BIODEGRADATION OF ALDEHYDES DISCHARGED FROM WASTEWATER TREATMENT PLANTS IN THE TAMA RIVER

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下水処理水として排出されたアルデヒド類の
多摩川での流下にともなう分解挙動

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多摩川および多摩川に放流される下水処理水, 下水処理水による清流復活事業の行われている呑川を対象に, アルデヒド類の濃度と水の臭気強度を測定し, アルデヒド類のさまざまな条件下での分解速度を検討した. 下水処理水のアセトアルデヒドは, 臭気閾値以上で存在していたが, 処理水の持つ臭気全体への寄与は大きくなると考えられた. アルデヒド類は, 半減期数時間で, 河川水中で容易に分解し, その分解速度は水温に依存し, 存在する微生物量が増加ほど速くなった.

Key Words : *acetaldehyde, formaldehyde, odour, wastewater treatment, degradation rate*

1. Introduction

Aldehydes as indoor air quality pollutants attract attentions due to allergic symptoms. Formaldehyde as well as total zinc is suspected of causing cancer and was discussed[1)] as a candidate for a regulatory item for the conservation of aquatic ecosystem in the environmental quality standard in Japan. Furthermore the concentration of acetaldehyde in effluents from wastewater treatment plants (WWTPs) is over the odour threshold level[2)]. Though exact contributions of identified compounds to combined odor of treated wastewater are not known[3)], the odorants in river water may add a limitation for the use of the space around the river for recreational purpose regardless of its toxicity.

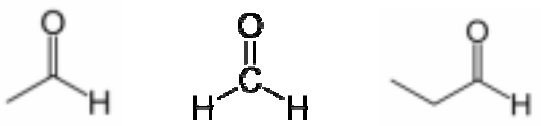
However, there are few reports on the measurement of aldehydes' concentrations and on the effect of treated wastewater on the odour of the receiving waters. The data accumulation on these issues is expected.

In this study, concentrations of aldehydes and threshold odour number(TON) were measured at urban rivers and for effluents from WWTPs. The target sites were the Tama River and the Nomigawa River, where treated wastewater from Ochiai WWTP is discharged for environmental restoration. Moreover, biodegradation experiments using the Tama River water and the Nomigawa River water with various conditions were conducted in order to clarify the fate of aldehydes in the rivers which receive effluents from WWTPs.

2. Material and Method

(1) Target Compounds

The target compounds in this study are acetaldehyde, formaldehyde and propionaldehyde.(**Fig.1**)



Acetaldehyde **Formaldehyde** **Propionaldehyde**

Fig.1 Target Compounds

(2) Field Observation

The concentrations of aldehydes and TON in the Tama River, effluents form the WWTPs located along the river and the Nomigawa River were measured in total seven times from July 2007 to January 2008. **Fig. 2** and **Table 1** show the points of the observation.

The water samples were taken with the plastic bucket tied with rope from the bank of the river or from the center of river bridges. The samples were collected with the brown glass bottles without head space before they were carried to the laboratory under low temperature. The aldehydes concentration, TON and COD were measured as soon as possible within the day.

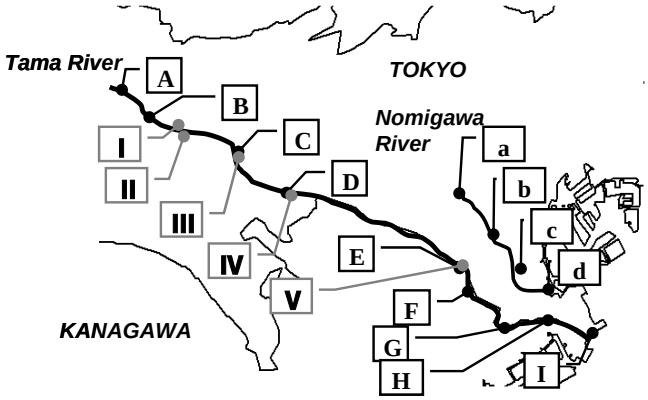


Fig.2 Points of the observation

Table 1 Points of the observation

the Tama River	**A-Ozaku**
	B-under the Haijima Bridge
	C-near the Kitatama Ⅱ WWTP
	D-near the Kitatama Ⅰ WWTP
	E-under the Maruko Bridge
	F-under the Gas Bridge
	G-under Route 15
	H-under Sangyo Road
	I-near the Ukisimabashi Park
WWTPs discharging wastewater into the Tama River	**Ⅰ-Kitatama Joryu WWTP**
	Ⅱ-Hachioji WWTP
	Ⅲ-Kitatama Ⅱ WWTP
	Ⅳ-kitatama Ⅰ WWTP
	Ⅴ-Todoroki WWTP
the Nomigawa River	**a-near Midorigaoka Station**
	b-under the Kitano Bridge
	c-under the Otaira Bridge
	d-under the Asahi Bridge

