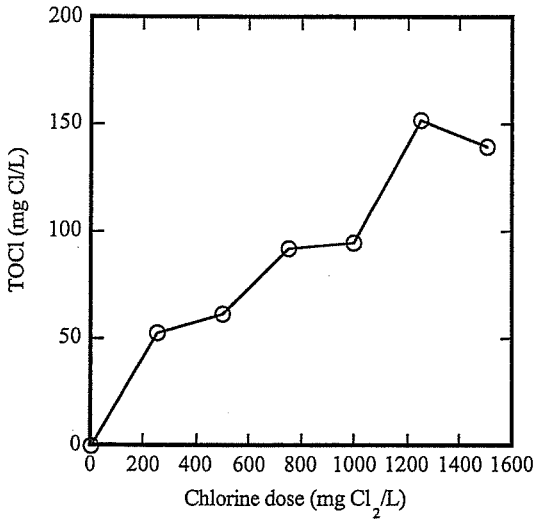


Figure 2. Effect of chlorine dose on TOCl formation. Conditions: NOM type, humic acid; TOC, 1000 mg/L; reaction time, 1 day; pH, 7.0; without bromide.

Table 1. Estimation of the activity inducing chromosomal aberrations of TOCl on TOX basis without bromide ion. Conditions: NOM type, humic acid; TOC, 1000 mg/L; reaction time, 1 day; pH, 7.0.

Chlorine dose ($mg Cl_2/L$)	Number of chromosomal aberrations (/100cells)	TOCl (mg Cl/L)	Activity per TOX (L/(100 cells mg Cl))
250	11	53.0	1.45
500	14	61.9	1.58
750	20	92.4	1.52
1000	22	95.1	1.62
1250	31	151.4	1.43
1500	32	139.6	1.60

Activity inducing chromosomal aberrations of brominated DBPs. TOBr increased with increasing bromide ion concentration (Figure 3), and TOCl decreased with increasing bromide ion concentration (Figure 4). The result of chromosomal aberration test is shown in Figure 5. The number of chromosomal aberrations increased with increasing bromide.

From the results in Figures 3-5 and the A_{TOCl} value obtained from Table 1, the number of chromosomal aberrations per TOBr was estimated for each condition (Table 2). In this estimation, the number of chromosomal aberrations caused by TOCl was calculated by multiplying TOCl by A_{TOCl} (=1.53). Then, this number was subtracted from the observed number of chromosomal aberrations to obtain the estimated number of chromosomal aberrations induced by TOBr. The number of chromosomal aberrations from TOBr on TOX basis fell in a

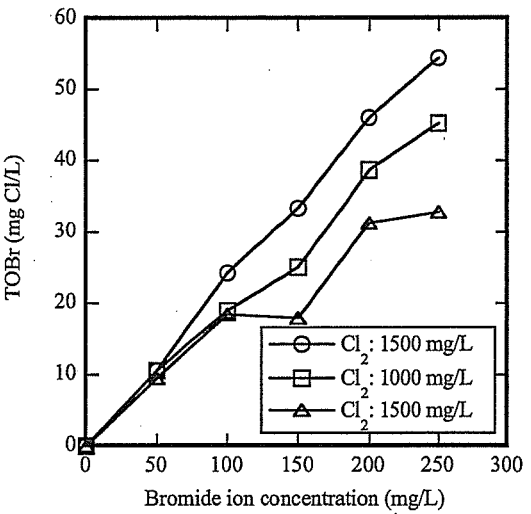


Figure 3. Effect of bromide ion concentration on TOBr formation. Conditions: NOM type, humic acid; TOC, 1000 mg/L; reaction time, 1 day; pH, 7.0. Note that TOBr concentration is expressed in mg Cl/L for comparison purpose.

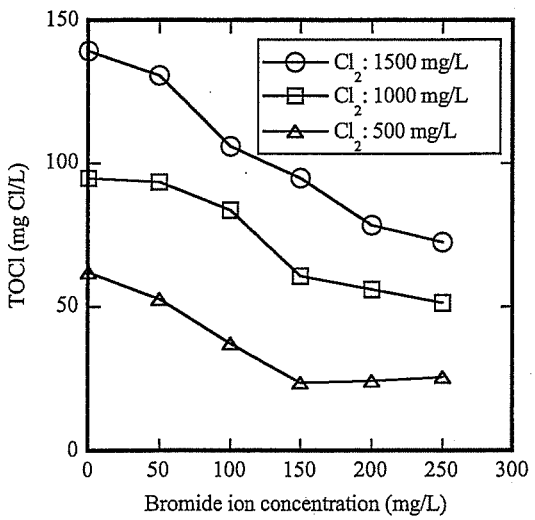


Figure 4. Effect of bromide ion concentration on TOCl formation. Conditions: see the caption of Figure 3.

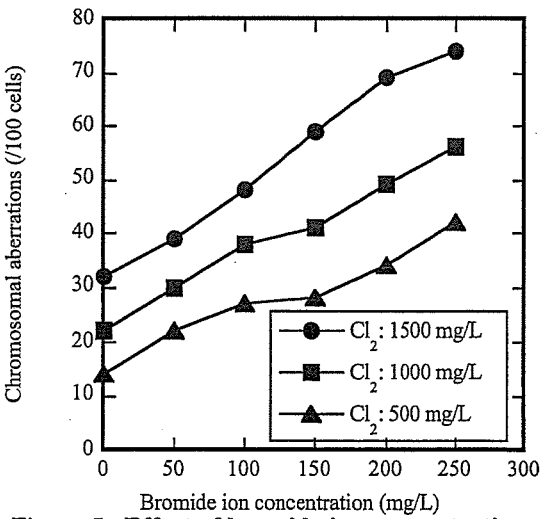


Figure 5. Effect of bromide ion concentration on TOCl formation. Conditions: see the caption of Figure 3.

relatively narrow range (6.37-8.91). The average value (A_{TOBr}) was 7.34 L/(100 cells mg Cl) and the standard deviation was 0.68 L/(100 cells mg Cl) (n=15). Based on this result, it was assumed that the number of chromosomal aberrations induced by TOBr on TOX basis did not change and was equal to A_{TOBr} to calculate the contribution of TOBr in the next subsection.

The ratio of A_{TOBr} to A_{TOCl} was 4.8. Therefore, it can be said that the mixture of brominated DBPs was approximately 4.8 times more toxic than TOBr on TOX basis. This result was in agreement with the evaluation based on the chromosomal aberration test on the reaction products between hypobromous acid and humic acid (i.e., only brominated products) and the ones from chlorination without bromide ion (chlorinated DBPs only) [8].

Table 2. Estimation of the activity inducing chromosomal aberrations of TOBr on TOX basis.
Conditions: see the caption of Figure 3. Also note that TOBr concentration is in mg Cl/L for comparison

Chlorine dose	Bromide ion	Number of chromosomal aberrations	TOCl	Chromosomal aberrations induced by TOBr	TOBr	Activity per TOX
(mg Cl_2/L)	(mg Br/L)	(/100cells)	(mg Cl/L)	(/100cells)	(mg Cl/L)	(L/(100 cells mg Cl))
500	50	22	53.0	10.4	9.6	7.60
	100	27	37.5	18.8	18.5	7.11
	150	28	23.5	22.9	17.9	8.91
	200	34	24.4	28.7	31.2	6.42
	250	42	25.6	36.4	32.9	7.74
1000	50	30	93.4	9.5	10.5	6.37
	100	38	83.6	19.7	18.9	7.31
	150	41	60.7	27.7	25.0	7.75
	200	49	55.9	36.8	38.7	6.65
	250	56	51.2	44.8	45.3	6.91
1500	50	39	131.3	10.2	10.6	6.76
	100	48	105.7	24.8	24.3	7.16
	150	59	94.6	38.3	33.4	8.02
	200	69	78.1	51.9	46.0	7.90
	250	74	72.4	58.1	54.5	7.47

