

# Mass Balance Study of Nonylphenol Ethoxylates and Their Metabolites in an Urban River Contaminated by Nonylphenol

Mamoru Motegi\*, Kiyoshi Nojiri, Shigeo Hosono and Kiyoshi Kawamura

Center for Environmental Science in Saitama  
914 Kamitanadare, Kisaimachi Kitasakitamagun, Saitama 347-0115, Japan

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\*E-mail: a0191338@pref.saitama.lg.jp

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In previous studies, an urban river called Kamo River was found to be polluted with nonylphenol (NP) by a rubber product manufacturing factory. To determine the contribution of the factory effluent to the river pollution, a mass balance study was conducted for NP, nonylphenol ethoxylates (NP $n$ EOs,  $n = 1-15$ ), and nonylphenol carboxylates (NP $m$ ECs,  $m = 1-10$ ) in the waters of the river and its 10 inflow channels. The total concentration of nonylphenolic compounds (T-NPCs) in the river water was 4.6 nM/L at the upstream sampling point and 54.6 nM/L at the downstream sampling point. T-NPCs concentration ranged from 0.4 to 487.1 nM/L in the waters of the inflow channels connected to the targeted river section, and the highest value was observed in the water of the inflow channel which receives the factory effluent. The mass flows of T-NPCs were 458.0 mM/day for Input (the upstream sampling point and outlets of 10 inflow channels) and 828.2 mM/day for Output (the downstream sampling point). The mass flow of the highly polluted inflow channel comprised 82.4% of Input. In comparison with the mass balance of chloride ion, the mass flow of T-NPCs in Output was still higher than that in Input. This phenomenon was attributed to the high mass flows of NP and NP $n$ EOs ( $n = 1-3$ ) in Output, and their potential source was determined to be the river sediment.

## 1. Introduction

Nonylphenol ethoxylates (NP $n$ EOs, where 'n' indicates the number of ethoxy (EO) units) are widely used as nonionic surfactants in detergents, pesticides, emulsifiers, and dispersants. Commercially produced NP $n$ EOs are a mixture of compounds with various numbers of EO units and frequently show a normal distribution pattern with a peak in concentration at around NP9EO.<sup>(1,2)</sup> In Japan, 18,000 tons of NP $n$ EOs were produced in 2003, and 1,200 tons of it were released into the environment in fiscal year 2003.<sup>(3)</sup> Commercial NP $n$ EOs with long EO chains that are released into the environment are mostly transferred to the water environment because of their low volatilization and high water solubility.<sup>(3-5)</sup>

In general, NP $n$ EOs with long EO chains discharged into the water environment are biodegraded by microorganisms into NP $n$ EOs with short EO chains and to nonylphenol carboxylates (NP $m$ ECs, where 'mECs' indicates the number of 'n-1' ethoxy units plus one terminal CH<sub>2</sub>COOH) by carboxylation of their terminal EO under aerobic condition.<sup>(5,6)</sup> Furthermore, nonylphenoxy monoethoxylate (NP1EO) and nonylphenoxy acetic acid (NP1EC) are transformed to nonylphenol (NP) by microorganisms under anaerobic condition. In sewage treatment plants (STPs), NP $n$ EOs in the influent are mainly transformed into NP $m$ ECs with short EO chains such as NP1EC and nonyl-

phenol monoethoxy acetic acid (NP2EC) during the treatment process under aerobic condition.<sup>(1,7-9)</sup> These phenomena are considered to occur also in the natural water environment.<sup>(10)</sup>

It is well known that NP is more toxic to fish than its precursors.<sup>(11)</sup> In addition, weak estrogenic effects on aquatic organisms have been confirmed for NP, nonylphenol diethoxylate (NP2EO), and NP1EC.<sup>(12-14)</sup>

Some European countries have introduced a regulatory environmental quality standard (EQS) for NP as 1  $\mu\text{g/L}$ ,<sup>(5)</sup> and a stringent EQS of 0.3  $\mu\text{g/L}$  has been introduced in Italy in 2003.<sup>(15)</sup> Although the EQS for NP has not been defined in Japan, the NP concentration often exceeded 1  $\mu\text{g/L}$  in some river waters.<sup>(16-19)</sup> Because an industry-level self-regulation banning the household use of NPnEOs as detergents began in 1998 in Japan, the pollution of river water with nonylphenolic compounds is considered to be attributable to industrial usage and is site-specific.<sup>(16,17)</sup>

