

## Key Features of Alcohol Ethoxylate (AE) Risk Assessment

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This document provides the results of the ecological risk assessment of alcohol ethoxylate (hereinafter “AE”, synonym: polyoxyethylene alkyl ether), a major non-ionic surfactant, conducted by the Research Center for Chemical Risk Management (CRM), the National Institute of Advanced Industrial Science and Technology (AIST). In Japan, this is the first comprehensive risk assessment that has revealed the current status of ecological risk in aquatic environment of AE as a mixture of homologues. The key features of AE risk assessment include the following:

- (1) To aim at a persuasive deduction based on solid theories and actual data, AE risk assessment is developed with conservative analyses of the actual data obtained for this risk assessment, as well as with original analyses applying newly developed methods and model estimations.
- (2) To aim at a homologue-based ecological risk assessment of AE with consideration to the differences among homologues, an estimation method to assess the risk of AE as a mixture of homologues, is proposed. This method is expected to be applicable for risk estimation of other mixtures similar to AE of which each homologue has similar mechanisms of toxicity.
- (3) Since the ecotoxicity data of individual homologues are unavailable, a neural network model has been developed to predict the ecotoxicity for each homologue on organisms in the environment based on existing data. The method used to develop this model is expected to be applicable for risk assessment of other chemical substances whose ecotoxicity information is not presently available.
- (4) To assess the ecological risk defined as the adverse effects on the persistence of fish populations, an extrapolation method has been developed, which enables to estimate the threshold concentrations of effects on the persistence of fish populations for each homologue with limited ecotoxicity data (acute  $LC_{50}/EC_{50}$  and chronic NOEC). It is expected that population-level ecological risk assessments for many other chemical substances with limited ecotoxicity data become feasible.
- (5) The first monitoring in Japan was conducted using LC/MS assay by bipyridinium derivatives (hereinafter “Pyr+/LC/MS method”), the latest analytical method for quantification of AE homologues, which revealed the compositions of AE homologues in commercial detergents marketed in Japan, influent and effluent of sewage treatment plants, and in aquatic environment. In addition, the data from the monitoring provided the information on both of the exposure concentrations and the half-life parameters for each homologue of AE in river water. These findings are the basic information required to elucidate AE ecological risk on a homologue-based, and are the

highly valuable data obtained for the first time in Japan.

- (6) Attempts are made to quantify the relationship of risk trade-off and to evaluate its cost-effectiveness involved in the alternative use of AE that has been implemented to reduce the risk of nonylphenol ethoxylate (hereinafter “NPE”).
- (7) A methodological approach for ecological risk assessment including the screening-level risk assessment by species sensitivity distribution analysis and the risk characterization by effect analysis on the persistence of fish population is demonstrated.
- (8) Risk management measures feasible for national and local governments, industries, manufacturers and consumers are respectively recommended.

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## Executive Summary

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### Chapter I Preface

This document provides the results of the ecological risk assessment of alcohol ethoxylate (hereinafter “AE”, synonym: polyoxyethylene alkyl ether) conducted by CRM. The risk of AE on human health have already been evaluated in many existing assessments, although no definite conclusion has been reached concerning the potential adverse effects of percutaneous exposures, it is concluded that there are little adverse effects with oral exposures of AE on human health. Therefore, in this risk assessment, the human health risk of AE is not evaluated.

The background premises for AE risk assessment are as follow:

- 1) AE is the major non-ionic surfactant and its volume of use continues to increase. AE, the most typical non-ionic surfactant, is mainly used in household detergents and approximately 170,000 tons of AE were manufactured in Japan in Fiscal Year (FY) 2003. Due to the concerns over endocrine-disruptive effects, chemicals such as nonylphenol (hereinafter “NP”), nonylphenol ethoxylate (hereinafter “NPE”) have been gradually replaced by AE in the recent years. In addition, with the current trend to favor downsized and liquid detergents, the demand for AE as an alternative for linear alkylbenzenesulfonate (hereinafter “LAS”) is also expected to increase. Furthermore, in 2004, AE was included in OECD's High Production Volume (HPV) Chemical List (OECD, 2004). Overall facts and trends indicate that the volume of AE use is expected to substantially increase in the future.
- 2) AE is one of the substances whose effects on aquatic organisms are of concern due to its ubiquitous

presence in the aquatic environment in Japan. The release data that were published by the Pollutant Release and Transfer Register (hereinafter “PRTR”) system indicated that AE was one of the top ten chemicals (top three chemicals in household use) with a significant volume of annual discharge to the environment. Since most AE is released into water, AE is frequently prevalent in the nationwide rivers in Japan. In setting the water quality criteria to protect aquatic organisms, which the Ministry of the Environment (MOE) promotes, linear AE is designated as one of the substances with a high priority (MOE, 2002).

3) AE is one of the chemical substances of which the need to conduct a risk assessment was identified.

In many existing risk assessments outside of Japan, it has been concluded that the current exposure level of AE has low potential of adverse effects affecting aquatic organisms. In the preliminary risk assessment conducted in Japan, however, AE was determined to have potential adverse effects on aquatic organisms, and the need of comprehensive risk assessment was identified (Chemicals Evaluation and Research Institute; CERI and National Institute of Technology and Evaluation; NITE, 2006).

4) AE risk should be assessed considering the differences in the properties of individual homologues.

AE products are mixtures comprising of numerous homologues, and each AE homologue shows different behaviors in the environment, different removal rates in sewage treatment plants, and different ecotoxicity in the aquatic environment. To obtain a comprehensive and accurate assessment, it is important to understand the environmental concentrations and ecotoxicity by homologue, however, there is no risk assessment having accomplished such assessment except the most recent published paper (Belanger *et al.*, 2006).

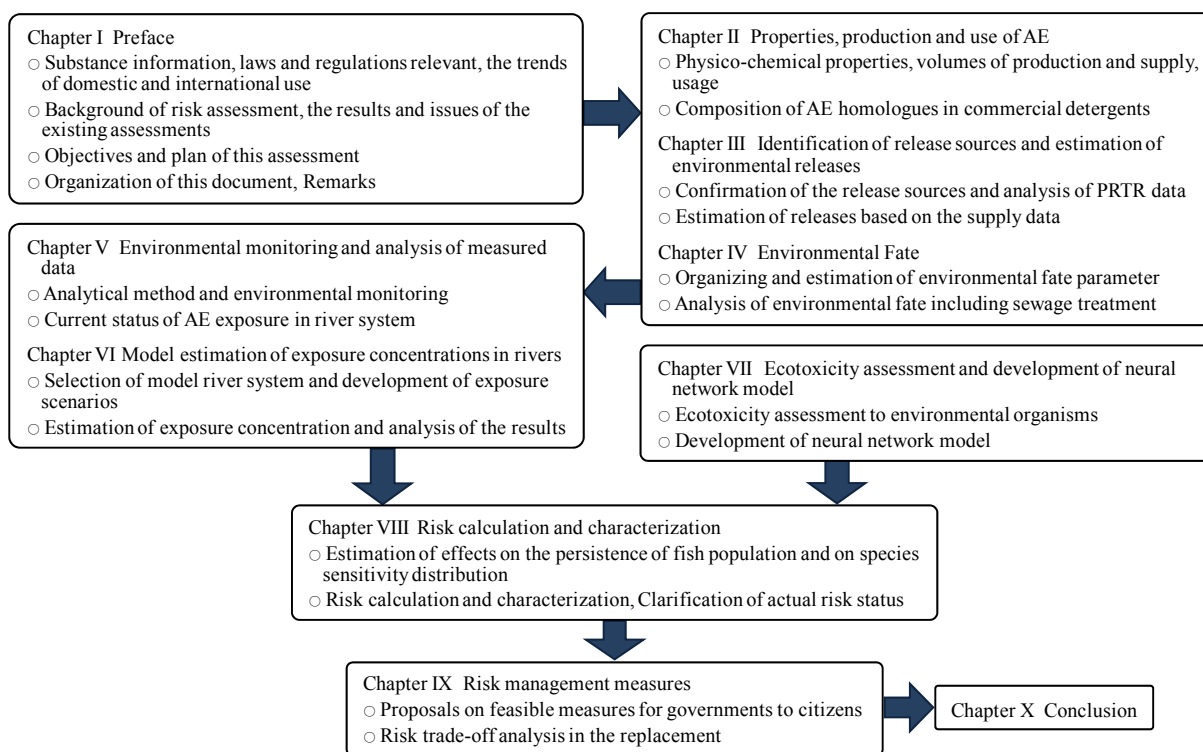
5) There is a social demand to confirm the validity of risk reduction measures where AE is used as an alternative to NPE. In recent years, AE has been used as an alternative for NPE in various industries in order to reduce the risk posed by releases of NPE. To fulfill such a social demand to confirm if using AE as an alternative for NPE is appropriate, it is necessary to conduct AE risk assessment including the elucidation of the risk trade-off involved with replacing NPE with AE.