Contribution of brominated DBPs to the activity inducing chromosomal aberrations of chlorinated humic acid. Under the assumption that the numbers of chromosomal aberrations induced by TOBr and TOCl on TOX basis do not change and these values are equal to A_{TOBr} and A_{TOCl}, respectively, the contribution of TOBr at each condition was obtained from these two values, TOBr (Figure 3), and TOCl (Figure 4). The contribution of TOBr was defined as:

$$\text{Contribution of TOBr (\%)} = \frac{\text{Number of chromosomal aberrations from TOBr}}{\text{Total number of chromosomal aberrations}} \times 100 = \frac{A_{TOBr} \bullet \text{TOBr}}{A_{TOCl} \bullet \text{TOCl} + A_{TOBr} \bullet \text{TOBr}} \times 100 \quad (3)$$

The contributions of TOBr at other conditions are shown in Figure 6. The contribution of brominated DBPs tends to be high at low chlorine-to-TOC ratio and high bromide-to-TOC ratio. Also, under the assumption that the relationship between the two ratios and the contribution of TOBr holds for real souse water, the contribution of brominated DBPs in drinking water can be estimated. For example, for a source water with TOC of 1.5 mg/L and bromide ion concentration of 75 μg/L, the contribution of TOBr was estimated to be 27.9%. Also, if the bromide ion concentration is above 150 μg/L for the same TOC level, the contribution of TOBr exceeds 50%. Considering that the average bromide concentrations in US source waters is 100 μg/L [1], it is not uncommon that the contribution of TOBr is close to or more than 50% in real drinking water

practice. The above estimation indicates that the contribution of brominated DBPs is not negligible even at relatively low bromide ion concentration.

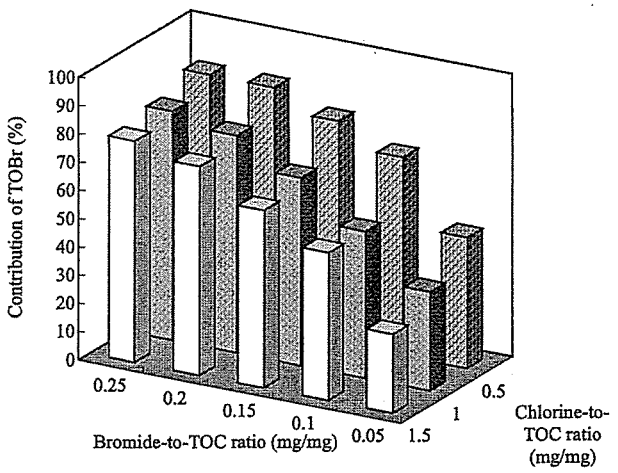
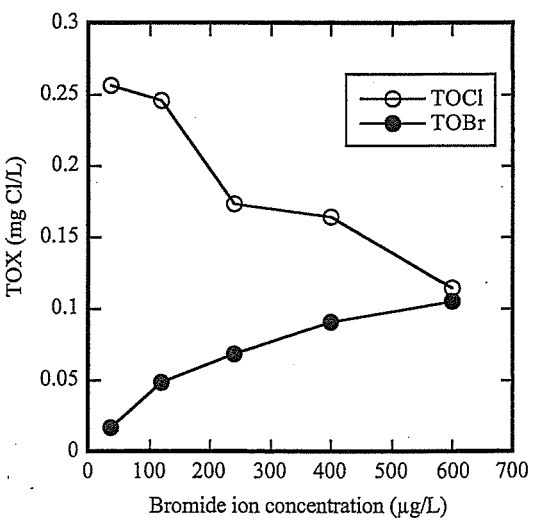


Figure 6. Contribution of TOBr to the activity inducing chromosomal aberrations of the reaction products from the chlorination of humic acid in the presence of bromide. Condition: see the caption of Figure 3. Note that both chlorine-to-TOC and bromide-to-TOC ratios were close to those in actual drinking water treatment practice.

Contribution of brominated DBPs to the activity inducing chromosomal aberrations of chlorinated Lake Biwa water

Effect of bromide ion concentration on TOBr, TOCl, and the activity inducing chromosomal aberrations. The trends of TOBr and TOCl formation for elevated bromide ion concentration were the same as for humic acid solution i.e., TOBr increased and TOCl decreased with increasing bromide ion concentration (Figure 7). Also, the number of chromosomal aberrations increased with bromide ion concentration (Figure 8).



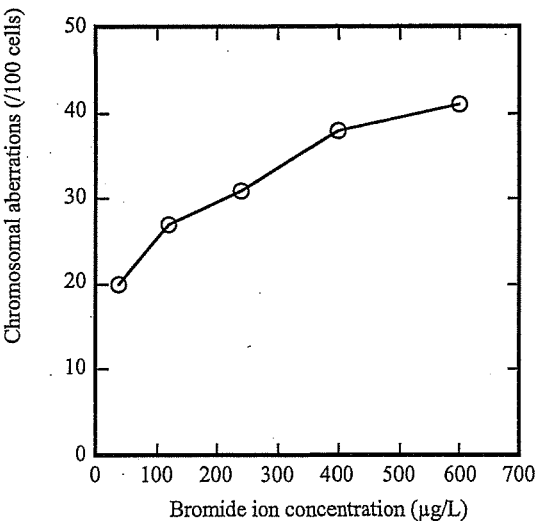


Figure 7. Effect of bromide ion concentration on TOBr and TOCl formation (Lake Biwa Water). Conditions: TOC, 1.88 mg/L; chlorine dose, 2.89 mg/L, pH, 7.0; reaction time, 1 day.

Figure 8. Effect of bromide ion concentration on the activity inducing chromosomal aberrations (Lake Biwa Water). Conditions: see the caption of Figure 7.

A_{TOCl} and A_{TOBr} values of chlorinated Lake Biwa water.

The A_{TOCl} and A_{TOBr} values of chlorinated Lake Biwa water were determined by multiple linear regressions. This was because bromide ion was present in Lake Biwa water, and it was impossible to obtain the samples that contain only chlorinated DBPs to estimate A_{TOCl} separately. The result of the regression is shown in Table 3.

The A_{TOCl} and A_{TOBr} values of the chlorinated Lake Biwa water were 1.00 and 6.58 L/(100 cells mg Cl) , respectively. Both the A_{TOCl} and A_{TOBr} values of chlorinated Lake Biwa water were close to the ones of chlorinated humic acid solution. Also, the A_{TOCl} and A_{TOBr} values of the chlorinated humic acid solution were recalculated by multiple linear regression for comparison. These values are in good agreement with the values obtained in the previous section.

The ratio of A_{TOBr} to A_{TOCl} was 6.58 for chlorinated Lake Biwa water (note that the ratio for chlorinated humic acid was 4.8). Thus, the contribution of TOBr to the toxicity of chlorinated water is not negligible even for a real source water.

The slight differences in A_{TOBr} (50%) and A_{TOCl} (10%) between Lake Biwa water and humic acid solution could be attributed to the difference in chemical structure of NOM. But, more comprehensive characterization of NOM would be necessary to elucidate the reaction pathways between NOM and hypohalous acids that are responsible for these difference. Also, it should be noted that A_{TOBr} and A_{TOCl} values were estimated under the assumption that the recovery of mutagenic compounds by solid phase extraction was 100%. This assumption is reasonable as the major fraction of mutagenic compounds is hydrophobic compounds, but may have caused some bias in A_{TOBr} and A_{TOCl} estimation.

Table 3. Summary of the activities inducing chromosomal aberrations on TOX basis.