(3) Biodegradation Experiment

The Tama River water and the Nomigawa river water with the addition of aldehydes at the concentration of 10 μg/L were kept in a temperature-controlled bath for 2 hours to 72 hours before the measurement of the change in the concentration of the aldehydes. Furthermore, the effects of temperature, the sampling location of river water and salinity on biodegradation rate were examined. **Table 2** shows the condition of each experiments.

(4) Threshold Odour Number(TON) Analysis

TON was analyzed by a method as shown in JWWA's manual[4] for water quality examination and JIS handbook(JIS-K-0102)[5], which recommends the use of more than 5 panels with the bottles of 3 different dilution ratios.

Table 2 Conditions of degradation experiments

Experiments	water temperature (℃)	Sampling Point
1) Biodegradation at different temperature	**5**	**Maruko Bridge**
	20	
	35	
2) Biodegradation in water taken at different locations	**20**	**Ozaku (Upstream of the Tama River)**
	20	**Maruko Bridge (Midstream of the Tama River)**
	20	**Midorigaoka (Upstream of the Nomigawa River)**
	20	**Kitano Bridge (Midstream of the Nomigawa River)**
3) Biodegradation in river water with different salinity	**20**	**Maruko Bridge (20km from the river mouth)**
	20	**Route1 (9km from the river mouth)**
	20	**Sangyo Road (6km from the river mouth)**
	20	**Ukishimabashi Park (1km from the river mouth)**

Table 3 Volume of Sample in Odour Test

Volume of water in preliminary examination (ml)	**200**	**40**	**10**	**4**
Volume of water in precise examination (ml)	**200**	**40**	**10**	**4.0**
	100	**28.5**	**8.0**	**2.9**
	67	**20**	**6.7**	**2.0**
	50	**13.3**	**5.0**	**1.3**
	40	**10**	**4.0**	**1.0**

a)Preliminary examination

200, 40, 10 and 4 ml sample water were diluted in the triangle flasks washed well to 200 ml with pure water. In addition, two additional flasks were filled only with pure water. Those flasks were warmed up to 45 degrees Celsius. The panels examined three flasks consisting of 1 sample and 2 banks after
shaking and chose one flask he/she can feel odour. If the panel can tell the right flask filled with the diluted sample, the case of the higher dilution was tried until his/her limitation of sensing odours.

b) Precise examination

In the precise examination, the panels did the same procedures, and dilution range of the precise examination was decided from the result of preliminary examination on **Table 3**. By repeating this process, threshold dilution ratio was obtained. The average of the panels' dilution ratio except for

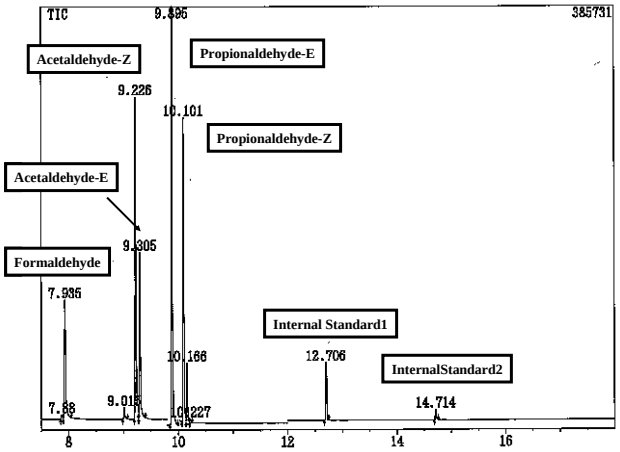


Fig. 3 Chromatogram of GC/MS measurement

the maximal and the minimal value was expressed in TON unit.

(5) Aldehydes Analysis

The aldehydes were analyzed by the method using GC/MS after the derivatization by pentafuluorobenzyl hydroxyl-amine-HCl(PFBOA), as written in the JWWA's manual[4] and Standard Method[6]. Acenaphthene-d_{10}, perylene-d_{12} and phenanthrene-d_{10} were used as surrogate standards for the quantification of the aldehydes.

Typical chromatogram of GC/MS measurement is shown in **Fig. 3** .