In our previous study on the Kamo River, which is a small urban river running through Saitama Prefecture in Japan, we found that the maximum concentrations of NP in the water and sediment were 3.7  $\mu\text{g/L}$  and 11,000  $\mu\text{g/kg}$  dry weight (dw), respectively.<sup>(19)</sup> In the sediment, NP1EO and NP2EO were also detected, but their concentrations were an order of magnitude lower than the NP concentration. In the river water, the total concentrations of NP, NPnEOs ( $n = 1-15$ ), and NPmECs ( $m = 1-10$ ) (T-NPCs) increased between Sites 1 and 2 (Fig. 1).

To identify the pollution sources of nonylphenolic compounds, a survey was conducted to determine their concentrations in the effluents from factories standing at the river basin. This survey was carried out in cooperation with the Department of Environment and Disaster Prevention, Saitama Prefecture Government from August to September 2004. The effluents were collected from each drain outlet of the factories. Results showed that 1.1  $\mu\text{g/L}$  (5.1 nM/L) of NP, 1,600  $\mu\text{g/L}$  (2,600 nM/L) of NPnEOs ( $n = 1-15$ ), and 1.6  $\mu\text{g/L}$  (5.3 nM/L) of NPmECs ( $m = 1-10$ ) were detected in a factory effluent (Fig. 2). The factory produces rubber products and is located at the right basin between Sites 1 and 2.

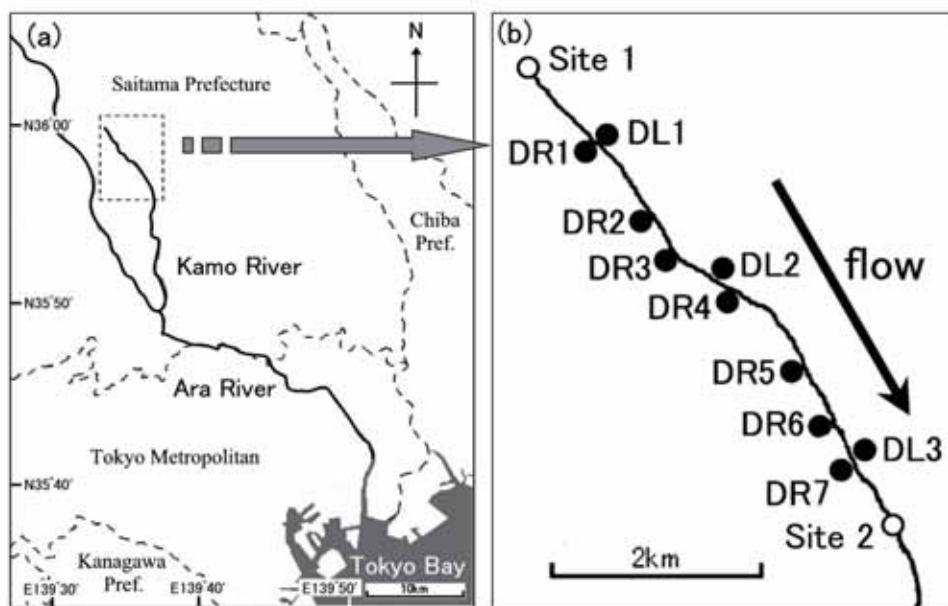


Fig. 1. (a) Location of the Kamo River and (b) sampling sites along the Kamo River (○: Sites 1 and 2) and its inflow channels (●: DR1–7, DL1–3).