	A_{TOBr}	A_{TOCl}	R^2	Adjusted R^2
Lake Biwa Water	6.58	1.00	0.985	0.646
Humic Acid (multiple linear regression)	7.36	1.54	0.973	0.894
Humic Acid (based on A_{TOCl} without bromide)	7.34	1.53	-	-

Contribution of brominated DBPs. From TOCl and TOBr values and A_{TOBr} and A_{TOCl} values (Table 3), the contribution of TOBr was estimated (Table 4). Even at the ambient bromide ion concentration (38.2 μg/L), the contribution of TOBr was more than 30%. Also, it was demonstrated that the contribution does exceed 50% for a real source water that contains bromide ion higher than 120 μg/L.

Table 4. Contribution of brominated DBPs to the activity inducing chromosomal aberrations of chlorinated Lake Biwa water.

Bromide ion concentration (μg/L)	Contribution of TOBr (%)
38	31.3
120	56.6
240	72.2
400	78.4
600	85.8

CONCLUSIONS

The combination of chromosomal aberration test and an analytical technique to differentiate total organic chlorine (TOCl) and total organic bromine (TOBr) revealed that brominated DBPs produced during chlorination is 5 to 7 times more mutagenic than chlorinated DBPs on TOX basis. The contribution of TOBr to the mutagenicity of chlorinated water could be more than 50% for a bromide-to-TOC ratio commonly found in source waters. From these results, it is concluded that brominated disinfection by-products (DBPs) can be significant contributors to the toxicity of drinking water. Thus, controlling of brominated DBPs is a critical issue for drinking water utilities that rely on source waters containing relatively high concentration of bromide ion.

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Occurrence of bromate in raw and finished waters for drinking water supply in Japan

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ABSTRACT

A nation-wide survey on bromate level in raw water and finished water was conducted at 87 waterworks in 2002 and 2003 prior to the determination of revised water quality standards for drinking water in Japan. Excess level(>10 μg/L) of bromate was detected from several finished water samples, which were taken from the waterworks with ozonation facilities. Increase of bromate in the finished water was chiefly due to formation in the course of ozonation, and addition by chlorination as impurity of commercially available and on-site produced sodium hypochlorite. Case of excess bromate in tap water after the enforcement of the revised standard and countermeasures are also described.

KEYWORDS

bromate, ozonation, sodium hypochlorite, water quality standards for drinking water

INTRODUCTION

Bromate is known as a positive mutagenic compound confirmed by both *in vivo* and *in vitro* tests such as Ames test, a chromosomal aberration test and a micronucleus test. It is also classified as IARC(International Agency for the Research on Cancer) Group 2B substances, i.e. "Possibly carcinogenic to humans". In recent years, existence of bromate(BrO_3^-) in drinking water has been one of great concerns. Bromate is hardly removed by conventional drinking water treatment system. Moreover, it is known that bromate level increases after ozonation due to oxidation of bromide into bromate(Haag and Hoigne, 1983). Dosing of sodium hypochlorite for chlorination also causes increase of bromate level in finished water because it contains

bromate as impurity.

Revised water quality standards for drinking water have been enforced in Japan since April 2004. Bromate was newly added as one of fifty standard items and its standard value was set at 10 μg/L. Chemical standards for drinking water treatments were also set at the same time and increase of bromate in finished water should be less than 5 μg/L at the maximum dosing of the chemicals. USEPA has already set the maximum contamination level of bromate for drinking water at 10 μg/L. WHO has also set the same level of guideline value in the latest Guideline of Drinking Water Quality, announced in September 2004.

This paper shows results of a nation-wide survey of bromate level in raw water and finished water in 87 waterworks, prior to the determination of the revised water quality standards for drinking water in Japan. Case of excess bromate in tap water and countermeasures are also described.

MATERIALS AND METHODS

Site selection and sampling

Sources of bromate in drinking water were assumed that; (1) bromate exists in raw water and remains after drinking water treatment, (2) bromide in raw water was oxidized into bromate by ozonation process, and (3) sodium hypochlorite for chlorination contains bromate as impurity. 87 waterworks were selected for sampling in this survey as shown in Figure 1. They contain 38 waterworks with ozonation facilities and 49 waterworks without ozonation. Chlorine agents used in the waterworks were on-site produced sodium hypochlorite with or without membrane separation in electrolytic bath, commercially available sodium hypochlorite and liquid chlorine.

Raw water and finished water samples were taken at each waterworks in November and December 2002. 1000 mL polyethylene bottles were filled without any bubbles, sealed tightly, transported in dark and cool condition, and immediately served for instrumental analyses of bromate, bromide and chloride. A questionnaire survey was also performed to each waterworks on operating conditions of ozonation(dose, locations, retention time, type of reactor) and chlorination(reagent, dose, locations). Water qualities and climate conditions(weather, air temperature, water temperature, pH, color, turbidity, potassium permanganate consumption, total organic carbon) in the sampling date were also included in the questionnaire.

In February 2003, follow-up survey was performed at 19 waterworks, in which bromate level in raw water was more than 0.5 μg/L, or that in finished water was more than 2.0 μg/L without ozonation, or more than 4.0 μg/L with ozonation.

Analytical procedures

All samples were filtered with 0.2 μm membrane filter prior to instrumental analyses. High levels of chloride and sulfate were also removed before analysis of bromate by filtering samples through silver cartridges and barium cartridges, respectively. Bromate was determined with ion chromatography by post-column reaction(Dionex AQ1120 with post-column reactor).

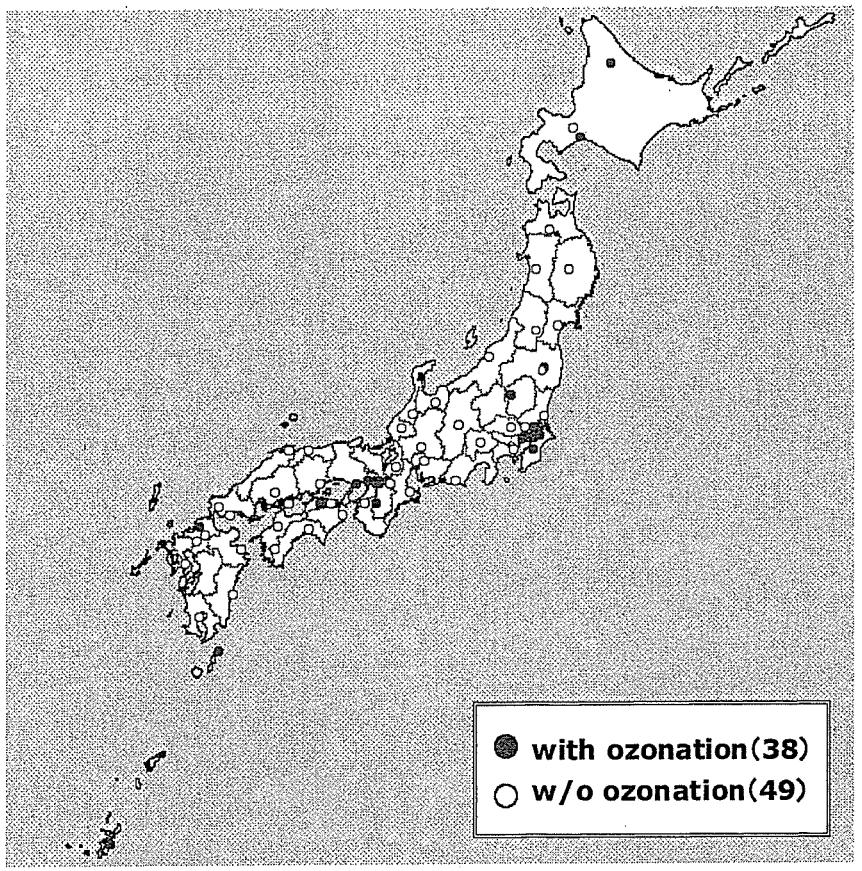

Figure 1 Location of 87 waterworks selected in the nation-wide survey

Table 1 Analytical conditions of ion chromatography by post-column reaction

Analytical instrument	Dionex AQ1120 with post-column reactor
Column	Dionex Ionpac AS-9HC (250mm x 4mm)
Guard column	Dionex Ionpac AG-9HC (50mm x 4mm)
Suppressor	ASRS-ULTRA 4mm in chemical mode
Eluent	9mM Na_2CO_3
Flow rate	1.0mL/min.
Temperature	40 C
Injection volume	500_L
Detection	UV/VIS 268nm