3. Results and Discussion

(1) Field Observation

The results of the average of two to three times measurements on TON at each observation point are shown in **Fig. 4**. The range of TON was 3~90 (TON) at the Tama River water, was 83~367 (TON) for effluents from the WWTPs and was 70~150 (TON) at the Nomigawa River water. Most of those measured TON values in this study were higher than the TON of available data. For example, Aoki *et al.* reports that TON of the effluent from a WWTP in Shiga prefecture was approximately 13.

To study the difference in the duplicated measurements, the value of TON at the same sampling point is shown in **Fig. 5**. In the figure, the dotted lines expressed a range between the double and the half. Though the second observation was conducted after 2 month of the first observation, 9 plots out of 13 plots were within the range and the other plots were not completely deviated from the range. This result suggested the high reproducibility of the examination of the TON analysis.

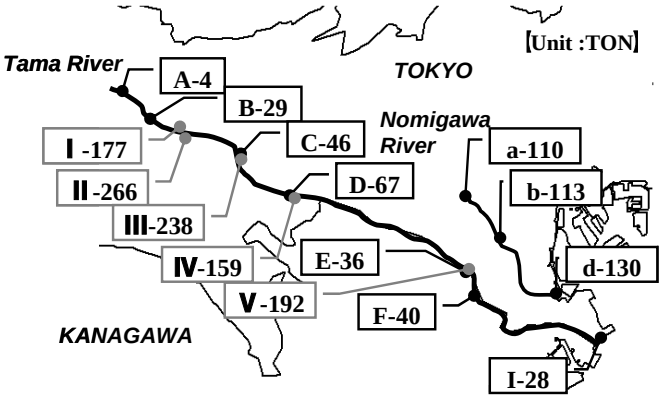


Fig. 4 TON at Observation Points

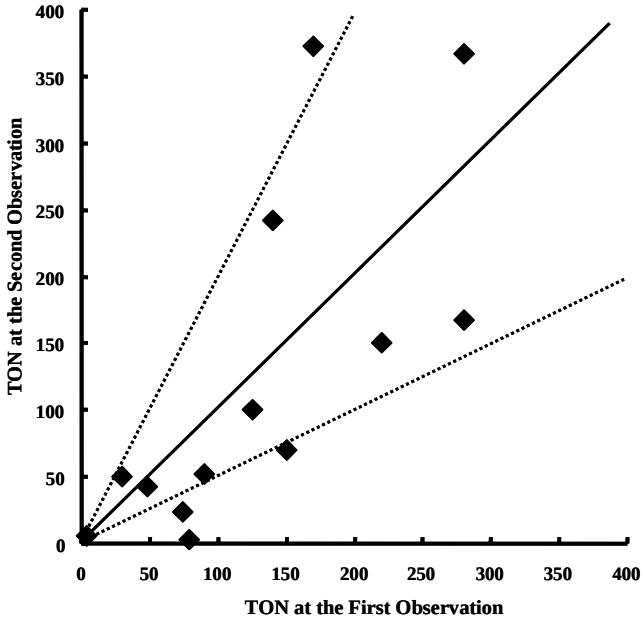


Fig. 5 TON of the first and second observations

The result of the average of two to three times measurements on the concentrations of acetaldehyde, formaldehyde and propionaldehyde at each observation point are shown in **Fig. 6**. The range of the concentrations of acetaldehyde was 0.4~4.5 μg/L at the Tama River, was 2.0~2.8 μg/L at the WWTPs and was 0~2.5 μg/L at the Nomigawa River. Acetaldehyde concentration was increased along with the flow direction in the river. The concentrations of acetaldehyde at the Tama River and the Nomigawa River were comparable or slightly higher than the range between 0~1.7 μg/L, observed at 170 points of water environments in Japan by the Ministry of the Environment in 2000[7]. The concentrations of acetaldehyde in the effluents from the WWTPs were slightly lower than those observed by Aoki *et al.*[2], who reported 5 μg/L for the effluent.

The range of the concentrations of formaldehyde was 0.3~2.5 μg/L at the Tama River, was 1.9~6.6 μg/L for the effluents from the WWTPs and was 1.4~4.2 μg/L at the Nomigawa River. The observed values for the Tama River and the Nomigawa River were comparable or slightly higher than the range between 0(N.D.)~2.6 μg/L, observed[8] by the Japanese Ministry of the Environment in 1999 for 130 points of the river. The concentrations of formaldehyde at the WWTPs were lower than 9 μg/L, detected in the Aoki's research.

Among target WWTPs, the plant Ⅴ discharges acetaldehyde and formaldehyde with the highest concentrations. The reason for these high concentration is the treatment process of the plant Ⅴ, which use the pure oxygen aeration method.