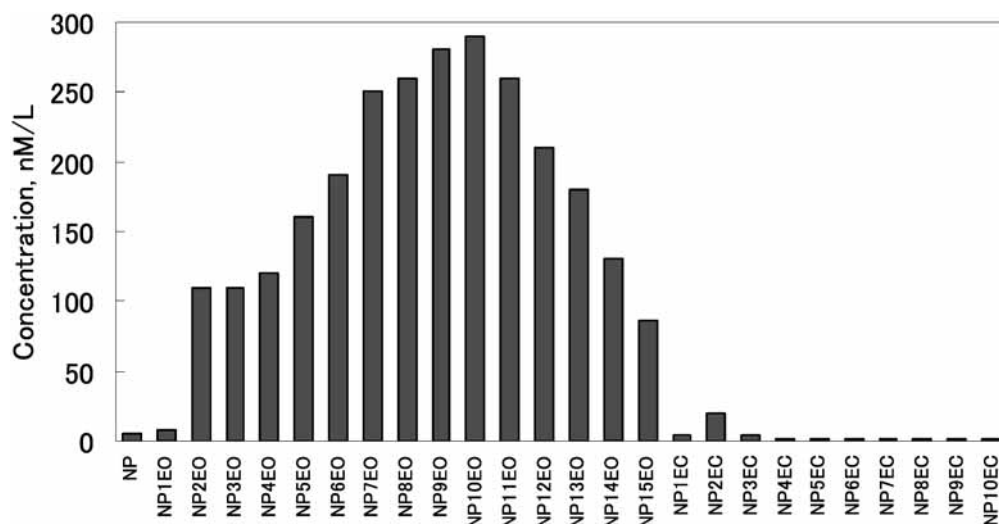


Fig. 2. Oligomer profile in concentration of nonylphenolic compounds in the effluent from a factory located at the basin of the Kamo River. The profile was similar to that of NP $n$ EOs used for industry, and showed a seminormal distribution pattern with a peak at NP10EO.

Under these circumstances, a mass balance study of these nonylphenolic compounds in the river water and its inflow channels was conducted between Sites 1 and 2 to determine the contribution of the factory effluent and to understand the behavior of nonylphenolic compounds in the river.

## 2. Materials and Methods

### 2.1 Study area and sampling

The Kamo River is a typical urban river located in Saitama Prefecture in Japan and a tributary of the Ara River, which is one of the major rivers in Japan (Fig. 1(a)). The Kamo River is 19.2 km in length, and its basin area is approximately 62 km<sup>2</sup>. A rubber overflow weir is constructed at the upstream point, which is 6.8 km from the confluence with the Ara River to keep seawater from entering and to ensure adequate water supply for agricultural purposes. Although the left basin has been almost completely covered by the sewerage system, its coverage ratio in the right basin is approximately half. Because effluents from STPs are discharged directly into the Ara River, they had no influence on the Kamo River.

The length of the river between Sites 1 and 2 is 5.6 km and approximately 10,000 persons living in the right basin are not served by the sewerage system in the study area. Site 1 is located at the uppermost stream of the river and is the outlet of an underground drain for domestic wastewater collected from the upper basin. Seven sampling points at the right basin (DR1–7) and three sampling points at the left basin (DL1–3) were selected as the main inflow channels (Fig. 1(b)). DR1–6 and DL1–2 are the outlets of drainage conduits. DL3 and DR7 are the outlets of an open channel and a brook, respectively. Site 2 is located at the downstream of these inflow channels.

The survey was conducted in February 2005, and rainfall was not observed for five days before the survey. The maximum water depths at the cross sections of Sites 1 and 2 were 0.2 and 0.45 m, respectively.

The details of sampling methods are described in our previous study.<sup>(19)</sup> A brief summary is explained as follows. Each water sample was collected from the surface at the sampling points. One liter of the sample was used for NP analysis, and another liter was used for NP $n$ EOs and NP $m$ ECs analyses. Each water sample was also collected in a polypropylene bottle to measure chemical oxygen demand (COD<sub>Mn</sub>), suspended solids (SS), chloride ion (Cl<sup>-</sup>), pH, and electrical conductivity (EC). Water temperature was measured on site.

## 2.2 Sample treatment and analytical methods

The details of sample treatment and analytical methods for nonylphenolic compounds are described previously by Motegi *et al.*<sup>(19)</sup> Briefly, each water sample was filtered through a glass fiber filter before extraction, and both filtered residue and filtrate were individually analyzed.

NP in the filtered residue and the filtrate was extracted with methanol and dichloromethane, respectively. After ethyl derivatization, a cleanup procedure using a Florisil Cartridge was adopted for each extract. NP was analyzed using a gas chromatograph (GC) mass spectrometer (MS) under the selected ion monitoring (SIM) mode.