Considering the above premises for risk assessment, three objectives of AE risk assessment are set as follows:

- 1) To assess the ecological risk of AE as a mixture of homologues at the fish population-persistence level, considering the differences among homologues of their environmental fate, distribution, exposure concentration and ecotoxicity, and to reveal the current status of ecological risk of AE in the environment.
- 2) To conduct a quantitative risk analysis including exposure scenarios assuming increases of AE use in the future, and to propose appropriate risk management measures based on the results.
- 3) To quantify the relationship of risk trade-off involved in replacing NPE or LAS with AE, and to

evaluate the cost-effectiveness of the substitutions. To provide some knowledge and reference information concerning the social acceptability of substance replacement for risk reduction based on these results.

AE is a Class 1 Designated Chemical Substance assigned by the “Law Concerning Reporting, etc. of Releases to the Environment of Specific Chemical Substances and Promoting Improvements in Their Management (hereinafter PRTR Law)”. As described below, AE contains an alkyl chain (carbon chain) in its molecule. However, the AE homologues designated by the PRTR law include only those with the alkyl chain lengths of 12-15. In this assessment, risks of all AE homologues existing in the environment are assessed including homologues currently designated by the PRTR law. The organization of this document is shown in Figure 1.



**Figure 1 The organization of this document**

## Chapter II

### Properties, production and use of AE

#### 1. Identification and physico-chemical properties

AE is nonexistent in the course of nature and is synthesized by adding polymerization of ethylene oxide to higher alcohol. Normally, AE commercial products contain homologues with varying numbers of alkyl chains and molecules of ethylene oxide (hereinafter “EO molecules”). In this risk assessment, the AE homologue is represented in the form of a combination of alkyl chain length and EO molecules, *i.e.*

described as  $C_iEO_j$  ( $i$ : number of alkyl chain;  $j$ : EO molecules).

Since each AE homologue is composed of different alkyl chains (hydrophobic) and EO molecules (hydrophilic), their physico-chemical properties vary. For example, the bioconcentration factor ( $BCF$ ) and octanol-water partition coefficient ( $K_{ow}$ ) are higher with an increase in the length of alkyl chains and a decrease in EO molecules.

## 2. Production and supply

AE production has been increasing since 2002 and the volume of production in FY 2003 was approximately 170,000 tons, which accounts for more than 30% of total non-ionic surfactants in Japan. AE homologues with  $C_{12-15}$ , as designated by the PRTR law, account for 60 to 80% of the total volume of AE supply in Japan.

## 3. Use

AE and other non-ionic surfactants are used in various industries and purposes with their characteristics of foaming, moistening, emulsifying, dispersing, cleaning, antistatic and corrosion proofing and softening.

The main use of AE is in household detergents and these detergents make up more than 70% of the total volume of AE ( $C_{12-15}$ ) supplied in Japan. AE is used in various industries such as textile, pulp and paper, laundry, leather, cosmetics, photographs, rubber and plastic products, agriculture (agricultural chemicals), construction work, petroleum and coal, and fuel, etc.

## 4. Composition of AE homologues in commercial detergents in Japan

The results of a contract research on AE homologue compositions conducted for this risk assessment, revealed the differences in the AE homologue compositions of each detergent. Many popular household detergents contained a significant amount of homologues with  $C_{12-15}EO_{0-15}$ , and most had an even-numbered carbon chain.

# Chapter III

## Identification of release sources and estimation of environmental releases

In this chapter, based on the PRTR and AE supply data, the major release sources of AE homologues with  $C_{12-15}$  designated by the PRTR law and the environmental media into which AE is released are identified, and the volume of AE releases into the environment is estimated (Figure 2).

### 1. Estimation of releases into the environment based on the PRTR data

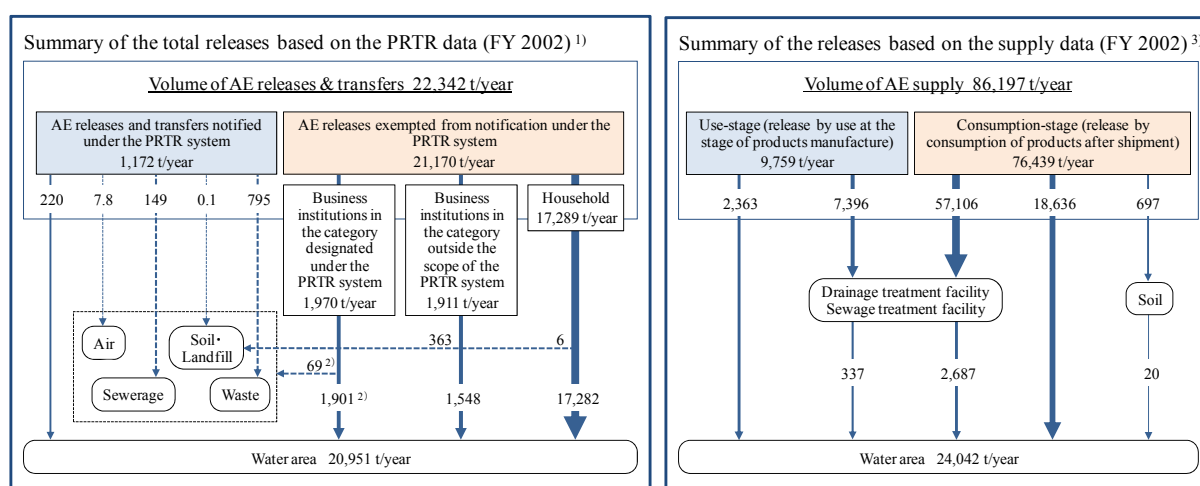
Using the PRTR data published in March 2005 (revised PRTR data in FY 2001 and 2002 ) (METI, 2005a; MOE, 2005), data concerning AE releases into the environment, and the outline of AE releases and transfers are summarized and shown in Figure 2 (left).

The PRTR law obliges “business institutions designated under the PRTR system” which meet the

specified criteria, to notify the volumes of releases and transfers of designated chemical substances, while the releases from business institutions exempted from notification are estimated by the government. Based on the total releases notified by the business institutions designated under the PRTR system, and those estimated by the government for the business institutions exempted from notification, it is estimated that AE of 22,342 tons/year in total was released in FY 2002, of which 77% (17,282 tons/year) was released from domestic wastewater. Nearly all the volume of AE environmental releases was released into water, and the releases into soils and air were negligible.

## 2. Estimation of releases into the environment based on the supply data

Based on the volume supplied by use, releases into the environment are estimated considering removal during en-route of releases (Figure 2, right). In this estimation, 24,042 tons/year of AE is considered to be released, which is not significantly different from the above estimation based on the PRTR data (22,342 tons/year). Also in the estimation by the supply data water is considered as the environmental medium into which virtually the entire volume of AE is released.



1) Compiled from METI (2005a) and MOE (2005).

2) Releases from business institutions in the categories designated under the PRTR system are allocated originally by CRM for this risk assessment in accordance with the composition ratio by medium (public water areas: 96.5%, others: 3.5%, see Table III.4).