The range of the concentrations of propionaldehyde was 0(N.D.)~1.2 μg/L at the Tama River, was 0.2~1.6 μg/L at the WWTPs and 0(N.D.) μg/L was at the Nomigawa River. Very low concentrations were detected for propionaldehyde in water environments. There are no previous data available for the comparison.

(2) Comparison with odour threshold

Generally, odour threshold concentrations of aldehydes within the gas phase is known[9], though that within the liquid phase is not clear. In the triangle odour flasks method, the odorants which were transferred from the sample water to the head space were measured after gas-liquid equilibrium was established in the flasks. The odour threshold concentration of aldehydes within liquid phase is formulated from the partial pressure calculated from the Henry's constant. The expressions are as follows.

$$H = \frac{P}{A} \tag{1a}$$

$$C_{liq} = \frac{C_{gas} \cdot M}{H} \tag{1b}$$

where H: Henry's constant
P: partial pressure of material in gas phase,
A: molar fraction,
C_{liq}: odour threshold concentration in liquid phase,
C_{gas}: odour threshold concentration in gas phase,
and M: molar weight.

From the expressions, the odour threshold concentration in the liquid phase of acetaldehyde is 0.99 μg/L, that of formaldehyde is 44.6 mg/L and that of propionaldehyde is 0.79 μg/L.

The concentrations of acetaldehydes detected in the downstream water of the Tama River and the Nomigawa River and most of effluents from WWTPs were higher than the odour threshold concentration in liquid phase. However, all of the concentrations of formaldehyde at observed points were lower than the odour threshold concentration, because the odour threshold concentration in liquid phase of formaldehyde is very high. Furthermore, most of the detected concentrations of propionaldehyde at observed points were also below the odour threshold concentration.

These analysis suggests that the contribution of acetaldehyde to the odour of environmental waters can be considered at the most sampling locations. On the other hand, the TON converted only from the concentration of acetaldehyde in the effluents was at most 6(TON). The contribution of acetaldehyde for the combined odour of the effluents from WWTPs would not be high because of much lower TON converted from acetaldehyde concentration than the measured TON.