NP1EO and NP2EO were extracted from the filtrate by solid phase extraction using a trifunctional octadecyl silica resin cartridge. In the case of filtered residue, NP1EO and NP2EO were extracted in the same manner as NP. After trimethylsilyl derivatization, a cleanup procedure using a Florisil Cartridge was adopted for each extract. These compounds were also analyzed using the GC/MS under the SIM mode.

The extractions of NP $n$ EOs ( $n = 3–15$ ) and NP $m$ ECs ( $m = 1–10$ ) from the filtered residue and the filtrate were performed with the same extraction methods as those for NP1EO and NP2EO. Measurements of NP $n$ EOs ( $n = 3–15$ ) and NP $m$ ECs ( $m = 1–10$ ) were performed using a high-performance liquid chromatograph MS under the SIM mode.

The detection limits of the individual nonylphenolic compounds in the filtered residue and the filtrate ranged from 0.003 to 0.01  $\mu\text{g/L}$  and from 0.003 to 0.1  $\mu\text{g/L}$ , respectively. Their average recoveries in the filtered residue ranged from 76 to 105%, and their relative standard deviations (RSDs) were below 9%. Those in the filtrate ranged from 55 to 98% and from 1 to 23%, respectively.

The concentrations of NP, NP1EO and NP2EO were not corrected by the recovery ratios, because their surrogates were added before the extraction. The concentrations of NP $n$ EOs ( $n = 3–15$ ) and NP $m$ ECs ( $m = 1–10$ ) were corrected by the recovery ratios to corresponding compounds for the accurate mass balance, because these chemicals were quantified by the absolute calibration method. The total concentration of nonylphenolic compounds in water was obtained by summing the concentrations in the filtered residue and the filtrate.

## 2.3 General parameters

The general parameters (COD<sub>Mn</sub>, SS, pH, and EC) were measured to characterize the water samples from the river and inflow channels. These parameters were determined according to the Japanese Industrial Standard K0102. Cl<sup>-</sup> in the filtrate was determined as a conserved substance in a mass balance study using an ion chromatographic analyzer (IC7000 series 2, YOKOGAWA, Japan).

## 2.4 Flow rate and mass flow

The flow velocities of water in the river and its inflow channels were measured using a portable electromagnetic flowmeter (TK-105X, TOHO DENTAN, Japan). The flow rate of water was calculated by multiplying the flow velocity and the cross-sectional area at each sampling point. Mass flows of nonylphenolic compounds and Cl<sup>-</sup> were calculated by multiplying their concentrations and the flow rate.

### 3. Results

#### 3.1 General parameters in water

Results of the measured parameters are summarized in Table 1. EC, SS, COD<sub>Mn</sub>, and Cl<sup>-</sup> at DR1, DR4, DR5, and DR7 in the right basin were higher than those at the other sampling points, and this suggested that their inflow waters were mainly comprised of domestic wastewater. On the other hand, the general parameter values were low at DL1–3 in the left basin, which is completely covered by the sewerage system.

COD<sub>Mn</sub> concentrations were 5.7 mg/L at Site 1 and 5.3 mg/L at Site 2. Those at DR1–7 in the right basin ranged from 3.3 to 46.6 mg/L, and those at DL1–3 in the left basin ranged from 1.2 to 3.5 mg/L. The SS concentration increased from 2 mg/L at Site 1 to 8 mg/L at Site 2. The concentration ranged from 1 to 26 mg/L at DR1–7, and was below 1 mg/L at DL1–3. pH was 7.4 at both Sites 1 and 2, and ranged from 7.1 to 8.0 at the outlets of the inflow channels (DR1–7 and DL1–3). The EC value increased from 31 mS/m at Site 1 to 45 mS/m at Site 2, and ranged from 22 to 61 mS/m at DR1–7 and from 22 to 33 mS/m at DL1–3. The Cl<sup>-</sup> concentration increased from 17.6 mg/L at Site 1 to 43.8 mg/L at Site 2. Although its concentrations at DL1–3 (7.2–14.7 mg/L) were lower than those of the river water, those at DR1–7 ranged from 9.8 to 70.3 mg/L. Water temperature was 12.7°C at Site 1 and 9.1°C at Site 2, and ranged from 6.9 to 19.1°C at the outlets of the inflow channels.