3) Original estimation in this risk assessment by CRM

**Figure 2 Releases of AE in FY 2002**

## Chapter IV Environmental Fate

In the previous chapter, releases of AE into air and soil are estimated to be negligible and nearly the entire volume of AE is assumed to be released into water after use. In this chapter, differences in physico-chemical properties among homologues are focused, and basic information on the environmental

fate of AE and its each homologue after release between and in environmental media are summarized.

Since nearly all environmental releases of AE are released into water, the processes controlling their environmental fate are considered to be transfer between media (volatilization, adsorption and bioaccumulation) and degradation.

#### 1. Transfer between media (volatilization, adsorption and bioaccumulation)

Judging from the existing reviews and the physico-chemical properties estimated by EPI Suite, the volatilization of each homologue of AE is at negligible level. Although the relation with EO molecules has not been clearly elucidated, it is found that the AE homologues are more easily adsorbed with increased length of alkyl chains. Furthermore, it has been shown that the bioaccumulation of AE homologues occurs from a low to a medium extent, being enhanced with increased length of the alkyl chains and decreased number of EO molecules.

#### 2. Degradation

AE homologues with fewer branches of alkyl chains, longer alkyl chains and fewer EO molecules have a propensity to degrade more rapidly. Commercial AE detergent products, meanwhile, generally comprise homologues with linear or low-branched alkyl chains, which rapidly degrade under both aerobic and anaerobic conditions. Consequently, biodegradation is an important process controlling the environmental fate of AE. The number of EO molecules is the more important determining factor for degradation rate compared to the length of alkyl chains. In addition, it is found that the high water temperature accelerates AE biodegradation, which suggests the need to consider the effects of water temperature in estimating exposure concentrations. The results of the environmental monitoring of AE indicate the AE removal rate in sewage treatment plants is 98% or higher.

## Chapter V

### Environmental monitoring and analysis of measured data

The analytical techniques for quantification of AE homologues were under development for along time, and the only available data on environmental concentrations by homologue in Japan were those reported by Maruyama *et al.* (2001). In recent years, however, a new technique for quantification was developed and reliable data have been published. This chapter introduces environmental monitoring and monitoring data obtained by this new quantification method, as well as analysis of exposures to the entire AE and by homologue, based on the actual monitoring data available on AE concentrations in the aquatic environment.

The analytical results of environmental exposures to the entire AE based on the available exposure concentrations by homologue indicate that AE exposure concentrations are several tens µg/L in the rivers near densely populated districts without adequate sewerage treatment systems, while the maximum AE

concentrations do not exceed 20 µg/L in effluent water of sewage treatment plants. Alcohol, one of the intermediates of AE biodegradation (homologues with EO<sub>0</sub>), was detected at all sampling sites at a higher concentration than homologues with other EO molecules, and the mean ratio relative to the entire AE concentration was 41%. Although not all alcohol detected was considered to be derived from AE, in this risk assessment, all concentrations including the detected alcohol, are assumed as environmental exposure concentrations of the entire AE. Further, it was confirmed that concentrations of AE individual homologues in river water were higher in winter. It is assumed that this is due to low water temperature in winter, which decreases the degradation rates of AE individual homologues as well as seasonal changes of water volume. In addition, the monitoring results in the Tama River showed that exposure concentrations of homologues designated by the PRTR law were approximately 60% of those of the entire AE (mean of all sampling sites).

The homologue compositions in the aquatic environment were investigated in the Tama and Tone Rivers (area in Gunma Prefecture). The results suggest that nearly 90% of AE detected in the Tama River comprised of homologues with an even-numbered carbon chain, indicating that AE was mainly released from households. In contrast, concentrations of homologues with an even-numbered carbon chain represented up to 70% of the entire AE concentration in the Tone River, suggesting that releases from industries, including textile industry, contributed to AE exposure concentrations significantly. Further, the comparison of homologue compositions in effluent water from sewage treatment plants by countries and that by processes from detergents to releases into the environment has revealed that homologue composition within an aquatic environment is site-specific.

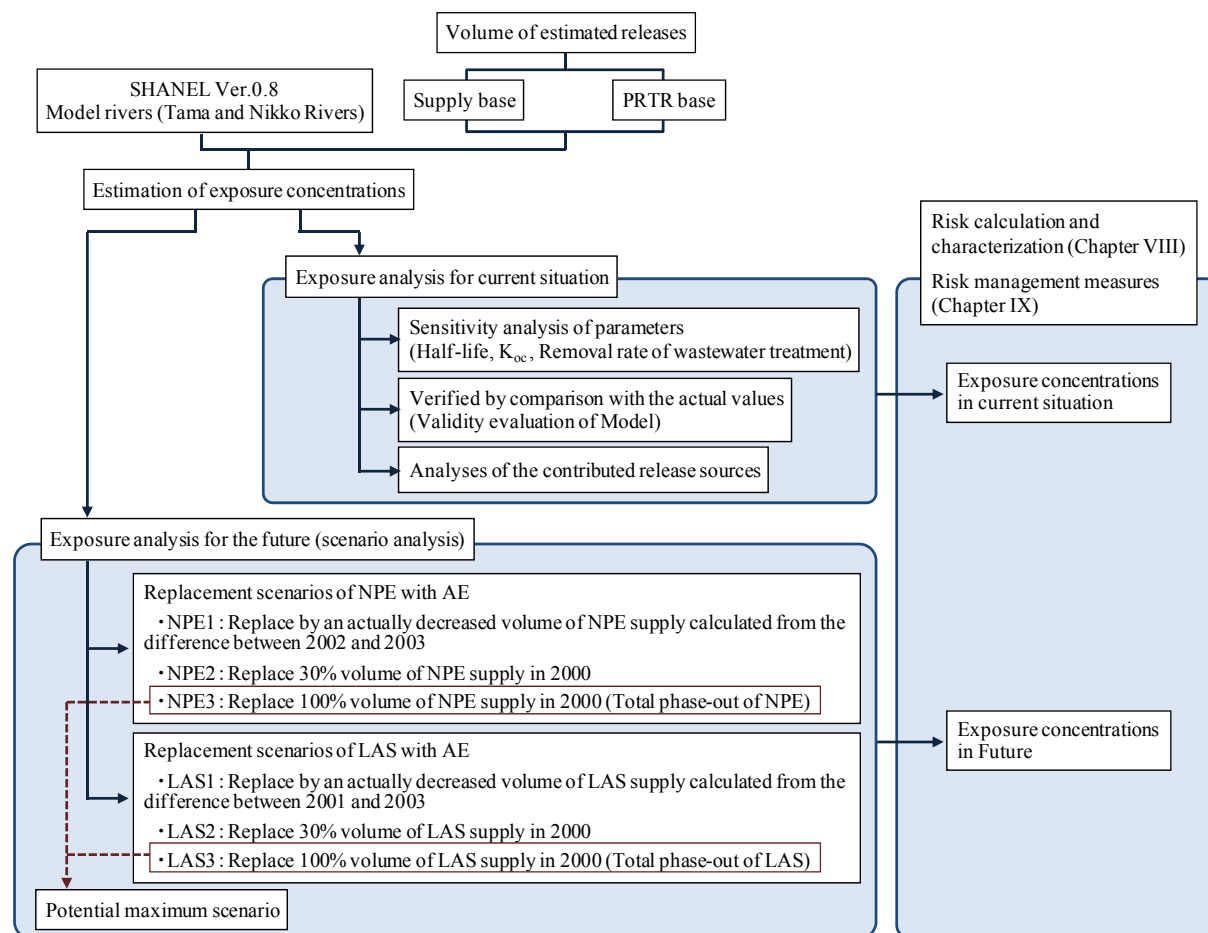
## Chapter VI

### Model estimation of exposure concentrations in rivers

To assess risk of AE that are ubiquitously present in nationwide rivers in Japan, clear understanding on the current conditions of exposures in each river basin is indispensable. However, the reliable monitoring data available include very little data with a limited number of river basins. In this chapter, to understand the current conditions of exposures to AE in nationwide rivers, the correlation between biochemical oxygen demand (BOD) and AE concentrations is investigated first, noticing the fact that a large amount of BOD data are available for each river basin across Japan. Based on the results of the analysis, the Tama and Nikko rivers are respectively ranked among the nationwide rivers, and selected as the two appropriate model river basins for estimating AE exposure concentrations employing SHANEL (Standardized Hydrology-based AssessmeNt tool for chemical Exposure Load). In addition to the estimation of the current exposure concentrations, several future exposure scenarios assuming a replacement of NPE and LAS with AE (*i.e.*, increase in AE use) are developed and future exposure concentrations are estimated in



accordance with these scenarios. Factors contributing to high exposures are also examined on the basis of estimated results. The contents and flow of exposure analyses are shown in Figure 3.

