Aquatic Risk Assessment of 2-Sulfonato Fatty Acid Methyl Ester Sodium Salt (MES)

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Abstract: The aquatic risk of 2-sulfonato fatty acid methyl ester sodium salt (MES) used in household detergents was assessed. The environmental exposure assessment expressed as predicted environmental concentration (PEC) was determined on the basis of monitoring results from the seven sites of four rivers in the urban area in Tokyo and Osaka. The 95 percentile as well as geometric mean of the MES concentration was found to exhibit a good correlation with the geometric mean of the Biochemical Oxygen Demand (BOD; the latter's regression was greater than 0.99). The predicted no effect concentration (PNEC) for the aquatic environment was estimated by performing chronic assays of algae and daphnia. The risk characterization ratio (RCR: PEC/PNEC) was less than 1. Therefore, it is concluded that MES will not adversely affect the aquatic environment in Japan.

Key words: risk assessment, surfactant, aquatic environment, PEC, PNEC

1 INTRODUCTION

In Japan, 2-sulfonato fatty acid methyl ester sodium salt (MES) has been used as one of the main surfactants in heavy-duty household granular detergents¹⁾. The eco-toxicological effects²⁾ and the biodegradability³⁻⁵⁾ of MES were reported previously. MES is readily and fully biodegradable under aerobic conditions; therefore, it can be removed efficiently by biological wastewater treatment systems such as activated sludge³⁻⁵⁾. It can also be biodegraded in environmental waters. The surfactants used in household detergents are discharged into waterways and some of the detergent material flows into rivers. Therefore, it is imperative to assess the environmental risk of detergent chemicals. In Japan, the human and the aquatic risk assessment of linear alkylbenzene sulfonate (LAS) and polyoxyethylene alkyl ether (AE), which are produced in high production volumes, have been proceeded by an extensive program of the Japan Soap and Detergent Association⁶⁾.

Organization for Economic Co-operation and Development (OECD) member countries decided to undertake the investigation of high production volume (HPV) chemicals in a co-operative way. These HPV chemicals include all chemicals reported to be produced or imported at levels greater than 1,000 tones per year in at least one member country

or in the European Union region. The Screening Information Data Set (SIDS) Initial Assessment Report (SIAR) has one primary purpose. It is the document through which the key scientific data on a chemical is presented for scientific and technical review and discussion by member countries. This review and discussion concludes at an assessment meeting (SIAM). One of the components of MES, hexadecanoic acid, 2-sulfo-, 1-methyl ester sodium salt (CAS No. 4016-24-4; C16-MES) was assessed and determined to be "low priority for further work" in the OECD-HPV Project "SIAM16"⁷⁾, where the term, "low priority for further work" means "low risk".

This paper reports the results of the aquatic risk assessment of commercial MES (C14 and C16) based on the predicted environmental concentration (PEC) determined from actual river monitoring data. The following two chemicals were subjected for the aquatic risk assessment: tetradecanoic acid, 2-sulfo-, 1-methyl ester sodium salt (CAS No. 4016-22-2; C14-MES) and hexadecanoic acid, 2-sulfo-, 1-methyl ester sodium salt (CAS No. 4016-24-4; C16-MES).

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2 ENVIRONMENTAL RISK ASSESSMENT

2.1 Assessment process

In the environmental risk assessment, chemical's concentrations measured or modeled in the environments were compared with extrapolations of available ecotoxicity data leading to predicted no effect concentration (PNEC; predicted concentration that to do not exhibit the harmful effects on aquatic organisms) values. The ecological risks posed by MES for aquatic ecosystems can be characterized and assessed on the basis of environmental exposure and hazard analysis. The environmental hazards are determined by a toxicological assay for three trophical levels of aquatic organisms—algae, invertebrates, and fish. Then, the effects on alga growth inhibition, daphnia acute immobilization and reproduction and fish acute toxicity of MES were reported earlier²⁾. These assay parameters were served as the evaluative criteria for ecotoxicity in the initial data set of the Law Concerning Examination and Regulation of Manufacture, etc. of Chemical Substances (Chemical Substances Control Law, Japan).

The PNEC for C14 and C16-MES were based on these aquatic toxicity data. On the other hand, predicted environmental concentration (PEC; potential exposure to the chemical in environment) was determined from monitoring results.

2.2 Environmental effects

The eco-toxicological tests for hazard assessment have been conducted with the OECD Guidelines for the Testing of Chemicals.

