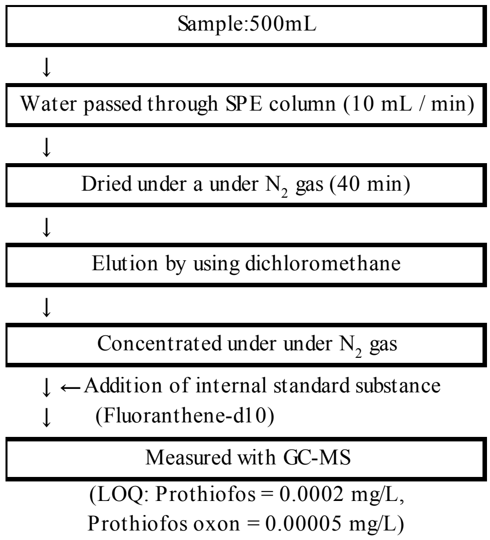

Fig. 5: Analytical Flow Chart for Prothiofos, Prothiofos oxon

Prothiofos is one type of Organophosphorus insecticide that is believed to produce prothiofos oxon by chlorination.[10] The sensitivity of the method introducing a sample into LC-MS/MS directly was insufficient. Thus, we adopted the method which measure Prothiofos and Prothiofos oxon by use of GC-MS with a solid phase extraction pre-processing using solid phase column packed with a Styrene divinylbenzene copolymer (Fig. 5).

Fluoranthene-d10 was used as an internal standard substance to lower variation in measurement with GC-MS.

After investigation, the LOQ for Prothiofos was determined to be 0.0002 mg/L, and the LOQ for Prothiofos oxon was determined to be 0.00005 mg/L. As calculating the detected value of Prothiofos, we sum the detected value of Prothiofos and the value that is converted from Prothiofos oxon's value to Prothiofos's one.

2.4 Result of the Occurrence Survey of Pesticides in Raw Water and Treated Water at Purification Plants

In the period of May to August (2014 to 2016), a period in which herbicides and other chemicals are sprayed onto paddy fields during rice cultivation, we conducted the occurrence survey at 8 water purification plants of Tokyo Waterworks in raw water and treated water of 6 pesticides for which we developed examination methods.

As the results of the survey, these 6 pesticides were not detected in treated water, but only Pyraclonil was detected in raw water at up to 5 water purification plants while the other 5pesticides were not detected in raw water(Table 5).

Although Pyraclonil was detected in raw water, it is believed that the Pyraclonil was removed during the water purification process because ozonation and biological activated carbon treatment were performed at the water purification plants where Pyraclonil was detected.

Table 5: Detection Status in Raw Water at Purification Plants

Pyraclonil		Raw water			
		May	June	July	August
2016	Max concentration (mg/L)	0.00007	0.00022	0.00012	N.D.
	Ratio among 8 plants	2/8	5/8	4/8	0/8
2015	Max concentration (mg/L)	0.00020	0.00032	0.00010	N.D.
	Ratio among 8 plants	1/8	4/8	4/8	0/8
2014	Max concentration (mg/L)	N.D.	0.00010	0.00005	N.D.
	Ratio among 8 plants	0/8	4/8	2/8	0/8

Pyraclonil was NOT detected in raw water,and the other 5 pesticides were NOT detected in either raw water or treated water.

3. Conclusion

Regarding the selection method of pesticides to be examined, we have established an effective and efficient selection method with reference to examination results from MHLW.

There were no established examination methods for 6 pesticides among the selected pesticides based on that method. Thus, we developed examination methods for them.

We were able to develop rapid methods that avoid complicated pre-processing and do not require large amounts of highly hazardous organic solvents as much as possible. Additionally, we were able to determine LOQ for all 6 pesticides that meet Guideline targets.

We conducted the occurrence survey of 6 pesticides which we developed the methods in raw water and treated water at 8 water purification plants using the newly developed examination methods. As the results of the survey, only one among the 6 pesticides was detected in raw water, while all of 6 pesticides were not detected in treated water.

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