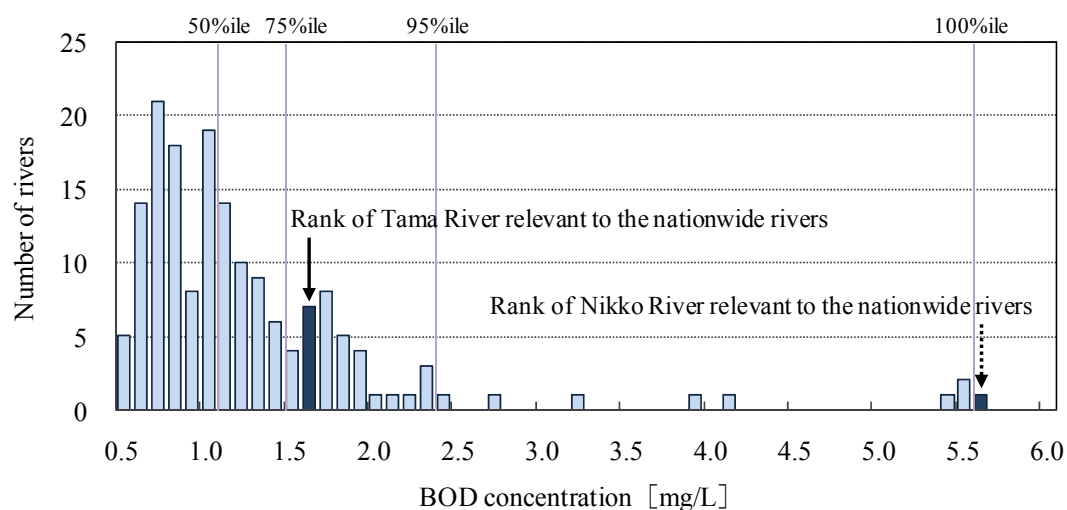


**Figure 3 Contents and flow of exposure analyses by SHANEL**

### 1. Ranking of the Tama River and Nikko River in the nationwide rivers

Although reliable monitoring data are limited, over 70% of AE supply is for household use, and AE is released mainly from households. In contrast, BOD is a water pollution indicator for domestic wastewater in the nationwide rivers and a significant amount of BOD monitoring data is available. As the first step of analysis, the AE and BOD concentrations obtained from the monitoring surveys in the same river are examined for their correlation. As a result, a considerably positive correlation between AE and BOD is confirmed, and thus it is judged that BOD can be used as a surrogate indicator to AE concentration for the screening purpose. In the second step, with BOD data (FY 2002) on 166 first class rivers in Japan by the Ministry of Land, Infrastructure and Transport (MLIT), BOD concentrations in the Tama and Nikko rivers are investigated. As a result, the Tama River is ranked as 129th (78 percentile) in ascending order in the water quality by BOD concentration (Figure 4). Since the Nikko River is not designated as a first class river, BOD concentration in this river that was surveyed by MOE is compared with the BOD concentration data

by MLIT. Consequently, BOD concentration in the Nikko River is higher than that in a river of 100 percentile (Figure 4). Therefore, based on the results of water quality ranking by BOD in the nationwide rivers, it is suggested that these two rivers selected as the model river for the analysis by SHANEL represent as those with high AE concentrations.



**Figure 4 Ranking of the Tama River and Nikko River in the Japanese nationwide rivers (river water quality ranking by BOD in FY 2002)**

[Compiled from MLIT (2005b) and NIES (2007)]

## 2. Current exposure status

The conditions for analysis of the current exposure status are as follows:

Model rivers: The Tama River and Nikko River

Estimation period: January to December 2000 (366 days)

Factors of AE physico-chemical properties\*: AE organic carbon-water partition coefficient ( $K_{OC}$ ), half-life (in the soil liquid phase, soil solid phase, river water, river sediment liquid phase and river sediment solid phase), and the removal rate in sewage treatment plants

Release volume: PRTR data in FY 2002 and AE supply data in FY 2002

\* AE half-life (in river water) is set as 0.3, 0.5 or 1.5 days respectively. For other physico-chemical properties, the maximum, minimum and 50 percentile values from references and estimations are used.

In this analysis, a sensitivity analysis is firstly conducted to identify factors of physico-chemical property having a significant effect on changes in exposure concentrations. It emerged that changes in exposure concentrations are highly dependent on the AE half-life in river water and when the AE half-life in river water is set as 0.3 day, the estimated values are closest to the measured values of AE with C<sub>12-18</sub> (in the analysis using the Tama River as a model).

In the second step, the contribution to exposure concentrations is estimated by release sources to identify a release source contributing to significant increases in exposure concentrations. Based on the results, in the

case of the Nikko River, it emerged that the textile industry is the biggest contributor to exposure concentrations, reflecting a regional characteristics that the textile industry concentrated in the areas along the Nikko River basin. Nevertheless, the contribution by the use of household detergents is markedly higher than that of other uses. In the Tama River meanwhile, the contribution of the use of household detergents is higher than that in the Nikko River. In addition, a contribution of metal and machinery industries, as well as textiles, is recorded, although not to a great extent in the Tama River.

The accuracy of overall estimations by SHANEL in the above is verified by comparison with the actual values monitored in the Tama River, which indicates that the estimated values with AE half-life in river water set at 0.3 day are relevant as exposure concentrations in risk assessment.

### 3. Future exposure analysis

AE has already been used as an alternative substance for NPE in industries. Likewise in Japan, similarly to European countries and the U.S., it is expected that LAS used for household purposes will be replaced with AE in the future. Assuming such a replacement, future AE exposure is analyzed using the scenarios of replacement shown in Figure 3. Based on the estimation results, it is anticipated that replacing LAS rather than NPE will result in higher AE exposure concentrations in the future.

## Chapter VII

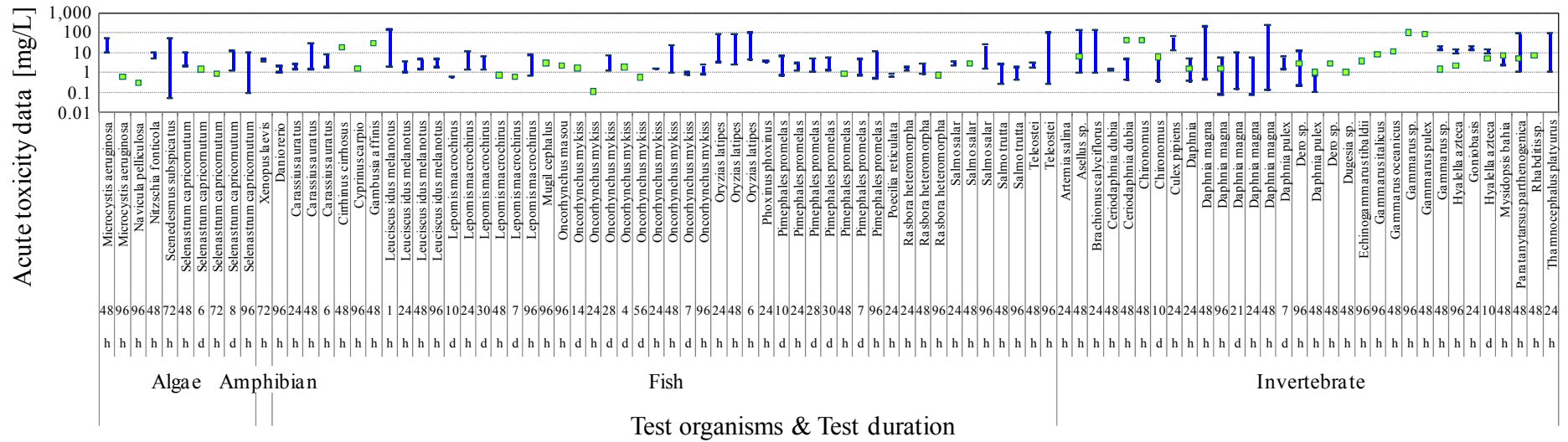
### Ecotoxicity assessment and development of neural network model