#### 3.2 Concentrations of nonylphenolic compounds

Table 2 shows the molar concentrations of nonylphenolic compounds in the water of the Kamo River and its inflow channels. The total concentrations of NP, NP<sub>n</sub>EOs ( $n = 1–15$ ) and NP<sub>m</sub>ECs ( $m = 1–10$ ), indicated by 'T-NPCs', were 4.6 nM/L at Site 1 and 54.6 nM/L at Site 2. At DR6, the maximum concentration of 487.1 nM/L was

Table 1  
General parameters in the waters of the Kamo River and its inflow channels.

| Unit   | COD <sub>Mn</sub><br>(mg/L) | SS<br>(mg/L) | pH  | EC<br>(mS/m) | Cl <sup>-</sup><br>(mg/L) | WT<br>(°C) |
|--------|-----------------------------|--------------|-----|--------------|---------------------------|------------|
| Input  |                             |              |     |              |                           |            |
| Site 1 | 5.7                         | 2            | 7.4 | 31           | 17.6                      | 12.7       |
| DR1    | 46.6                        | 26           | 7.6 | 61           | 42.6                      | 7.8        |
| DL1    | 2.1                         | <1           | 7.9 | 24           | 7.2                       | 19.1       |
| DR2    | 6.1                         | 3            | 7.5 | 28           | 9.8                       | 11.3       |
| DR3    | 3.3                         | 1            | 7.1 | 22           | 13.9                      | 14.6       |
| DL2    | 1.2                         | <1           | 7.4 | 22           | 9.5                       | 11.5       |
| DR4    | 10.8                        | 8            | 7.4 | 55           | 63.5                      | 11.9       |
| DR5    | 11.2                        | 5            | 7.4 | 44           | 34.0                      | 12.1       |
| DR6    | 7.5                         | 3            | 7.6 | 29           | 13.8                      | 16.7       |
| DL3    | 3.5                         | <1           | 8.0 | 33           | 14.7                      | 6.9        |
| DR7    | 18.0                        | 12           | 7.1 | 57           | 70.3                      | 10.3       |
| Output |                             |              |     |              |                           |            |
| Site 2 | 5.3                         | 8            | 7.4 | 45           | 43.8                      | 9.1        |

Abbreviations are as follows; COD<sub>Mn</sub>: chemical oxygen demand, SS: suspended solids, EC: electrical conductivity, Cl<sup>-</sup>: chloride ion, WT: water temperature.

Table 2  
Concentrations of nonylphenolic compounds in the water of the Kamo River and its inflow channels.

| Sampling site | Type         | NP  | NP1EO<br>+NP2EO | NP1EC<br>+NP2EC | NP <i>n</i> EOs<br>( <i>n</i> = 3–15) | NP <i>m</i> ECs<br>( <i>m</i> = 3–10) | T-NPCs* |
|---------------|--------------|-----|-----------------|-----------------|---------------------------------------|---------------------------------------|---------|
| Input         |              |     |                 |                 |                                       |                                       |         |
| Site 1        | River        | 0.4 | 1.2             | 0.4             | 2.5                                   | ND**                                  | 4.6     |
| DR1           | Drainage     | 3.6 | 6.3             | ND              | 0.9                                   | 0.6                                   | 11.4    |
| DL1           | Drainage     | ND  | 0.3             | 0.4             | 0.3                                   | ND                                    | 1.0     |
| DR2           | Drainage     | 0.8 | 3.8             | 2.5             | 4.3                                   | 1.2                                   | 12.6    |
| DR3           | Drainage     | ND  | 0.5             | ND              | 1.1                                   | ND                                    | 1.6     |
| DL2           | Drainage     | ND  | ND              | ND              | 0.4                                   | ND                                    | 0.4     |
| DR4           | Drainage     | 0.5 | 3.3             | 0.1             | 2.4                                   | ND                                    | 6.2     |
| DR5           | Drainage     | 0.7 | 3.2             | ND              | 2.6                                   | 0.7                                   | 7.2     |
| DR6           | Drainage     | 6.1 | 93.6            | 7.3             | 375.3                                 | 4.7                                   | 487.1   |
| DL3           | Open channel | ND  | ND              | ND              | 1.1                                   | 0.6                                   | 1.7     |
| DR7           | Brook        | 0.3 | 1.2             | ND              | 1.7                                   | 1.5                                   | 4.8     |
| Output        |              |     |                 |                 |                                       |                                       |         |
| Site 2        | River        | 7.0 | 21.2            | 0.9             | 24.5                                  | 1.0                                   | 54.6    |

Unit: nM/L

\*T-NPCs: NP + NP*n*EOs (*n* = 1–15) + NP*m*ECs (*m* = 1–10).