Table 2 Analytical conditions of ion chromatography

Analytical instrument	Dionex DX320
Column	Dionex Ionpac AS-9HC (250mm x 4mm)
Guard column	Dionex Ionpac AG-9HC (50mm x 4mm)
Suppressor	ASRS-ULTRA in external mode
Eluent	9mM Na_2CO_3
Flow rate	1.0mL/min.
Temperature	35 C
Injection volume	100_L
Detection	UV/VIS 205nm (bromide ion) electrical conductivity (chloride ion)

Determination limit was 0.02 μg/L. Bromide and chloride were measured by ion chromatography (Dionex DX320). Table 1 and 2 show analytical conditions of ion chromatography by post-column reaction and ion chromatography, respectively.

RESULTS AND DISCUSSION

Figure 2 shows histograms of bromate level in raw water taken at 87 waterworks. Bromate level in 62 raw water samples was less than the determination limit(0.02 μg/L). In the case of river water samples in urbanized areas, bromate level was around 0.5 μg/L. Maximum bromate level was 1.6 μg/L, which was probably due to effluent from a waste landfill site located at upstream of the waterworks. Thus, bromate originally exist in raw water was not significant in most waterworks. Bromide level in 53 raw water samples was less than the determination limit(0.50 μg/L) as shown in Figure 3. In 7 samples, bromide level was higher than 100 μg/L and maximum level was 445 μg/L. Potential of bromate formation by ozonation might be much higher in these waterworks than others.

At 27 out of 38 waterworks with ozonation facilities, bromate levels in the finished water samples were higher than 1.0 μg/L, which is equivalent to 10% of the revised water quality standard value(10 μg/L) as shown in figure 4. Two finished water samples contained higher bromate than the standard value and the maximum observed bromate was 21.5 μg/L. The waterworks with the highest bromate in finished water also observed the highest bromate(1.61 μg/L) and bromide(0.35 mg/L) in its raw water. Moreover, it uses on-site produced sodium hypochlorite without membrane separation, which may contains much bromate as described latter. There is a possibility that multiple sources of bromate caused the highest bromate level in the finished water observed in the survey.

In the finished water samples without ozonation, bromate level was lower than that with ozonation as Figure 5. However, 11 out of 49 samples contained bromate higher than 1.0μg/L, which was certainly due to the impurity of bromate in the chlorine agents. Table 3 shows increase

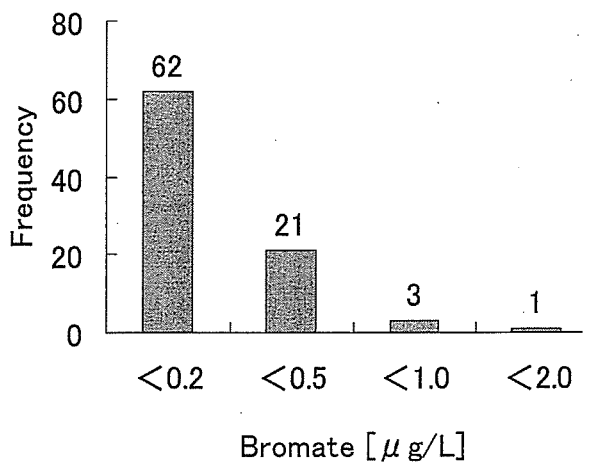

Figure 2 Bromate level in raw water at 87 waterworks

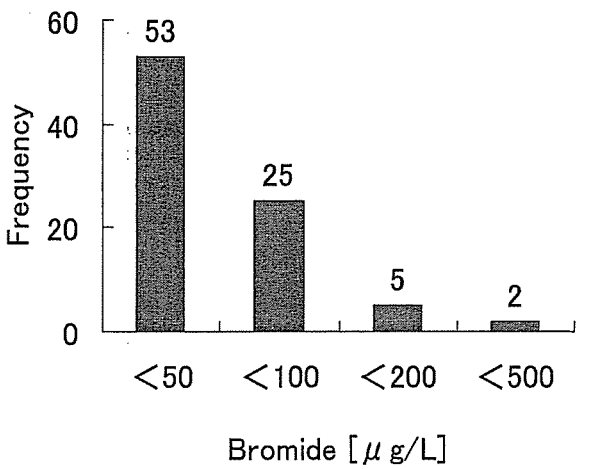

Figure 3 Bromide level in raw water at 87 waterworks

of bromate in the raw and finished water samples at 49 waterworks without ozonation. On-site produced sodium hypochlorite without membrane separation caused much increase of bromate(0.50 - 3.99 μg/L) compared to that with membrane separation(0.22 - 0.71 μg/L). Higher dosing ratio of the former sodium hypochlorite is part of the reasons of much bromate increase because available chlorine level in the former was the lowest(1%) as shown in Table 3. Bromide as impurity of raw salts might also affect the bromate in both type of on-site produced sodium hypochlorite. Ozaka *et al.* pointed that bromide level in raw salts for on-site production of sodium hypochlorite was much varied depending on purity and production method of the salts (Ozaka *et al.*, 2003).

It is noticeable that specific commercially available sodium hypochlorite also increased bromate level in the finished water up to 6.33 μg/L, which was higher than the chemical standards of for drinking water treatments(up to 5 μg/L). 7 out of 9 waterworks, where increase of bromate level was more than 1.0 μg/L, used commercially available sodium hypochlorite for chlorination. Other 2 waterworks used the on-site produced sodium hypochlorite without membrane separation. Increase of bromate level after dosing of liquid chlorine was not over 0.52 μg/L at 11 waterworks.

Figure 6 shows results of the follow-up survey at 19 waterworks, in which bromate level in the raw water was more than 0.5 μg/L, or that in the finished water was more than 2.0 μg/L without ozonation, or more than 4.0 μg/L with ozonation. Bromate level in 19 finished water samples was less than the previous survey at most waterworks, partly due to decrease of ozone and/or chlorine dosing ratio. Colder water temperature compared to the previous survey might be also one of the reasons of less bromate formation, especially in the course of ozonation. However, 2 out of 11 finished water samples with ozonation still contained excess bromate, which was taken from the same waterworks as in the previous survey. Increases of bromate in the course of chlorination were 0.13 μg/L by liquid chlorine, 2.8 - 3.0 μg/L by on-site produced sodium hypochlorite, and 0.42 - 5.0 μg/L by commercially available sodium hypochlorite.