#### 1. Ecotoxicity assessment with existing toxicity data

In this chapter, an ecotoxicity database built from the existing AE toxicity study data is presented first, and the ecotoxicity of AE is assessed. Of the three domains, *i.e.* aquatic and terrestrial organisms and microorganisms and protozoa, aquatic organisms had the highest sensitivity to AE. Furthermore, of the aquatic organism it seems that invertebrates had the highest sensitivity, followed by fish, algae and aquatic plants (Figures 5 to 6).

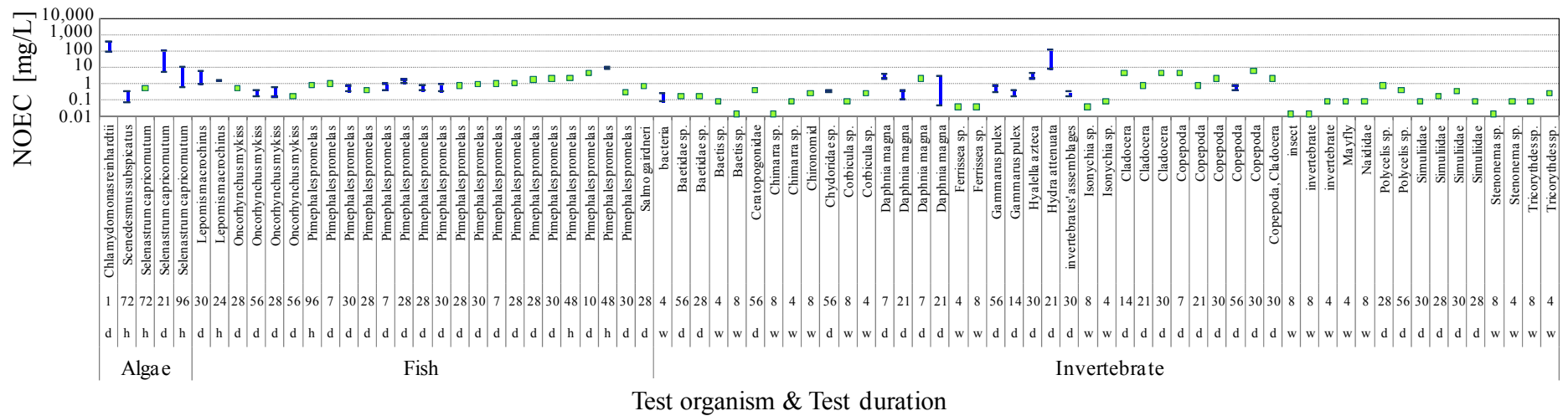
In addition, it is found that although the majority of AE is removed by wastewater treatment, the intermediates (including the homologues of EO<sub>0</sub>) that are more ecotoxic than their AE parent homologues at per unit concentration can be produced mainly with reduction of EO chains during biodegradation process.

## Executive Summary



1) The dot and bar indicate the geometric mean and the range of the reported toxicity data, respectively.

**Figure 5 Summary of reported acute toxicity test data of AE on aquatic organisms (Algae: EC50, Other: LC50)**



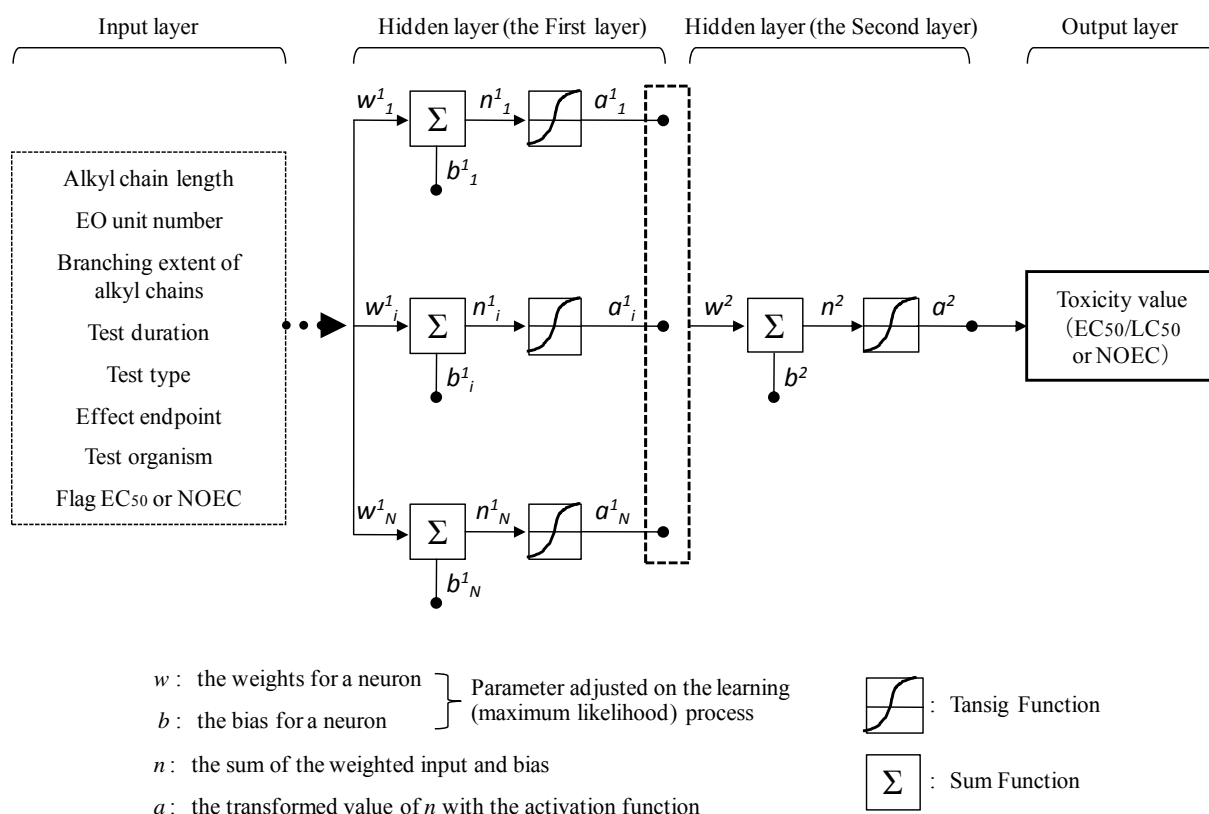
1) The dot and bar indicate the geometric mean and the range of the reported toxicity data, respectively.

**Figure 6** Summary of reported chronic toxicity test data of AE on aquatic organisms

## 2. Model prediction of ecotoxicity by homologue

Information on ecotoxicity of AE individual homologues could not be obtained from the published data. Several prediction models for ecotoxicity by homologue were previously proposed, but all had some limitations (*e.g.* linear extrapolation). A new neural network model has been, thus, developed to predict effect concentrations on reproduction and survival (chronic toxicity index: NOEC, acute toxicity index: LC<sub>50</sub>/EC<sub>50</sub>) of organisms by homologue, which are essential for the analysis of effects on the persistence of populations (Figure 7).

When values predicted by this model are compared with those measured from toxicity studies, it is confirmed that this model can predict ecotoxicity by homologue with higher accuracy than the conventional models, and therefore, the values predicted by this model are judged to be relevant as basic data for risk assessment.



