

Construction of an Effective and Efficient Pesticide Examination System

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Keywords: Pesticide; instrumental analysis; examination method

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.

$$DI = \sum_i \frac{DVi}{GVi} \dots (1) \quad DI: \text{Detected index value} \quad DVi: \text{Detected value of pesticide } i \quad GVi: \text{Target value of pesticide } i$$

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				(2)Toxicity scores		
Shipment volume(t/yr)	Score	Shipment volume(t/yr)	Score	ADI	Score	
Less than 1	1	40 to less than 50	5	6	1 or more	1
1 to less than 10	2	50 to less than 60		7	0.1 to less than 1	2
10 to less than 20	3	60 to less than 70		8	0.01 to less than 0.1	3
20 to less than 30	4	70 to less than 80		9	0.001 to less than 0.01	4
30 to less than 40	5	80 or more		10	below 0.001	5

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

(3)Detection status scores		(4)Degradability scores		(5)Water solubility scores	
Detected concentration	Score	Biodegradability	Score	$\log P_{ow}$	Score
Below LOQ	0	4 or more	1	6 or more	1
Between LOQ and 1/10 of target value	3	3 to less than 4	2	4 to less than 6	2
1/10 of target value or above	5	2 to less than 3	3	2 to less than 4	3
		1 to less than 2	4	0 to less than 2	4
		below 1	5	-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 fell 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.

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.

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

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 Guidelines³⁾ 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	
	DVB/CAR/PDMS	AQUA Trap-1	Methanol	5 mM ammonium acetate methanol solution	
			Mobile phase B 0.5% formic acid aqueous solution	Mobile phase B 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		Quantitative determination
	76	73	180	151	309
	Qualifier ions	Qualifier 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 (CS₂) 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 CS₂ after decomposing with a reducing 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.

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 CS₂ measurements, a GC-MS equipped with a multifunctional auto-sampler was used to study the development of an examination method, and this can extract CS₂ automatically after adding the reducing agent, so many samples can be measured continuously. As for the reducing agent, we used ascorbic acid.

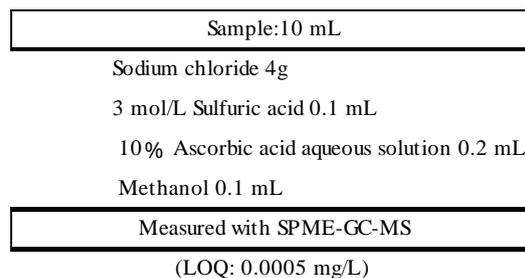


Fig. 1: Analytical Flow Chart for Dithiocarbamate Pesticide

Then, we investigated the conversion ratio of the six types of Dithiocarbamate

pesticides to CS₂. 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 CS₂ 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.

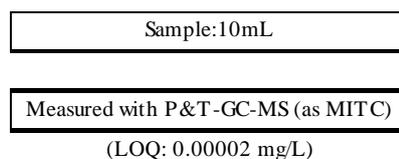


Fig. 2: Analytical Flow Chart for Dazomet and Metam

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-methylphosphinicpropionic 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).

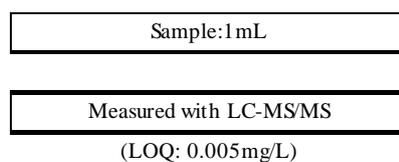


Fig. 3: Analytical Flow Chart for Glufosinate and MPPA

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)

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

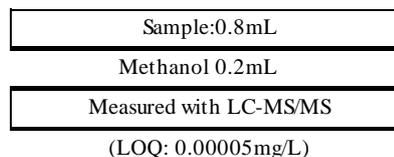


Fig. 4: Analytical Flow Chart for Pyraclonil

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)

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).

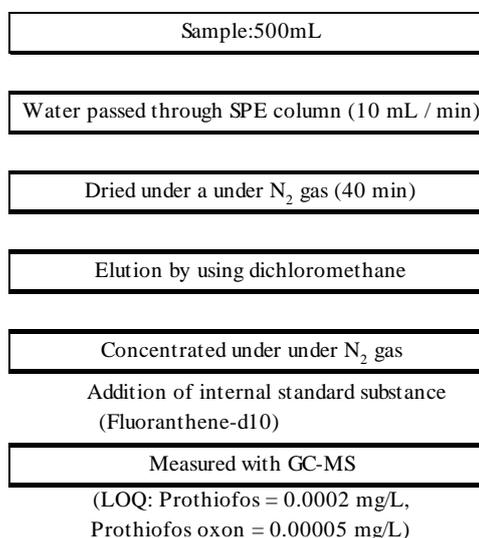


Fig. 5: Analytical Flow Chart for Prothiofos, Prothiofos oxon

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 5 pesticides 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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