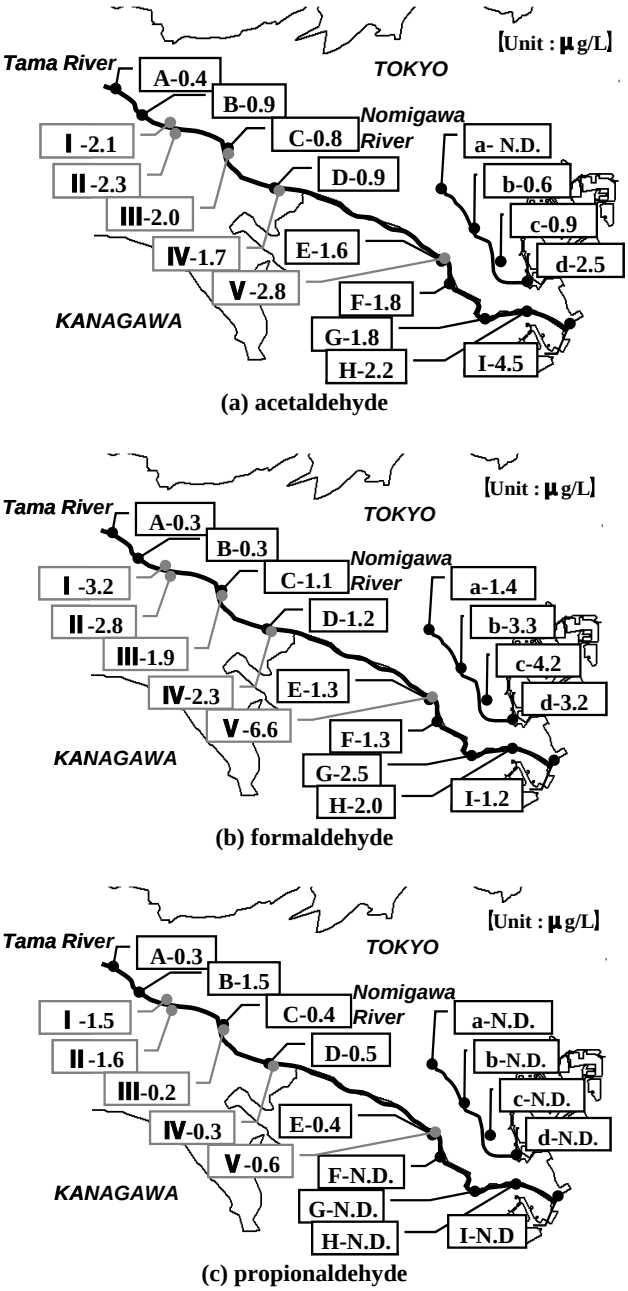


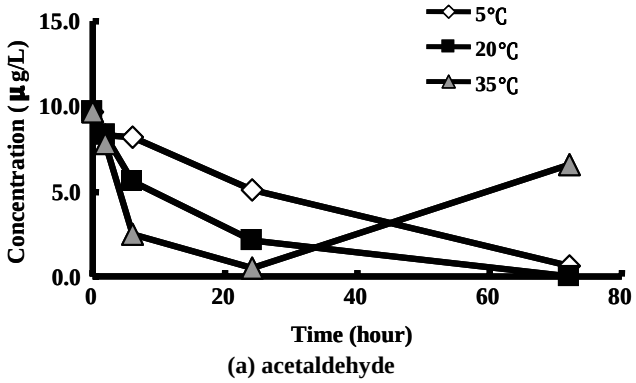
Fig. 6 Concentrations of aldehydes at Observation Points

(3) Biodegradation Experiment

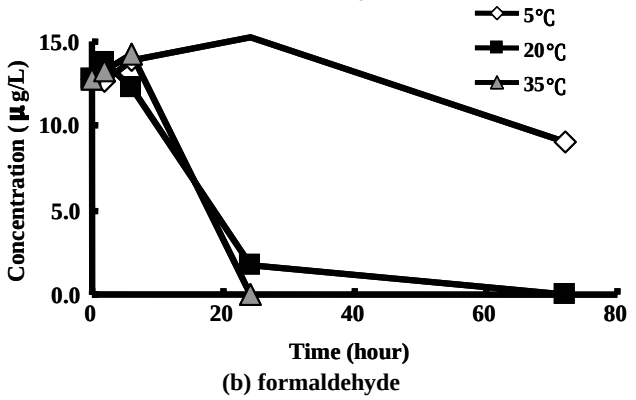
1) Biodegradation at different temperature

Fig. 7 shows the concentrations of aldehydes in the degradation experiment using midstream of the Tama River water at 5, 20 and 35 degrees Celsius. The concentrations of acetaldehyde decreased by half in 26 hours at 5 degrees Celsius, in 8.5 hours at 20 degrees Celsius and in 4.5 hours at 35 degrees Celsius. The concentrations of formaldehyde decreased by half, in 16 hours at 20 degrees Celsius and at 35 degrees Celsius but didn't decreased by half at 5 degrees Celsius during 72 hours. The concentrations of propionaldehyde decreased by half in 18 hours at 5 degrees Celsius, in 4 hours at 20 and at 35 degrees Celsius.

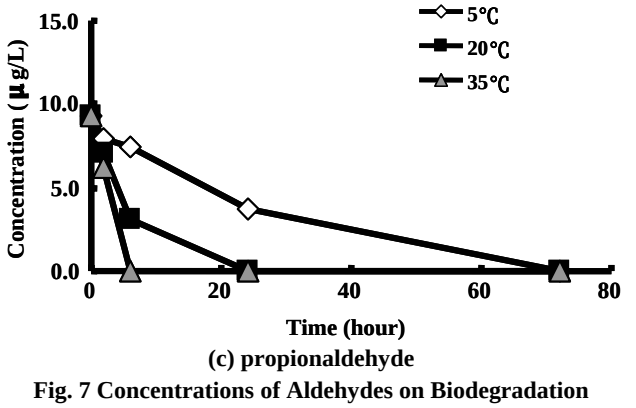
Consequently, it is considered that the biodegradation rates of the aldehdyes increased with the increase in temperature.



(a) acetaldehyde



(b) formaldehyde



(c) propionaldehyde

Fig. 7 Concentrations of Aldehydes on Biodegradation Experiment at Different Temperature

2) Biodegradation in water taken at different locations

Fig. 8 shows the concentrations of aldehydes in the degradation experiment using upstream and midstream water of the Tama River and the Nomigawa River at 20 degrees Celsius.