**Figure 7 Architecture of Neural Network Model**

## Chapter VIII

### Risk calculation and characterization

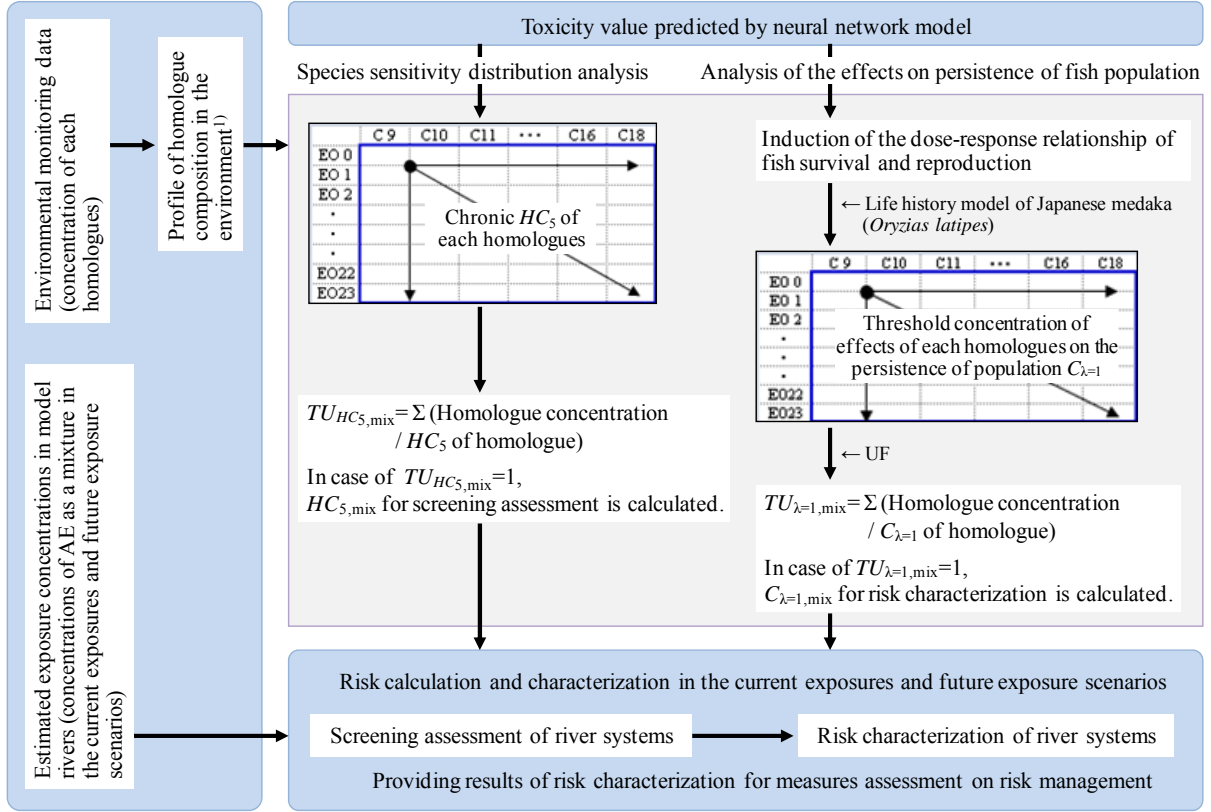
#### 1. Framework for risk calculation and characterization

The flow and the concept for risk calculation and characterization is presented in Figure 8, with the

effects on the persistence of fish population as the endpoint. In addition, a species sensitivity distribution is employed for the screening-level assessment. During the analysis of effects on the persistence of fish populations, Japanese medaka (*Oryzias latipes*) is selected as the model organism. Based on laboratory toxicity data, the concentration that makes the population growth rate (hereinafter “ $\lambda$ ”) of the test organism decreased to 1, is proposed to be the threshold concentration of effects on the persistence of fish populations. Ecotoxicity data for survival and reproduction of fish that are absolutely imperative for deriving the threshold concentration of effects on persistence of fish populations for each homologue (hereinafter “ $C_{\lambda=1,i,j}$ ”) are estimated by the developed neural network model.

Two sets of values for AE exposure concentrations, *i.e.*, measured values ( $C_{12-18}EO_{0-23}$ ) and estimated values in the Tama and Nikko rivers by the SHANEL model are applied to risk calculations. The former is used to estimate  $HC_{5,mix}$  (hazard concentration affecting 5% of the organism species in the environment), and  $C_{\lambda=1,mix}$  (threshold concentration of effects on the persistence of fish population), which are described below, to calculate the ecological risk posed by each homologue and to elucidate the overall risk of the homologues designated by the PRTR law. The latter is used to characterize risks with the current status of the rivers (presence/absence of risks and their level), to identify release sources, and to estimate future risks.

Based on the assumption that the toxic effects of individual homologues on organisms act in an additive manner, the risk of AE, a mixture of plural homologues, is quantified by the dose accumulation method, as shown in Formula 1. The risks of individual homologues can also be assessed by toxic unit (hereinafter “ $TU$ ”), the ratio of an exposure concentration divided by the concentration of toxic effect of individual homologues. Further, the total value of  $TU$  for each homologue provides a value representing the risk of the entire AE homologues.



1) Profile of homologue composition estimated from the AE exposure concentrations in river water that were previously corrected to be a concentration of only containing the AE-derived alcohol

**Figure 8 Framework of AE ecological risk calculation and characterization**

$$AE \text{ risk} = TU_{mix} = \frac{C_1}{EC_{x_1}} + \frac{C_2}{EC_{x_2}} + \dots + \frac{C_n}{EC_{x_n}} = \sum_{i=1}^n \frac{C_i}{EC_{x_i}} \quad (1)$$

$C_i$ ; Environmental concentration of number  $i$  homologue.

$EC_{xi}$ ; A concentration at which  $i$  homologue independently has an effect on  $x$  % of organisms in the environment (e.g.  $EC_{10i}$  represents as the effect concentration of number  $i$  homologue that independently has an adverse effect on 10% organisms in the environment).

$C_i/EC_{xi}$ ;  $TU$ , risk of number  $i$  homologue ( $TU$ ), relative potency of number  $i$  homologue in a mixture.

$TU_{mix}$ ; Risk of AE: a mixture of plural homologues.