\*\*ND denotes not detected and is set to zero for T-NPCs concentration. Detection limits for NP, NP1EO+NP2EO, NP1EC+NP2EC, NP*n*EOs (*n* = 3–15), and NP*m*ECs (*m* = 3–10) are 0.3, 0.3, 0.1, 0.2, and 0.6 nM/L, respectively.

detected, and its value was nine times higher than that at Site 2. T-NPCs concentrations at DR1–7 (except for DR6) were in the range of 1.6 to 12.6 nM/L and only that at DR3 was lower than that at Site 1. T-NPCs concentrations at DL1–3 ranged from 0.4 to 1.7 nM/L.

Individual nonylphenolic compounds were classified into five groups: NP, NP1EO + NP2EO, NP1EC + NP2EC, NP*n*EOs (*n* = 3–15), and NP*m*ECs (*m* = 3–10). NP concentrations at Sites 1 and 2 were 0.4 and 7.0 nM/L, respectively. NP concentrations at DL1–3 were below the detection limit (<0.3 nM/L), and those at DR1–7 ranged from not detected (ND) to 6.1 nM/L. NP concentrations at Site 2 and DR6 exceeded 1 µg/L (4.5 nM/L); however, their levels were not very different from those of the other water samples.

The NP1EO+NP2EO concentrations in river water increased from 1.2 nM/L at Site 1 to 21.2 nM/L at Site 2, and the NP*n*EOs (*n* = 3–15) concentration also increased from 2.5 nM/L at Site 1 to 24.5 nM/L at Site 2. The concentrations of NP1EO+NP2EO and NP*n*EOs (*n* = 3–15) at DR6 were 93.6 and 375.3 nM/L, respectively, and were the highest among the samples. On the other hand, those at DR1–7 (except for DR6) and DL1–3 ranged from ND (<0.3 nM/L) to 6.3 nM/L and from 0.3 to 4.3 nM/L, respectively.

The NP1EC+NP2EC concentrations at Sites 1 and 2 were 0.4 and 0.9 nM/L, respectively. These compounds were detected from four inflow waters out of 10 inflow waters, and the maximum concentration was 7.3 nM/L at DR6. NP*m*EC (*m* = 3–10) concentrations at Sites 1 and 2 were ND (<0.6 nM/L) and 1.0 nM/L, respectively. The concentration was detected from six inflow waters out of 10 inflow waters, and the maximum concentration was 4.7 nM/L at DR6.

### 3.3 Oligomer profile of nonylphenolic compounds in concentration ratio

Figure 3 shows the distribution patterns in concentration ratio for oligomers of nonylphenolic compounds at DR6 and Site 2. The concentration ratio denotes the ratio of the concentration of individual nonylphenolic compounds to T-NPCs. The NP2EO ratio at DR6 was the largest. The concentration ratio decreased largely according to the increase in the EO unit until NP6EO, and presented a weak peak at NP8EO and NP9EO. Although the NP2EC ratio was the largest among NP $m$ ECs ( $m = 1-10$ ), it was only 1.4%. On the other hand, the distribution pattern at Site 2 presented a peak at NP1EO, and also showed high concentration ratios of NP, NP2EO, and NP3EO. The concentration ratios of NP $n$ EOs with long EO chains ( $n \geq 4$ ) at Site 2 were clearly lower than that at DR6. As for the distribution patterns of Site 2 and DR6, the concentration ratios of NP and NP1EO were much higher at Site 2 than that at DR6.