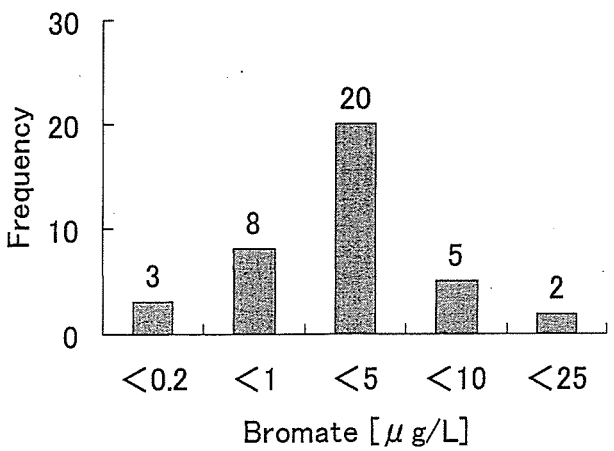

Figure 4 Bromate level in finished water at 38 waterworks with ozonation

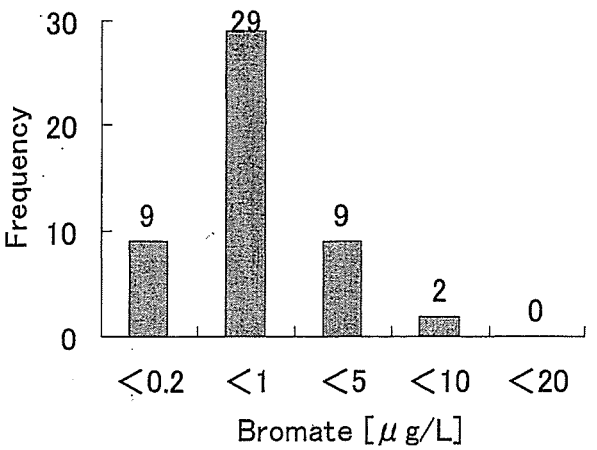

Figure 5 Bromate level in finished water at 49 waterworks w/o ozonation

Table 3 Increase of bromate level between the raw and finished water samples at 49 waterworks without ozonation

Chlorine agent	No. of samples	Available Chlorine [%]	Increase of bromate ion [μg/L]
On-site produced sodium hypochlorite (w/o membrane separation)	3	1	0.50 ~ 3.99
On-site produced sodium hypochlorite (with membrane separation)	5	5	0.22 ~ 0.71
Commercially available sodium	30	10 or 12	0 ~ 6.33
Liquid chlorine	11	12	0 ~ 0.52

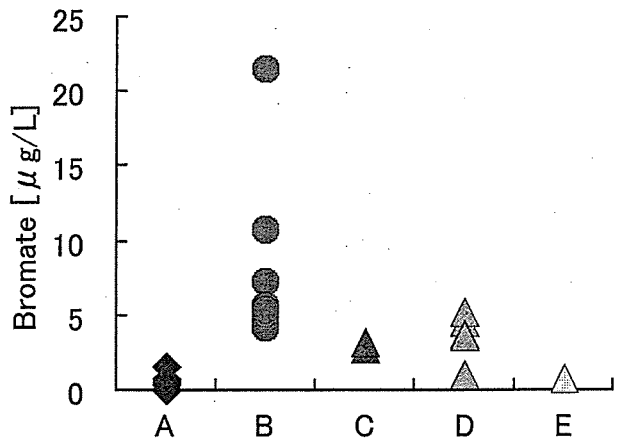

Figure 6 Bromate in raw and finished water at 19 waterworks
(Follow-up survey in Feb. 2003)
A: Raw water
B: Finished water (Ozonation)
C: Finished water
(On-site produced sodium hypochlorite)
D: Finished water
(Commercially available sodium hypochlorite)
E: Finished water (Liquid chlorine)

Case of excess bromate in drinking water and countermeasures

Excess of bromate in drinking water have been reported from several waterworks since the enforcement of the water quality standards for drinking water in April 2004. In the case of a small water utility located in Hokkaido Prefecture, 147 μg/L of bromate, which was 14.7 times higher than the standard value, was detected in tap water just after they started measurement of bromate in April 2004. Finished water taken from the utility still contained 168 μg/L of bromate on the remeasurement. The local municipality restricted usage of the water for drinking and cooking, and distributed drinking water from neighboring water utilities by plastic canteens for nearly a week.

Source of the bromate contamination in the drinking water was identified as its commercially available sodium hypochlorite purchased from a local supplier. It contained extremely high level of bromate up to 668 mg/L. Bromate was not detected in its raw water. After the sodium hypochlorite was replaced with new one, which contained 19 mg/L of bromate, bromate in finished water decreased to 2 μg/L and the restriction was released. The water utility has increased the frequency of bromate measurement in tap water from every 3 months to every month. It has also continued investigation of bromate in the sodium hypochlorite for chlorination and asked the local supplier to submit a component analysis sheet of the sodium hypochlorite.

In June 2004, Ministry of Health, Labour and Welfare has promoted awareness of bromate contamination in sodium hypochlorite for drinking water treatment. This advised every waterworks and local municipalities as to; (1) confirmation of bromate level in both commercially

available and on-site produced sodium hypochlorite, (2) appropriate use and storage of sodium hypochlorite taking account of bromate increase and available chlorine decrease that may occur under high temperature, (3) attention to chlorination in high dosing ratio against ammonium nitrogen, iron, and manganese in raw water, and so on.

CONCLUSION

The nation-wide survey of bromate level in drinking water, sampled at various waterworks in Japan, determined excess level of bromate in several finished water samples. Increase of bromate in the finished water was chiefly due to formation in the course of ozonation process and addition in chlorination process as impurity of commercially available and on-site produced sodium hypochlorite. Result of the survey was utilized for the determination of the revised water quality standards for drinking water in Japan.

It is concluded that potential of excess bromate in the drinking water is very high at a number of waterworks, where ozonation and/or chlorination in high dosing ratio are performed especially in summer seasons. It is recommended to control dosing ratio and retention time in ozonation and chlorination process, and to make routine check of sodium hypochlorite quality on bromate and available chlorine level.

ACKNOWLEDGEMENT

This survey was promoted and financially supported by Ministry of the Environment from FY 2001 to 2003. The authors are grateful to research committee on "Existence of Hydrophilic and Persistent Toxic Chemicals in the Drinking Water Resources, Control by Drinking Water Treatments, and Risk Assessment", Ministry of Health, Labour and Welfare.

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B－39 浄水塩素処理過程におけるハロ酢酸生成に関わる化学構造のスクリーニング

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1. はじめに

浄水塩素処理過程で生成する消毒生成物のうち，ハロ酢酸(HAA)は，検出濃度・頻度が高い物質群の一つである。また，臭素を含む一部のものが非常に高い毒性を示すため，近年注目を集め始めており，その生成機構解明の重要性も高まってきている。しかしながら，現在までに生成機構がほぼ明らかにされている消毒副生成物はトリハロメタン(THM)のみであり，HAAの生成機構については不明な点が多い。

そこで，本研究では，HAA 生成機構解明の一環として，様々な化合物の塩素処理からの HAA 生成量を測定し，その生成量に大きな影響を与える化学構造の特定を試みた。さらに，共存する臭化物イオンの HAA 生成特性に及ぼす影響も調査した。

2. 実験方法

表 1 に調査対象とした 44 種の有機化合物を示す。その選定にあたっては，芳香族化合物では，THM 生成に大きな影響を与えるとされるフェノール性ヒドロキシル基と，天然溶存性物質中に多く含まれるカルボキシル基の，数および位置関係に着目した。脂肪族化合物の選択では，カルボキシル基とともに，β-ジケトン構造形成に重要なカルボニル基に特に注意を向けた。

表 1:測定対象化合物

芳香族化合物	脂肪族化合物
フェノール	クロトン酸
レゾシノール	マレイン酸
カテコール	コハク酸
ヒドロキノン	フマル酸
サリチル酸	クエン酸
m-ヒドロキシ安息香酸	3-ケトグルタル酸
p-ヒドロキシ安息香酸	グリオキシル酸
フロログルシン	蟻酸
o-メトキシフェノール	ピルビン酸
o-クレゾール	アセトアルデヒド
バニリン酸	酢酸
安息香酸	アセトン
フタル酸	乳酸
没食子酸	アセチルアセトン
5-ヒドロキシイソフタル酸	プロピオン酸
2,4-ジヒドロキシ安息香酸	1-プロパノール
2,5-ジヒドロキシ安息香酸	エチレングリコール
3,5-ジヒドロキシ安息香酸	グルコース
2,3-ジヒドロキシ安息香酸	スクロース
2,6-ジヒドロキシ安息香酸	マルトース
3,4-ジヒドロキシ安息香酸	ラクトース
	アリルアルコール
	グルコサミン