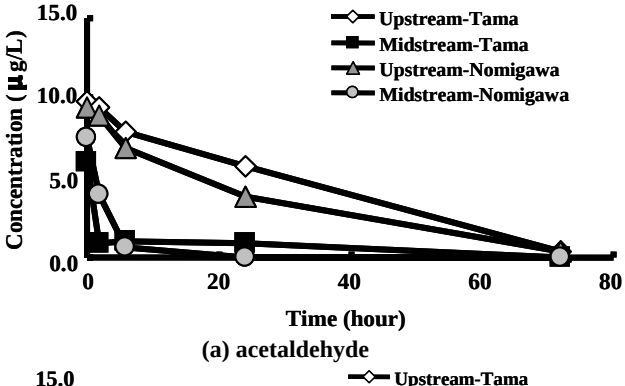
The concentrations of acetaldehyde decreased by half in 35 hours in upstream and in 1.5 hours in midstream water of the Tama River and in 18 hours in upstream and in 2.5 hours in midstream water of the Nomigawa River. The concentrations of formaldehyde decreased by half in 48 hours in upstream and in 12 hours in midstream water of the Tama River and in 60 hours in upstream and in 19 hours in midstream water of the Nomigawa River.

Consequently, it is considered the biodegradation rate of the aldehdyes increased with the presence or the activity of microorganisms contained in the samples.

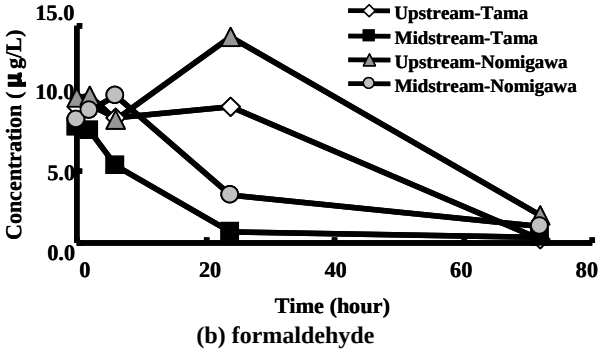
3) Biodegradation in river water with different salinity

Fig. 9 shows the concentrations of aldehydes in the degradation experiment using river water which were taken from midstream to estuary of the Tama River at 20 degrees Celsius.

The concentrations of acetaldehyde decreased by half by 6 hours in all of the river water and the rates of biodegradation were slightly lower in the case of higher salinity water. However, a slightly different tendency was observed for formaldehyde.



(a) acetaldehyde



(b) formaldehyde

Fig. 8 Concentrations of Aldehydes on Biodegradation Experiment in water taken different locations

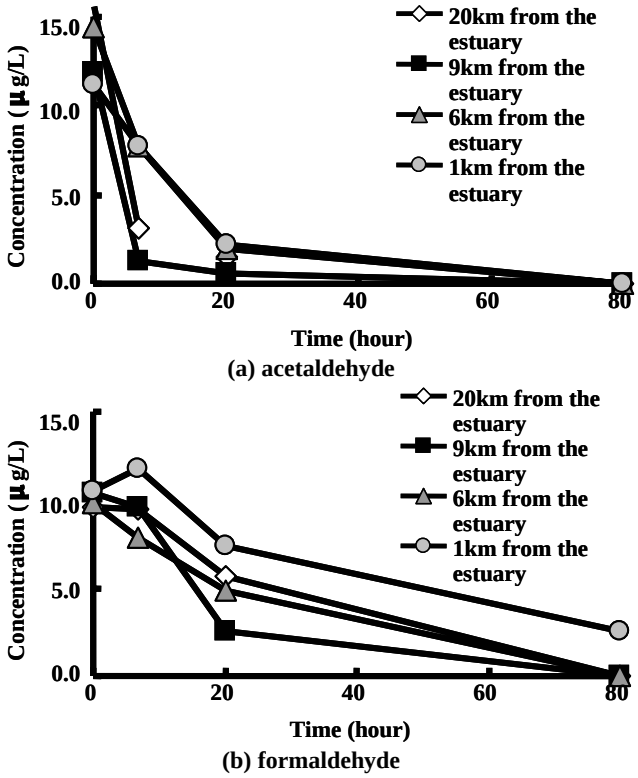


Fig. 9 Concentrations of Aldehydes on Biodegradation Experiment in river water with different salinity

(4) Relationship among water quality parameters

Fig. 10 shows the relationship between TON, aldehydes and other water quality parameters in this field observation.

In the **Fig. 10 (a)** of TON – acetaldehyde relation and the **Fig. 10 (b)** of TON – formaldehyde relation, the plots of the Tama River water, the effluents from WWTPs and the Nomigawa River were concentrated in certain areas in the figure, respectively. Slight positive correlations between acetaldehyde concentration and odour were observed for effluents and for the Tama River water cases respectively.

In the **Fig. 10 (c)** of acetaldehyde – formaldehyde relation, the tendency that the concentrations of the acetaldehyde increased with the increase in formaldehyde was suggested except for the Nomigawa River's cases, where acetaldehyde concentrations were below detection limits in the case of the locations near the discharge points of treated wastewater.