## 2. Estimation of $HC_{5,mix}$ and $C_{\lambda=1,mix}$

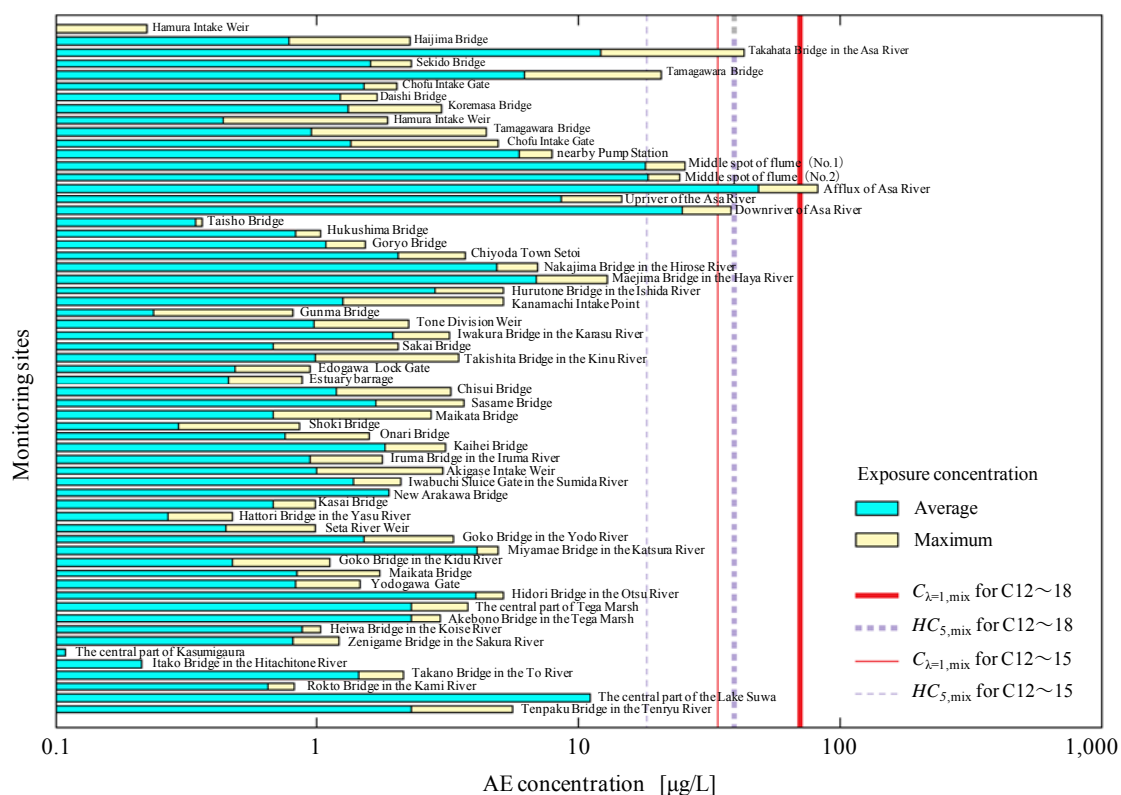
To conduct a risk assessment with a screening assessment and a risk characterization of the rivers in Japan, a hazard concentration affecting 5% of the organism species in the environment ( $HC_{5,mix}$ ) and a threshold concentration of effects on the persistence of fish populations ( $C_{\lambda=1,mix}$ ) are estimated by employing the environmental composition of homologues (composition of AE homologues derived from the concentrations of individual homologues corrected by excluding the alcohol originated from the substances other than AE) that has been derived from the monitoring data in winter from the Asa River. As a result,  $HC_{5,mix}$  and  $C_{\lambda=1,mix}$  of AE are estimated to be 39 and 70  $\mu\text{g/L}$ , respectively and those of the AE

designated by the PRTR law are consequently estimated to be 18 and 34  $\mu\text{g/L}$ .

### 3. Results of risk calculation and characterization

Based on the results of the risk characterization with the current AE exposure levels, AE risks are judged to be at “the level of no concern” in almost all the rivers with the monitoring data (Figure 9). Nevertheless, in the river basins in densely populated districts with low coverage rate of sewerage treatment systems, such as the Asa River in Hino, Tokyo, AE concentrations in the aquatic environment can exceed  $HC_{5,\text{mix}}$  or  $C_{\lambda=1,\text{mix}}$ . In other words, it is considered that there are risks, to a certain extent, in local water bodies in the vicinity of a densely populated area with inadequate sewerage treatment systems. In estimation of the future AE risk with the assumption of increases in AE use, similar to the current risk, it is considered that AE concentrations in the aquatic environment in districts with inadequate sewerage treatment system may be increased, and the risk may probably reach a level of concern. For example, in the Nikko River basin with inadequate sewerage treatment systems (72% throughout the entire Aichi Prefecture), if the current AE use increases to 120%, it is expected that the risk on persistence of fish populations would be of concern.

In addition, by using measured exposure concentrations ( $C_{12-18}\text{EO}_{0-23}$ ), it is estimated that the risk of all homologues designated by the PRTR law ( $TU_{C12-15}$ ) would be approximately 50 to 60% of the risk of the entire AE ( $TU_{C12-18}$ ).



**Figure 9 Summary of the results in risk calculation and characterization  
for all of monitoring study rivers ⇒ See frontispiece color Fig. (12)**



## Chapter IX

### Risk management measures

#### 1. Major proposals for risk management and reduction

##### 1.1 Extending the range of homologues designated by the PRTR law

As described above, the homologues designated by the PRTR law ( $C_{12-15}$ ) in the aquatic environment pose approximately 50 to 60% of the risk of the entire AE. In order to understand more accurately current status of AE risk for better management, a proposal is made to initiate a project to obtain and evaluate toxicity data required for the ultimate purpose of extending the range of homologues designated by the current PRTR law to homologues of  $C_{12-18}EO_{0-23}$  which can be quantitatively analyzed. The maximum initial costs of this project required to extend the range designated by the PRTR law are estimated to be approximately 1.7 million yen.

##### 1.2 River water monitoring

To conduct river water monitoring is proposed for correctly managing the AE risk. In particular, for river basins close to densely populated districts with inadequate sewerage treatment systems and large release sources, there is a greater need to monitor AE concentrations.

It is still expensive to conduct analyses with the latest quantitative method that provides accurate homologue composition. To conduct cost-effective monitoring, following considerations are recommended to be taken: 1) rivers with high exposure concentrations should be monitored with high priority; 2) seasonal characteristics whereby exposure concentrations increase in winter should be considered; and 3) composite samples by sampling at different timing of the same sampling points are effective for reducing monitoring cost.

##### 1.3 Production and consumption with awareness to AE homologue properties

AE ecotoxicity is determined by the distributions of C chain lengths and EO molecules. AE biodegradation, which is an important process to determine AE environmental exposure concentrations, is significantly influenced by EO molecules. In addition, the distributions of EO molecules can be controlled in the manufacturing process to some extent. Therefore, AE manufacturers, including raw material and detergent manufacturers, and consumers using these products, can minimize the AE risk if they produce or use AE products with awareness to ecotoxicity and the biodegradation properties of AE homologues.

##### 1.4 Reduction of AE releases

Since it is expected that AE use continues to increase in the future, reduction of releases in all stages of the life-cycle of AE, *i.e.* production, use and discharge, is critical as future risk reduction measures.

Since AE is removable by wastewater treatment, treated by sewage is one of the major risk reduction measures. Considering the fact that more than 70% of AE supply is used for household detergents, the first

priority is to provide sewerage treatment systems (including individual septic tanks) in densely populated areas. The cost of AE reduction by wastewater treatment is estimated to be 67,730 yen/kg-AE. In this estimation, sewage treatment plants were assumed to be exclusively for AE removal, however, in reality, other substances including pollution loads are removed, meaning the actual cost may be quite lower than the estimation stated above. Next, for risk reduction measures for AE in industry use, reducing releases from the top six industries of AE use, specifically from the textile industry, is considered to be effective.

## 2. Assessment of social acceptability on replacing NPE or LAS with AE

Recently, NPE has been replaced with AE for the purpose to reduce risk with NPE. In order to judge whether the above replacement actually reduces ecological risk in rivers or not, the risk trade-off is quantified in this section including the case of LAS replacement with AE. To obtain basic information used to judge the validity of replacement, cost-effectiveness is assessed. In addition, the overall environmental effects of AE, LAS and NPE are compared across all life-cycle stages of production, use and discharge.

The results of the risk trade-off assessments show that replacing both NPE and LAS with AE can reduce the ecological risk in aquatic environment.

Next, a practicable analysis on cost-effectiveness of replacing NPE with AE is conducted and the results are described below. Three kinds of scenarios (see Figure 3) are developed as follows: NPE1 (a replacement that was actually performed in industries), NPE2 (where 30% of NPE is replaced across all industries), and NPE3 (100% of NPE is replaced across all industries). The results of the analysis indicate that NPE1 scenario is the most cost effective means of risk reduction.

Finally, environmental effects throughout all stages of production, use and discharge are compared between AE, LAS and NP (and/or NPE), based on the four viewpoints of biodegradation, ecotoxicity, environment-friendly production and the presence/absence of endocrine disrupting concerns. It is suggested that the degree of adverse effects on the environment is in an order of NP and/or NPE > LAS > AE.

Consequently, it is suggested that replacement with AE represents an effective strategy for the total risk reduction of surfactants in rivers.