ハロ酢酸で分析の対象としたものは，$CH_{3-m-n}Br_nCl_m$-COOH(n, mは0,1,2,or3かつm+n ≥1)で表される9種である。塩素処理の条件は，化合物濃度が3 mg-C/L，塩素濃度が30 mg/L(次亜塩素酸を添加)，pH=7，反応時間=24時間とし，その結果生成するHAA生成量を測定した。これに加え，臭化物イオン(Br)が4 mg/L存在する条件でも同様の塩素化実験を行い，その影響も調査した。

HAA濃度の測定は，HAAを酸性メタノール法[1]でメチル化，液液抽出した後，それをGC/MS(GC:Agilent 6890 series GC system, MS:JEOL JMS-AX505H型)で測定して行った。

3. 実験結果

測定した HAA 生成量をもとに化合物を分類したものが表 2 および 3 である。本研究と同条件で塩素処理した場合のクロロホルム($CHCl_3$)生成量も，文献[2]から値が得られる化合物については付記した。

4. 考察

4.1 HAA 生成量と $CHCl_3$ 生成量の比較

HAA 生成量と $CHCl_3$ 生成量の比較した結果を図 1 に示す。HAA 生成量が大きい化合物は，$CHCl_3$ 生成量もおおむね大きく，化合物の次亜塩素酸へ反応性自体が，両物質の生成に重要であると考えられる。

表2:芳香族化合物の分類 (各生成量(μmol/mg-TOC, 右横に付記)により I ～Vに分類した)

	I (0-0.18)		II (0.18-0.4)	III (0.4-1.5)	IV(1.5-5)	V (5-)
	I a(0-0.04)	I b(0.04-0.18)				
HAA (Br⁻なし)	カテコール 安息香酸 フタル酸 2,5-DHB 2,3-DHB	ヒドロキノン 3,4-DHB	o-クレゾール 没食子酸 2,4-DHB 2,6-DHB	レゾシノール サリチル酸	フェノール *m*-HBA *p*-HBA o-メトキシフェノール バニリン酸 3,5-DHB	フロログルシン 5-ヒドロキシイソフタル酸
HAA (Br⁻)	カテコール 安息香酸 フタル酸	ヒドロキノン 2,5-DHB 2,3-DHB 3,4-DHB		レゾシノール o-クレゾール 没食子酸 2,4-DHB	サリチル酸 *m*-HBA *p*-HBA o-メトキシフェノール バニリン酸 3,5-DHB 2,6-DHB	フロログルシン 5-ヒドロキシイソフタル酸
$CHCl_3$ (参照: 文献 2)) (Br⁻なし)		ヒドロキノン サリチル酸 没食子酸	*p*-HBA バニリン酸	フェノール o-メトキシフェノール	フェノール	レゾシノール フロログルシン 3,5-DHB

注)DHBはジヒドロキシ安息香酸, HBAはヒドロキシ安息香酸のそれぞれ略称である

表 3:脂肪族化合物の分類 (分類法は表２の場合と同様)

	I (0-0.18)			II (0.18-0.4)	III (0.4-1.5)	IV(1.5-5)	V (5-)
	I a(0-0.04)		I b(0.04-0.18)				
HAA (Br⁻なし)	クロトン酸 マレイン酸 コハク酸 フマル酸 グリオキシル酸 蟻酸 酢酸 乳酸	プロピオン酸 1-プロパノール エチレングリコール グルコース スクロース マルト-ス ラクトース アリルアルコール グルコサミン	ピルビン酸 アセトアルデヒド アセトン			クエン酸	3-ケトグルタル酸 アセチルアセトン
HAA (Br⁻)	クロトン酸 マレイン酸 コハク酸 フマル酸 グリオキシル酸 蟻酸 酢酸 乳酸	プロピオン酸 1-プロパノール エチレングリコール グルコース スクロース マルト-ス ラクトース アリルアルコール	ピルビン酸 アセトアルデヒド アセトン				クエン酸 3-ケトグルタル酸 アセチルアセトン
$CHCl_3$ (参照: 文献 2)) (Br⁻なし)	コハク酸 フマル酸 グリオキシル酸 蟻酸	酢酸 乳酸 エチレングリコール グルコース	ピルビン酸		クエン酸		3-ケトグルタル酸

特に脂肪族化合物については, 両生成量間の相関は高い。一方, 芳香族化合物では脂肪族に比べてばらつきが大きく, 化学構造に対する依存性が高いと推察される。

4.2 芳香族および脂肪族化合物からの HAA 生成特性の比較

芳香族化合物からの HAA 生成量はトリハロ酢酸＞ジハロ酢酸＞モノハロ酢酸の順であった。特にモノハロ酢酸の生成量は非常に小さく, 検出されない場合が多かった。

一方, 脂肪族化合物の場合, 芳香族化合物に比べて, いずれの生成量も小さいものが多かった。また, その生成特性も異なり, ジハロ酢酸の生成量が圧倒的に大きかった。

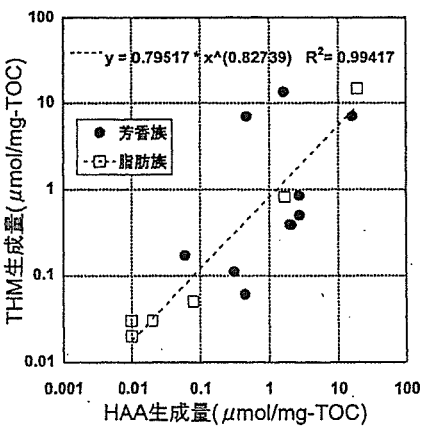

図 1:THM($CHCl_3$)と HAA 生成量の比較

4.3 化学構造と生成量の関係の考察

(1)芳香族化合物 : 芳香環に置換した官能基のうち, 特に活性化効果が強いフェノール性ヒドロキシル基(-OH 基)に着目して各化合物を再分類し, 表2における分布状態, および一般的傾向をまとめたものを表4に示す。

表 4:-OH 基による芳香族化合物の分類

分類		分布	一般的な傾向
-OH基を持たない化合物		Ia,	生成量は非常に低い
モノフェノール類		II～V	-OH基を持たない化合物よりHAA生成量は大
ジフェノール類		Ia～IV	$CHCl_3$ 生成量>HAA生成量 レゾシノール類の生成量が大
	レゾシノール類	II～IV	HAA生成量はモノフェノール類より小 $CHCl_3$ 生成量はモノフェノール類より大
トリフェノール類		II, V	フロログルシン>>没食子酸

●ジフェノール類では, -OH基が互いにメタ位の関係にあるレゾシノール類からの生成量が圧倒的に高い。この理由としては, -OH基がメタ位の関係にある場合には, β-ジケトン構造を形成可能で, -OH基に挟まれた炭素の反応性が大きく増加することが挙げられる。また, その他の化合物については, 塩素化を含まない酸化反応が主体となっていると考えられる。

●ジフェノール類は, 次亜塩素酸に対する反応性は, モノフェノール類と同等以上と考えられるが, HAA生成量では相対的に小さかった。これは, 次亜塩素酸の大部分が$CHCl_3$生成に使われるためと推察される。

●-OH基を3つ持つ化合物である, フロログルシンと没食子酸の間のHAA生成量の相違は大きいが, 前者には3つの-OH基が互いにメタ位に置換していることがその理由と考えられる。後者の場合では, -OH基に挟まれた炭素が更なる-OH基で置換されるため, レゾシノールより低い生成量を示したと推定できる。