In the **Fig. 10 (d)** of TON – water temperature relation, the tendency that the TON increased with the increase in water temperature was suggested. This result suggested that the river water and effluents from WWTPs in a hot season have more intensive odour than that in a cool season.

In the **Fig. 10 (e)** of acetaldehyde – COD relation and the **Fig. 10 (f)** of formaldehyde – COD relation, a slight positive correlations were observed. This suggests that better removal of total amount of organic matters leads to better removal of aldehydes.

4. Conclusions

In this study, the concentrations of aldehydes and threshold odour number(TON) at the Tama River water, effluents from WWTPs and the Nomigawa River water were measured. Moreover, to clarify the fate of aldehydes in the rivers which receive effluents from WWTPs, biodegradation experiments using the Tama River water and the Nomigawa River water with various conditions were conducted.

The conclusions of this study were summarized as follows:

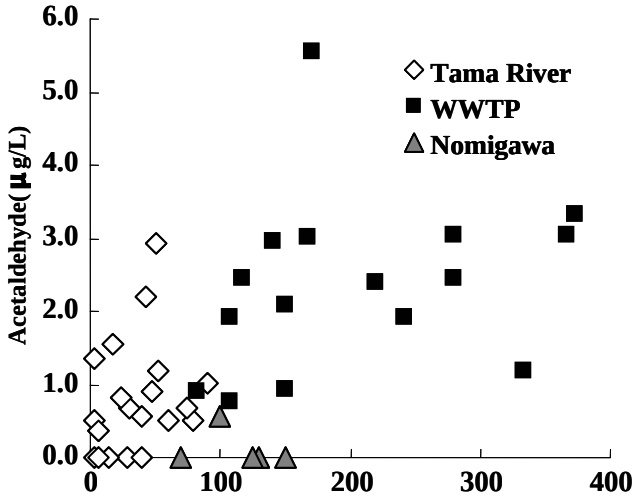
(1) The range of TON was 3~90 (TON) at the Tama River, was 83~367 (TON) at the WWTPs and was 70~150 (TON) at the Nomigawa River. Most of those measured TON values in this study were higher than the reported TON of available data.

(2) A high reproducibility of the TON analysis by 5 panels with 3 flasks in this study was suggested.

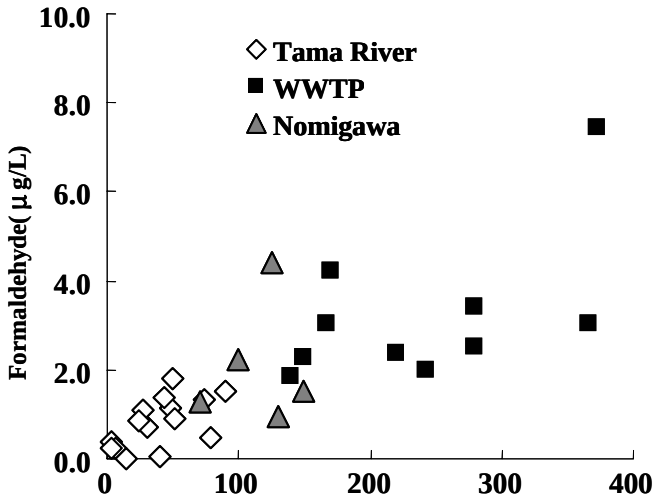
(3) The range of the concentrations of acetaldehyde was 0.4~4.5 μg/L at the Tama River, was 2.0~2.8 μg/L at the WWTPs and was 0~2.5 μg/L at the Nomigawa River. The range of the concentrations of formaldehyde was 0.3~2.5 μg/L at the Tama River, was 1.9~6.6 μg/L at the WWTPs and was 1.4~4.2 μg/L at the Nomigawa River. The concentrations of the aldehydes increased along with the flow direction in the river. These observed values of acetaldehyde and formaldehyde for the Tama River and the Nomigawa River were comparable or slightly higher than the range, observed by the Japanese Ministry of the Environment. The range of the concentrations of propionaldehyde was lower than 1.6 μg/L.

(4) Contribution of acetaldehyde to the odour of environmental waters can be considered at the most sampling locations. But the contribution of acetaldehyde for the combined odour of the effluents from WWTPs would not be high because of much lower TON converted from acetaldehyde concentration than the measured TON.