Results of the algae growth inhibition test, daphnia acute immobilization test, daphnia reproduction test, and fish acute toxicity test have been reported²⁾ and summarized in **Table 1**. Based on the available toxicity data, daphnia are considered to be most sensitive to MES. Therefore, the results of the daphnia reproduction test are used for calculating the PNEC. When only short-term toxicity data

are available, an assessment factor of 1000 is applied to their lowest L(E)C50 value. In this case, the two chronic assays—algae and daphnia—are available; therefore, an assessment factor of 50 can be applied according to the guidelines of EC⁸⁾. Subsequently, the PNECs of C14-MES and C16-MES are calculated as 82 and 4.2 $\mu\text{g/L}$, respectively.

2.3 Environmental exposure assessment

2.3.1 Monitoring of river water

A monitoring program was carried out from June 2004 to March 2006 in order to determine the concentrations of MESs in rivers. The seven sites of four urban rivers (Tamagawa ; Hamura-seki, Tamagawara-bashi, Denenchouhu-seki, Arakawa ; Chisui-bashi, Sasame-bashi, Edogawa ; Kanamachi and Yodogawa ; Hirakata-ohashi) that receive the effluents from municipal sewage treatment plants and also a limited number of untreated household drains in Tokyo and Osaka were selected. The sampling was performed in June, September, December, and March in order to understand the seasonal variation of water quality.

MESs were extracted with chloroform as methylene blue active substances and prepared for LC/MS analysis by concentration and clean up using solid phase extraction. This monitoring study was entrusted to the Chemicals Evaluation and Research Institute, Japan (CERI).

2.3.2 Monitored concentration of MES in river water

Table 2 lists the results of the MES analysis and **Fig. 1** shows the seasonal change of the MES concentration at each sampling site. The determination limit for C14MES and C16MES were 0.03 and 0.05 $\mu\text{g/L}$ respectively in this study. The MES concentration decreases in June and September. The seasonal variations of the MES concentration indicate the disappearance of MES by biodegradation in river water. Therefore, MES does not accumulate in the aquatic environment. It appears that in these months, the

Table 1 Summary of Effects of MES on Aquatic Organisms²⁾.

Organisms	Effects	C14-MES	C16-MES	Test Guideline
Green Alga (<i>Pseudokirchneriella subcapitata</i>)	72 h Growth Inhibition	EC50 > 100 NOEC: 56 mg/L	EC50 > 9.0 NOEC: 9.0 mg/L	OECD 201
Daphnids (<i>Daphnia magna</i>)	48 h Acute Immobilization	EC50: 17.2 mg/L	EC50: 1.24 mg/L	OECD 202
	21 d Reproduction	EC50: 6.81 NOEC: 4.10 mg/L	EC50: 0.70 NOEC: 0.24 mg/L	OECD 211
Medaka (<i>Oryzias latipes</i>)	96 h Acute	LC50: 24 mg/L	LC50: 1.3 mg/L	OECD 203

Table 2 Concentration of MES in River Water.

Sampling date (month)	MES Alkyl Chain	Tamagawa			Arakawa		Edogawa	Yodogawa
		Hamura-seki	Tamagawara-bashi	Denenchoufu-seki	Chisui-bashi	Sasame-bashi	Kanamachi	Hirakata-ohashi
2004.6	C14	<0.03 $\mu\text{g/L}$	0.03 $\mu\text{g/L}$	<0.03 $\mu\text{g/L}$	<0.03 $\mu\text{g/L}$	0.03 $\mu\text{g/L}$	<0.03 $\mu\text{g/L}$	<0.03 $\mu\text{g/L}$
	C16	<0.05	0.05	<0.05	<0.05	(0.03)	<0.05	<0.05
2004.9	C14	<0.03	0.03	<0.03	<0.03	0.09	<0.03	<0.03
	C16	0.05	0.06	(0.02)	<0.05	(0.04)	<0.05	0.03
2004.12	C14	<0.03	0.04	0.11	0.14	0.35	0.05	(0.02)
	C16	<0.05	0.1	0.52	0.38	0.68	0.18	0.04
2005.3	C14	<0.03	0.06	0.16	0.24	0.33	0.2	<0.03
	C16	<0.05	0.17	0.46	0.77	0.66	0.27	<0.05
2005.6	C14	<0.03	0.04	<0.03	<0.03	0.08	<0.03	<0.03
	C16	<0.05	0.05	(0.02)	<0.05	(0.04)	<0.05	<0.05
2005.9	C14	<0.03	(0.02)	<0.03	<0.03	0.04	<0.03	<0.03
	C16	<0.05	(0.02)	<0.05	<0.05	(0.03)	<0.05	<0.05
2005.12	C14	<0.03	<0.03	(0.02)	0.11	0.03	0.04	0.05
	C16	<0.05	0.08	0.09	0.34	0.08	0.08	0.19
2006.3	C14	<0.03	<0.03	0.03	0.05	<0.03	0.03	(0.01)
	C16	<0.05	0.09	0.17	0.12	0.54	0.06	(0.03)

Determination limit: C14 = 0.03 $\mu\text{g/L}$, C16 = 0.05 $\mu\text{g/L}$

(): detected under determination limit

Fig. 1 Seasonal Change of MES Concentration.

rate of biodegradation of MES is faster than that in December and March because of a favorable river water temperature. Moreover, a relatively high flow rate is observed in June and September, there for, it is assumed that the dilution ratio is high in these months. Further, the aerobic biodegradation process of activated sludge and

anaerobic digestion process of excess sludge were not inhibited by MES and the toxicity to fish was rapidly and significantly reduced by the biodegradation⁹⁾. Based on the monitoring results, the detection ratio of C14/C16 was determined as 32/68. This detection ratio was nearly reflected the consumption of raw materials.