(2)脂肪族化合物：脂肪族化合物で生成量が大きいのは, アセチルアセトン, 3-ケトグルタル酸, クエン酸の3つのみであり, その他の化合物はすべて表3のIに属する。上記の3つの化合物に共通する特徴としては, β-ジケトン構造を持つため, 典型的なケト-エノール互変異性を示し, ハロホルム反応を通しての HAA および $CHCl_3$ 生成が可能なことである。ここで, クエン酸については、塩素存在下で脱カルボキシル基反応を起こした後に, 3-ケトグルタル酸になって初めて, ケト-エノール互変異性を示すことに注意を有する。さらにこのことは, HAA 生成量が 3-ケトグルタル酸>クエン酸である理由の一つであるとも考えられる。

4.4 臭化物イオンの影響

臭化物イオン(Br^-)が存在すると, 芳香族化合物からの HAA 生成量は一般的に 1.5 倍程度に増加することが明らかとなった(図 2)。このことは, Br^-が次亜塩素酸に酸化されて生成する次亜臭素酸が, 芳香環に対して次亜塩素酸よりも高い反応性を持つことを反映しているといえる。

一方, 脂肪族化合物からのHAA生成量はBr^-が存在してもあまり変化しなかった。しかし, アセチルアセトン等からは毒性の非常に強いモノブロモ酢酸の生成が確認された。

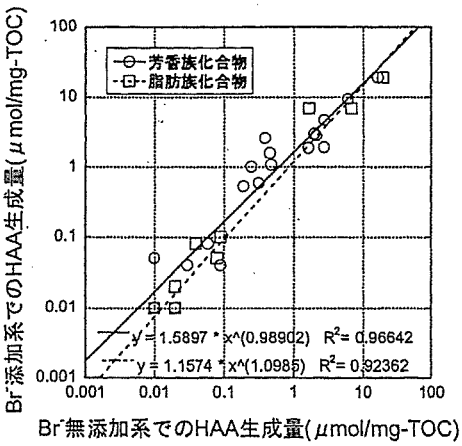

図 2:Br^-の HAA 生成に与える影響

5. まとめ

以下, 本研究で得られた知見のうち, 主なものを列挙する。

●一般的に, モノフェノール類はジフェノール類よりHAAを多く生成する。

●THM($CHCl_3$)生成量とHAA生成量の間に, 特に脂肪族化合物において, 良い相関が見られた。

●Br^-が存在することで芳香族化合物ではHAA生成量が増加した。脂肪族ではこの傾向は小さかった。

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Screening level analysis for monitoring pesticide in river water using a hydrological diffuse pollution model with limited input data

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Abstract To predict rice-farming pesticide concentrations in river water with imprecise model inputs for screening-level analysis, a basin-scale runoff model was developed. The Monte Carlo method was applied to create estimates of input data regarding agricultural work schedules and parameters for pesticide decomposition and sorption in solids and water. The prediction accuracy of the model was evaluated when used with non-optimised pesticide parameters; the model was calibrated using hydrological data alone without reference to observed pesticide concentration data. Overall, predictions for the pesticide concentrations were successful within order-of-magnitude accuracy. The pesticide rankings according to the predicted concentration roughly agreed with those observed. The success of screening-level analysis indicates that the model prediction can help in selection of pesticides to be monitored and in determining the monitoring schedule for the river basin.

Keywords Modelling; pesticides; pollutograph; prediction; runoff; water quality

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Nomenclature

$a_{W,V}$	infiltration rate coefficients of the rice paddy field (m/s).
$a_{W,in}$, $a_{W,out}$	irrigation and drainage rate coefficients of the rice paddy field, respectively (s^{-1})
a_V	vertical flow rate coefficient (s^{-1})
a_H	lateral flow rate coefficient (m/s)
A	area of the compartment (m^2)
B	length on a side of a square grid (m)
C_1 and C_2	concentration in each compartment (kg/m^3)
D	diffusion coefficient (m^2/s)
L	distance between compartments (m)
L_R	river length in a compartment
h	water level of the compartment (m)
h_0	depth of the compartment (m)
h_W	water depth of the rice paddy field (m)
$h_{W,0}$	objective water depth of the rice paddy field (m)
I	slope (dimensionless)
n_M	Manning coefficient ($m^{2/3}s/m^3$)
q_D	solute diffusion rate between compartments (kg/s)

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q_W	flow rate of spill-over irrigation divided by the paddy area (rate of continuous irrigation in order to keep a certain water depth and to prevent hot water damage: extra amount of irrigated water spill over from the outlet of the paddy, m/s)
Q_V	vertical flow rate (m^3/s)
Q_R	river flow rate (m^3/s)
Q_H	lateral flow rate (m^3/s)
$Q_{W,in}$	irrigation rate (flow rate of water to the paddy field, m^3/s)
$Q_{W,out}$	drainage rate (flow rate of water from the paddy field, m^3/s)

Introduction

A wide range of possible sources of diffuse pollution, including pesticides, have been found to originate on farms. In Japan, the fate of rice-farming pesticides and their concentrations in river water are particularly important issues for management of drinking-water supplies, because (1) more stringent regulations have been promulgated for pesticide concentrations in drinking water and (2) rice-farming pesticides run off to river water at higher rates than do other pesticides used in upland fields. Rice-farming pesticides are dusted directly over the ponding water of paddy fields, and thus are more likely to contaminate river water by spill-over following rainfall or by water-ponding depth control, etc. Although the annual pesticide consumption for upland fields in Japan is no less than that for rice paddy fields, most of the pesticides detected in river water are those used in rice farming (Matsui *et al.*, 2002). The prediction of pesticide concentrations in river water is of practical importance when used as a screening-level analysis, providing order-of-magnitude accuracy with minimal investment in time and resources in water-quality monitoring (Dabrowski *et al.*, 2002). Screening-level analysis is important for selecting pesticides to be monitored and determining the monitoring schedule for river basins where different pesticides are applied from year to year.

While many models and their applications have been reported, few have been applied to rice-farming pesticides in runoff from rice-paddy fields (Inao and Kitamura, 1999; Li and Migita, 1992). Moreover, no attempt has been made to predict rice-farming pesticide concentrations in river water in a large catchment area that constitutes the local primary source of drinking water, probably owing to the difficultly of acquiring input data. Such data include the name of each pesticide product dusted, the quantity used, the dates of pesticide dusting, the varieties of rice planted, the dates of transplantation of rice seedlings, the time-variation patterns of water depth of rice-paddy ponding, parameter values of pesticide decomposition, and parameter values of pesticide sorption. Accordingly, the objective of this research is to predict rice-farming pesticide concentrations in river water with imprecise model inputs and no parameter optimization for a screening-level analysis.

Model description

Compartment model

A compartment model was used to describe the movement of pesticides in a river basin and to create pesticide pollutographs. In the model, a river basin was divided into a grid of 1 km × 1 km grid cells. Each grid cell was subdivided into 12 compartments, including a river-water (R) compartment, a river-bed (S) compartment, and paddy-field-soil (X and Y) compartments (Figure 1). Water and pesticides from all compartments except

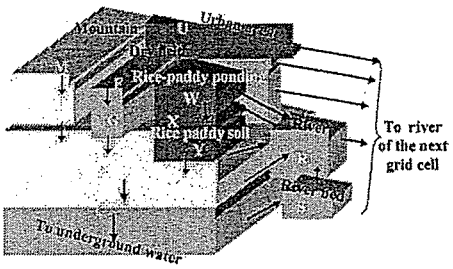

Figure 1 Compartment model in a grid cell and flow directions

the C compartment move laterally to the R compartment of one of the immediately surrounding eight grid cells, specifically, to the cell along the steepest downhill slope from the source cell. Lateral movement from the C compartment goes to the R compartment of the next grid cell via the S compartment of that grid cell. The irrigation water in the W compartment comes from the R compartment of the same grid cell. Vertical flows from all compartments except the R and S compartments are downward.