## **Chapter X**

### **Conclusion**

#### 1. Summary of the exposure assessment

AE is a non-ionic surfactant whose production and use has been increasing in recent years. Over 70% of the total volume of AE is used in household detergents. AE are mixtures of numerous homologues, of which those designated under the PRTR law account for 60 to 80% of the total volume of AE consumed in Japan.

The major emission sources of AE are households and textile industry, and nearly all volume of AE is

ultimately released into public water bodies. Since each group of AE homologues has unique physico-chemical properties, their environmental fates are also highly variable. However, all groups of AE homologues used in common household detergents are readily biodegradable, with a high removal rate of 98% or more by sewage treatment plants. Thus, exposure concentrations of AE are closely related to the coverage rate of sewerage treatment system.

The measured concentrations of each AE homologue in environmental waters suggest that AE present in aquatic environment are mainly from household. Since the exposure levels of AE tend to increase in winter (summer/winter ratio for average concentrations: 0.39), consideration should be given to seasonal factors when determining ecological risk management measures. Furthermore, the measured exposure concentrations demonstrate that the exposure concentrations of those AE homologues designated by the PRTR law represent approximately 60% of the total AE concentration.

In order to obtain an accurate understanding of the current status of environmental exposure to AE, the exposure concentrations in the Tama River and the Nikko Rivers have been estimated employing the SHANEL model. Comparison of the exposure estimates derived from this model with the measured river concentrations confirms that the estimates obtained are close enough to the measured data, and can therefore represent the environmental concentrations of all AE homologues ( $C_{12-18}$  range) to be used for risk characterization.

Furthermore, since the use of AE is expected to increase in the future, several alternative scenarios have been developed to estimate future AE exposure concentrations with increased use of AE as a substitute for NPE and LAS (see Figure 3). Based on the estimation results, it is anticipated that replacing LAS rather than NPE will result in higher AE exposure concentrations in future.

## 2. Summary of the ecotoxicity assessment

Based on a review of the existing toxicity test data, aquatic organisms have been found to be highly sensitive to the toxic effects of AE, meaning it is relevant to consider that the ecological risk of AE can be appropriately evaluated by focusing on its adverse effects on the aquatic organisms. It has also been shown that AE homologues vary in terms of their ecotoxicity, *i.e.* the toxicity of AE rises with an increase in the length of the C chains and a decrease in the number of EO molecules.

A new neural network model has been developed to predict the toxicity of individual homologues. Comparison of the predictions derived from this model with existing toxicity test data confirms that these predictions are more accurate (*i.e.* closer to the test data) than those from other existing models, thus proving the new model as sufficiently reliable for use in the risk assessment.

## 3. Summary of risk calculation and characterization

In the ecological risk assessment, the effects on the persistence of fish populations are defined as the endpoint for risk characterization. In addition, a species sensitivity distribution analysis is also employed

for the screening-level assessment.

The results of risk characterization based on the measured environmental concentrations suggest that with the present use of AE (the current status of AE exposures), the risk is below the level of concern in almost of the cases if the wastewater is appropriately treated. However, it has also been shown that there is risk, with certain probability, for local water bodies in the vicinity of densely populated areas without adequate sewerage treatment systems.

Moreover, the exposure scenarios assuming a future increase in AE use (see Figure 3) estimate higher exposure concentrations in the rivers near a densely populated area with no or inadequate sewerage treatment systems (including individual septic tanks), suggesting that, as with the present situation, such areas are considered to have little capacity against future AE risk.

Furthermore, based on the results of the risk calculation for each homologue, it is estimated that the AE homologues with C<sub>12-15</sub> designated by the PRTR law in aquatic environment accounts for 50 to 60% of the environmental risk posed by the entire AE (C<sub>12-18</sub>) observed in the monitoring study.

#### 4. Summary of risk management measures

The results of the risk assessment indicate that although there is little need to urgently introduce risk reduction measures with the current status of AE exposures, some risk management measures should be determined to address the future increase of AE use. Specific measures that have been proposed include: i) extending the range of AE homologues designated by the PRTR law to include C<sub>12-18</sub> from C<sub>12-15</sub>; ii) conducting monitoring studies (by employing the latest analytical method of quantification); iii) promoting production and consumption of products containing AE considering the physico-chemical properties of individual AE homologue (in particular, controlling the number of EO molecules); iv) developing emissions reduction measures that encompass all stages of AE life-cycle, *i.e.* production, use and discharge (in particular, reducing the environmental releases of AE through the implementation of wastewater treatment regimes); and v) enhancing information sharing.

#### 5. Quantification of the risk trade-off involved in replacing NPE or LAS with AE

In recent years AE has been used as a substitute for NPE in various industries in order to reduce the environmental risk posed by releases of NPE. Similarly, there has also been a global trend towards replacing LAS with AE. However, it has not been examined whether such substitution is truly effective as a measure to reduce ecological risk nor has its cost-effectiveness been determined. Hence, in this risk assessment, a quantitative analysis of these alternatives is performed considering the changes in the magnitude of the ecological risk as well as the cost-effectiveness of substitution.

The results of this analysis show that replacing both NPE and LAS with AE can reduce ecological risk. Moreover, the replacement of NPE with AE, which is currently being undertaken by industries, is suggested as a highly cost-effective replacement.

## 6. Future tasks

This risk assessment conducted an ecological risk assessment of AE at the fish population-persistence level taking into consideration of the property differences among individual homologue, and finally proposed risk reduction measures based on the results.

A series of analysis methods that have been newly developed in the assessment process, *i.e.* an ecological risk assessment method for mixtures using the dose accumulation concept, extrapolation of effects on the persistence of fish population using NOEC and LC<sub>50</sub>/EC<sub>50</sub>, a quantification method for the risk trade-off, and a neural network model, which provide valuable information for ecological risk assessments of chemical substances other than AE in the future. In addition, AE homologue compositions in detergents and aquatic environment together with half-lives of individual homologues, which were examined and obtained as the basic information for risk characterization, represent the first measured values in Japan and are extremely valuable.

The fact remains that the uncertainty due to insufficient information on properties of individual AE homologue (physico-chemical properties, environmental fate, ecotoxicity, etc.) could not be completely eliminated. A future task will be to clarify the properties of individual homologues. In addition, in order to understand the fate of AE within aquatic environment, accumulation of its monitoring data is necessary. In future, it is preferable to verify and update the assumption and uncertainty factor used in this risk assessment when new information on physico-chemical properties and environmental fates of individual AE homologues become available.

## 7. Caution and limitation in applying the information obtained in this risk assessment

In the process of conducting risk assessment summarized in this document, two kinds of parameters are used, *i.e.* intrinsic parameters that are related to homologues and organisms, and variable parameters that depend on time and place.

The former includes the degradation rates of individual homologues  $C_iEO_j$  ( $i$ : carbon number of alkyl chain;  $j$ : EO molecules), the threshold concentration of effects on the persistence of fish population,  $C_{\lambda=1,i,j}$  (Table VIII.5 in Chapter VIII), and the hazard concentration affecting 5% of the organism species,  $HC_{5,i,j}$  (Table VIII.2 in Chapter VIII).

On the other hand, the latter is the AE exposure concentrations and homologue compositions in aquatic environment. There are three determining factors related to: i) differences in rivers (each river has its own hydrologic and thermal properties); ii) interannual differences in the same river (even in the same river, annual climate conditions vary, and therefore, hydrologic and thermal properties, as well as seasonal change characteristics, may be subject to change); and iii) difference in AE raw material (AE is produced from petroleum and natural oil materials, of which ratios may vary and can have an effect on homologue compositions). In other words, AE exposure concentrations and the homologue compositions are

parameters in an aquatic environment that vary according to time and place.

The threshold concentration of effects on the persistence of fish populations ( $C_{\lambda=1,\text{mix}}$ ) for risk characterization and the hazard concentration affecting 5% of the organism species ( $HC_{5,\text{mix}}$ ) for screening assessment used in this risk assessment are based on measured data (in winter) of monitoring in highly exposed areas (the Asa River and Kawakita Canal in Hino, Tokyo), and therefore, it should be noted that these values reflect specific homologue composition of a certain river system.