2.3.3 Prediction of environmental concentration

The environmental exposure assessment is an integral part of the ecological risk assessments. The environmental concentration is determined either from the monitoring results or by calculation according to the environmental exposure model (specific discharge conditions, emission volume, flow rate, environmental fate, biodegradation, removal in sewage treatment plants, etc.)⁸⁾. In this report, the PECs of MES are determined from the monitoring data of river water adopting the newly proposed statistical analysis.

The statistical MES concentrations obtained from raw data were listed in **Table 3**. From a conservative point of view, in the risk assessment, the 95 percentile of the observed data was used as the PEC; it is expected to be relatively high value in the environment. The maximum value is often applied when the data are limited. Some times the PEC determined directly from the only monitoring data is not in agreement with results of the sampling sites. Moreover, it is inadequate for representing the entire estimation area. The maximum and 95 percentile are restricted in the monitored area. Therefore, in order to expand the interpretation and application of monitoring data, a statistical analysis was attempted to determine a reasonable PEC for a wide range of environmental water bodies that containing

relatively polluted and unmonitored rivers.

In the entire country, the biochemical oxygen demand (BOD) of river water is determined as a water criterion. It is assumed that the MES concentration is correlated with the BOD because both originate from household drains. **Table 4** shows the BOD of river water measured in parallel with MES. The BOD was measured according to JIS K0102 (Testing methods for industrial wastewater)¹⁰⁾ by CERI.

For the raw data obtained by monitoring for two years (**Fig. 2**), the correlation coefficient between the MES concentration and the BOD was obtained as 0.418 ($r^2 = 0.174$); this indicates a poor correlation. Another study was conducted to redetermine the correlation. In this case, the raw data were classified into three groups according to the water quality level represented by BOD. The 95 percentile and geometric mean of the MES concentration were calcu-

Table 3 Statistical Values of Measured MES Concentration.

	C14-MES	C16-MES	C14 + C16
Geometrical Mean	0.03 µg/L	0.04 µg/L	0.08 µg/L
95 Percentile	0.21	0.57	0.72
Max.	0.35	0.77	1.03

$$\text{MES } (\mu\text{g/L}) = 0.077 (\text{BOD, mg/L}) + 0.024; r^2 = 0.174$$

Fig. 2 Correlation between MES Concentration and BOD Obtained from Raw Data.

Table 4 BOD of River Water Measured in Parallel with MES.

Sampling	Tamagawa			Arakawa		Edogawa	Yodogawa
	Hamura -seki	Tamagawara -bashi	Denenchoufu -seki	Chisui -bashi	Sasame -bashi	Kanamachi	Hirakata -ohashi
2004.6	1.4 mg/L	2.0 mg/L	2.1 mg/L	1.4 mg/L	2.9 mg/L	3.5 mg/L	1.6 mg/L
2004.9	<1	1.4	1.5	1.1	3.1	<1	<1
2004.12	1.0	1.7	1.1	1.3	2.5	1.4	1.2
2005.3	1.4	2.9	1.7	2.0	6.4	2.6	1.7
2005.6	<1	2.2	1.8	1.5	4.5	2.4	1.1
2005.9	<1	1.2	1.0	<1	2.8	<1	<1
2005.12	<1	4.5	1.5	2.0	4.0	1.8	1.8
2006.3	1.0	<1	2.1	2.2	7.7	1.7	1.4

Kankyo Nenpo: Japan Soap and Detergent Association (2005, 2006)

lated for every group and compared with the geometric mean of the BOD of each group in order to examine the correlation. The 95 percentile and geometric mean of the MES concentration exhibited a good correlation with the geometric mean of the BOD; the value of r^2 was greater than 0.9 (Fig. 3). In this statistical analysis, the raw data were classified into the following ranges of the BOD: below 1 mg/L(clean water), 1.1-2 mg/L(a little polluted water), and above 2.1 mg/L(lightly polluted water). The next regression equations were obtained.

$$\text{MES 95\%ile } (\mu\text{g/L}) = 0.3521 (\text{BOD Geo. mean, mg/L}) - 0.044; r^2 = 0.924$$

$$\text{MES Geo. mean } (\mu\text{g/L}) = 0.0428 (\text{BOD Geo. mean, mg/L}) + 0.007; r^2 = 0.992$$

These correlations showed that the MES concentration is influenced by water quality. It was indicated that the accidental dispersion of the grab sample of the monitoring

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Fig. 3 Correlation of BOD Geometric Mean Value with 95 Percentile of MES Concentration and with Geometric Mean.

data was amended to reduce the contingency by the classification mentioned above¹¹). This statistical analysis method was appeared to be suitable for determining the PEC based on the monitoring data.