A set of differential mass-balance equations describing the dynamics of a solute (pesticide) and water in each compartment was formulated, based on the law of conservation of mass for the pesticide and the water. In the hydrology (water flow) part of the model, the rates of lateral water flow into and out of the W compartment ($Q_{W,in}$ and $Q_{W,out}$, respectively) are described as functions of the water level (h_W) in the compartment:

$$Q_{W,in} = Aa_{W,in} \max(0, h_{W,0} - h_W) + Aq_W \tag{1}$$

$$Q_{W,out} = Aa_{W,out} \max(0, h_W - h_{W,0}) \tag{2}$$

The water depth in the paddy field (h_W) is artificially controlled at various levels according to weather conditions and the growth stage of the rice. The desired water level in the rice paddy field ($h_{W,0}$) and the spill-over irrigation flow rate (q_W) are input variables, which are determined by the rice farming schedules.

Vertical flow from the W compartment ($Q_{W,V}$) is described as a function of water level in the rice paddy field; this water goes into the X compartment beneath the W compartment in the same grid cell:

$$Q_{W,V} = a_{W,V}A\left(\frac{h_W}{h_{W,0}}\right) \tag{3}$$

The rates of lateral flow (Q_H) from the M, F, and U compartments are described by the Manning equation:

$$Q_H = \frac{A}{B}h\frac{1}{n_M}h^{2/3}I^{1/2} \tag{4}$$

The rates of lateral interflow from the X, Y, N, G, B, and C compartments are described as a function of the water level in the compartment and the slope of the compartment:

$$Q_H = a_H I\left(\frac{A}{B}\right)h \tag{5}$$

Vertical flows from the X, Y, M, N, F, G, B, and C compartments are described as a function of percentages of each water content, which is equivalent to the water level

relative to the compartment height:

$$Q_V = a_V A\left(\frac{h}{h_0}\right) \tag{6}$$

The Manning equation is also used to describe the flow rate in the R compartment:

$$Q_R = \frac{A}{L_R} h \frac{1}{n_M} h^{2/3} I^{1/2} \tag{7}$$

For solute movement between compartments, advection and diffusion are considered. Solute advection is given as the product of the concentration and water flow rate calculated from Eqs. 1–7. However, the maximum real concentration for each solute is limited by its solubility in water, so any amount of pesticide over the solubility limit must exist in the solid phase and is not subject to movement. The rate of solute movement by diffusion between compartments is given by the linear driving force model:

$$q_D = A\frac{D}{L}(C_1 - C_2) \tag{8}$$

Within a compartment, both the solute concentration and the water level are assumed to be uniform, each represented by a single variable. For example, rainfall is assumed to mix completely and uniformly with pesticides in the paddy-field-water (W) compartment. If a compartment consists of multiple subelements (soil–solid and soil–water), a dynamic equilibrium exists between the dissolved and sorbed fractions at all times; sorption processes are considered to be instantaneous and are described by a single constant (the solid–water partition coefficient) in the linear equilibrium relationship. Therefore, once the concentration in one phase is known, the concentration in the other phase can be calculated. Degradation of pesticides in each compartment follows first-order kinetics. The processes of pesticide uptake by plants and pesticide evaporation into the atmosphere were not considered in this model. The flow rate coefficient in each type of compartment (e.g. W, X) is assumed to be a single value (for each compartment) throughout the entire set of grid cells in the basin. These assumptions were made to reduce the total number of hydrologic parameters, even though the target river basin was divided into numerous grid cells, which prevented excessive uncertainty in determining the model parameter values.

Site description and model application

The Chikugo River basin (1882 km^2; Figure 2) was selected to test the model and to predict rice-farming pesticide concentration. The Chikugo River basin includes rice-paddy fields (261 km^2) cultivated by 22,860 farmers dusting with more than 100 kinds of pesticides. The Chikugo River basin was divided into 1882 grid cells. The catchment area comprised 22,584 compartments. A set of 45,168 equations was solved to describe the movements of water and a pesticide in the river basin. The model equations were solved as a system of ordinary differential equations by Gear's stiff method from the IMSL MATH/LIBRARY.

Application of the compartment model to the river basin required geographic data. The altitude of each compartment was determined from Geographic Information System (GIS) data (Geographical Survey Institute, 1999), and water flow directions between compartments were determined based on the direction of the steepest gradient. The GIS data (Geographical Survey Institute, 1990) were also used to calculate the areas of the compartments (e.g., paddy field, river, forest) in each grid. However, the GIS data available were old and may not reflect current land utilization. The area of the paddy fields, which

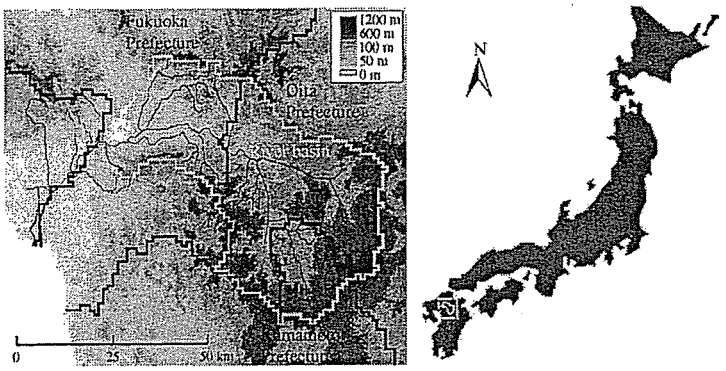

Figure 2 Location of Chikugo River and the target river basin

is the most important geographical information used in this study, was corrected with data published by the local governments (Census Statistics Office, 1997, 2002), which include data on the percentage of rice-paddy area removed from cultivation due to compulsory adjustments in production. The fallow paddy fields were regarded as upland field compartments.

Model inputs

Thirteen pesticides (Table 1 and Figure 3) were selected for verifying the model predictions, according to quantity consumed in the target river basin and detection in river water at high concentrations and frequency. Each pesticide is included as an active substance in several commercial pesticide products on the market. Pesticide dusting, irrigation, and drainage are the processes that most affect pesticide runoff among the numerous factors regarding agricultural work. Many factors (e.g., aerobic/anaerobic conditions, soil–sediment organic content) also affect pesticide decomposition and its partition between soil and water. Although some information has been reported and is available for these model inputs, the reported values for input parameters are subject to different kinds of uncertainties (Dubus *et al.*, 2003). Therefore, a single reported value would not be appropriate to represent an input parameter in a whole area. It is more reasonable to assume that all rate parameter uncertainties are random. Model input data sets of

Table 1 Properties of each pesticide (British Crop Protection Council, 1994, 2003; U.S. Environmental Protection Agency, 2004)

Pesticide	Water solubility, mg/L	Soil sorption coefficients, Koc (mL/g)	Half-life in soils (days)
Daimuron	1.2 at 20 °C	959, 6855	50
Mefenacet	4 at 20 °C	3063	23–223
Thiobencarb	30 at 20 °C	3170	14–21, 180–240
Bromobutide	3.54 at 25 °C	652, 10430	31–64
Pyrazolate	0.056 at 25 °C	7855, 29830	8–10, 10–20
Esprocarb	4.9 at 20 °C	581, 7952	30–70
Pretilachlor	50 at 20 °C	254, 1159	30
Pyributicarb	0.32 at 20 °C	1885	13–18
Bensulfuron-Methyl	67 at 25 °C	370	88.5, 28–140
Cafenstrole	2.5 at 20 °C	738, 13950	7
Cyhalofop-butyl	0.44 at 20 °C	1371, 9280	0.083–0.42
Pyrazosulfuron-ethyl	9.76 at 20 °C	10, 455	28
Dimethametryn	50 at 20 °C	254, 1357	140