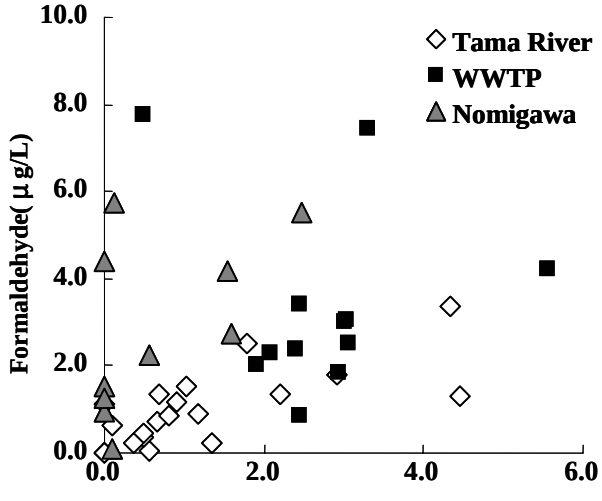
(5) Half life time of acetaldehyde in the Tama River water in the degradation experiment was 1.5~35 hours and that of formaldehyde was 5~48 hours. Biodegradation rates of the aldehdyes increased with the increase in temperature and with the increase in the presence or the activity of microorganisms contained in the samples.



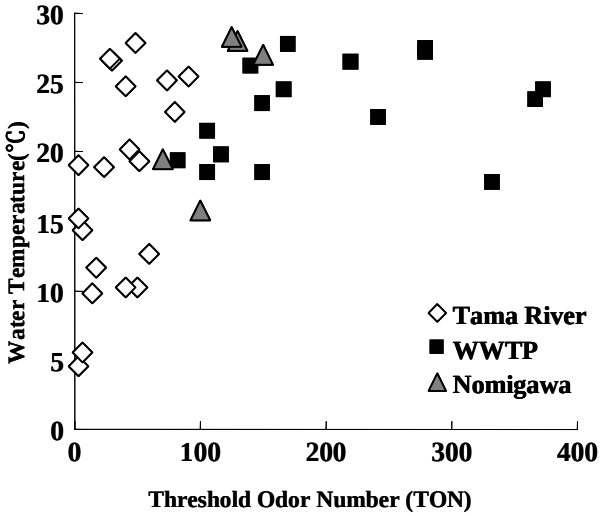
(a) TON – acetaldehyde



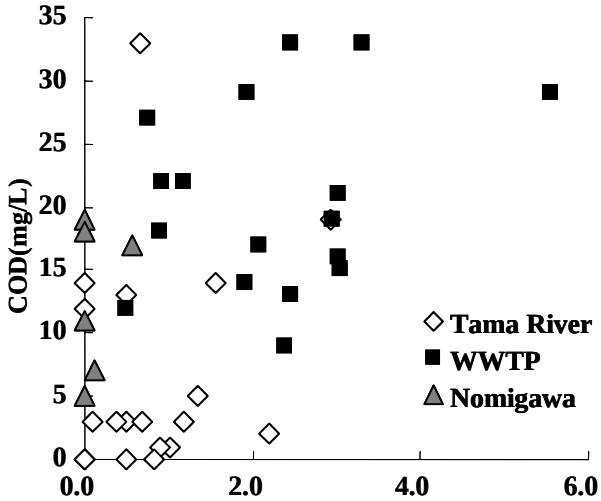
(b) TON – formaldehyde



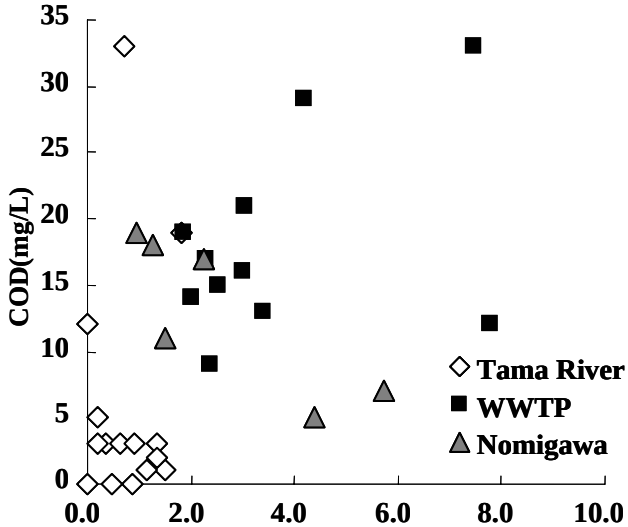
(c) acetaldehyde – formaldehyde



(d) TON – water temperature



(e) acetaldehyde – COD



(f) formaldehyde – COD

Fig. 10 Relationship between TON, aldehydes and other water quality parameters

Tendency that river water and effluents from WWTPs in a hot season have more intensive odour than that in a cool season was suggested.

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