Table 5 shows the 95 percentile and geometric mean of the MES concentration determined by the BOD based on the correlation in Fig. 3. The BOD applied to the calculation of MES concentration was estimated by assuming the environmental water quality standards in accordance with the classification of public water areas in Japan, to assess the MES concentration corresponding with the water quality. In the risk assessment, the 95 percentiles in Table 5 were considered as the PECs.

3 RISK ASSESSMENT

The aquatic (environmental) risk of MES was assessed by comparing the PEC with PNEC. The maximum concentrations of C14-MES and C16-MES in the monitored area were 0.35 and 0.77 $\mu\text{g/L}$, respectively. They were less than the PNECs of C14-MES (82 $\mu\text{g/L}$) and C16-MES (4.2 $\mu\text{g/L}$). In the next assessment, more polluted areas were considered according to the above-mentioned statistical analysis. For C14 and the C16 homologues, the PECs of the 95 percentile of the MES concentration for a BOD of 5 mg/L were 0.65 $\mu\text{g/L}$ and 1.07 $\mu\text{g/L}$, respectively, as shown in Table 5. Further, water with a BOD of 5 mg/L(moderately polluted water) is sufficient for fisheries. The PECs of C14-MES and C16-MES in a heavily polluted area with a BOD of 10 mg/L, which is considered to be unsuitable for aquatic organisms, are calculated as 1.32 $\mu\text{g/L}$ and 2.16 $\mu\text{g/L}$, respectively. All the PECs were less than the PNECs. In Japan, a rare case is reported in which the BOD of public water areas reaches 10 mg/L Therefore, it was concluded that MES poses a low ecological risk in almost all aquatic environments in Japan. MES can be removed effectively by

Table 5 The Predicted Environmental Concentration (PEC) of MES according to BOD.

Estimated BOD	C14		C16		C14 + C16	
	95%ile	Geo. Mean	95%ile	Geo. Mean	95%ile	Geo. Mean
1 mg/L	0.12 $\mu\text{g/L}$	0.02 $\mu\text{g/L}$	0.19 $\mu\text{g/L}$	0.03 $\mu\text{g/L}$	0.31 $\mu\text{g/L}$	0.05 $\mu\text{g/L}$
2	0.25	0.03	0.41	0.06	0.66	0.09
3	0.38	0.05	0.63	0.09	1.01	0.14
5	0.65	0.08	1.07	0.14	1.72	0.22
8	1.05	0.13	1.72	0.22	2.77	0.35
10	1.32	0.17	2.16	0.27	3.48	0.44

The BOD is estimated by assuming the environmental water quality standards in accordance with the classification of public water areas in Japan.

conventional biological wastewater treatment systems because it is readily and fully biodegradable under aerobic conditions³⁻⁵.

It has already been assessed that the surfactants—LAS, alcohol ethoxylates, and alkyl amine oxide—in household detergents pose a low risk; in this case also, the PECs are less than the PNECs⁶. Despite the high consumption of these surfactants, their environmental concentrations are distributed under the PNEC. It is considered that the prevalence of wastewater treatment systems and ready biodegradability have resulted in the low concentration of these surfactants.

4 CONCLUSIONS

This report demonstrated that the aquatic risk assessment of 2-sulfonato fatty acid methyl ester sodium salt (MES) and concluded under.

- 1) A statistical analysis method; examined the correlation with BOD was employed efficiently to predict the environmental concentration of MES based on the monitoring data.
- 2) The predicted no effect concentrations (PNEC) of C14 and C16-MES were estimated to 82 and 4.2 $\mu\text{g/L}$ respectively.
- 3) The predicted environmental concentrations (PEC) of C14 and C16-MES were predicted to be 0.65 and 1.07 $\mu\text{g/L}$ for BOD 5 mg/L (moderately polluted area), and 1.32 and 2.16 mg/L for BOD 10 mg/L (heavily polluted area), respectively.
- 4) It was confirmed that the PECs were less than the PNEC even in such areas as supposed to be heavily polluted; the risk characterization ratio (RCR: PEC/PNEC) was less than 1. Under the integrated concern, it was concluded that MES poses a low risk in aquatic environments in Japan.

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