### 3.4 Mass flow of nonylphenolic compounds and chloride ion

The mass flows of T-NPCs and Cl<sup>-</sup> in the river and its inflow channels are summarized in Table 3. The mass flows at Site 1 and the outlets of the inflow channels were defined as 'Input', and that at Site 2 was defined as 'Output'. Input and Output of T-NPCs were 458.0 and 828.2 mM/day, respectively. The percentage of Output was approximately 180% of Input. The mass flow at DR6 was the highest and comprised 82.4% of Input. The mass flows at Site 1, DR2, and DR4 were higher than those at the other places, but ranged from 4.1 to 4.8%. Only 0.5% of Input was observed in the mass flows at DL1–3 in the left basin.

To examine the mass balance of T-NPCs, the mass flows of Cl<sup>-</sup>, a highly conserved substance in water, was calculated. The mass flows of Cl<sup>-</sup> in Input and Output were 480.9 and 664.1 g/day, respectively. The percentage of Output was approximately 140% of Input. Each water sample was taken at one point and once at

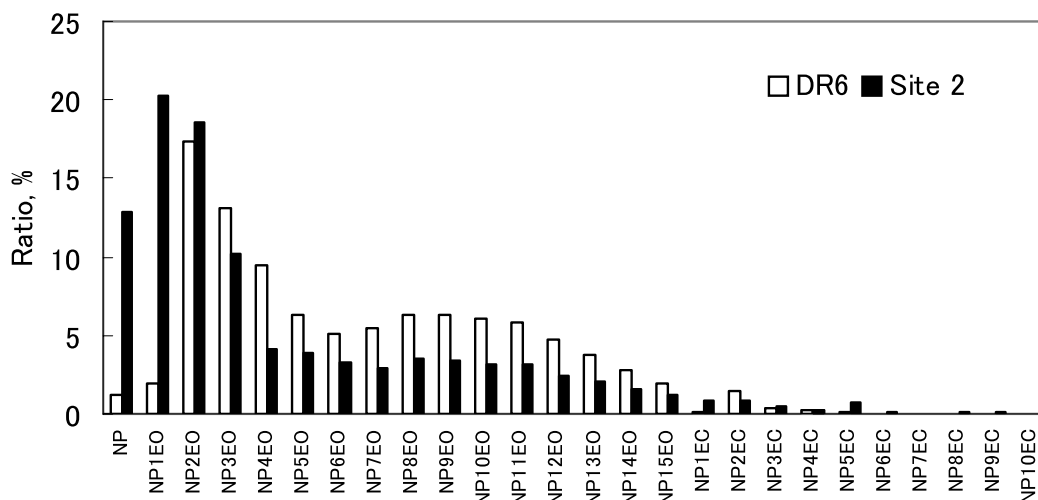


Fig. 3. Oligomer profiles in concentration ratio of nonylphenolic compounds in the waters at DR6 and Site 2.

The concentration ratio denotes the ratio of concentration of individual nonylphenolic compounds to T-NPCs. The oligomer profile of nonylphenolic compounds in the river water at Site 2 seemed to shift to NP and NP $n$ EOs with short EO chains as compared with that in the inflow water at DR6.

Table 3  
Mass flow of nonylphenolic compounds and chloride ion in the water of the Kamo River and its inflow channels.

| Sampling site | Distance from Site 1 (km) | Flow rate (m <sup>3</sup> /sec) | T-NPCs*            |                       | Chloride ion (Cl <sup>-</sup> ) |                     |
|---------------|---------------------------|---------------------------------|--------------------|-----------------------|---------------------------------|---------------------|
|               |                           |                                 | Mass flow (mM/day) | Mass flow ratio** (%) | Mass flow (g/day)               | Mass flow ratio (%) |
| <b>Input</b>  |                           |                                 |                    |                       |                                 |                     |
| Site 1        | 0.0                       | 0.0470                          | 18.6               | 4.1                   | 71.5                            | 14.9                |
| DR1           | 0.9                       | 0.0002                          | 0.1                | 0.0                   | 0.6                             | 0.1                 |
| DL1           | 0.9                       | 0.0143                          | 1.2                | 0.3                   | 8.9                             | 1.8                 |
| DR2           | 1.6                       | 0.0185                          | 20.0               | 4.4                   | 15.6                            | 3.2                 |
| DR3           | 2.0                       | 0.0110                          | 1.5                | 0.3                   | 13.2                            | 2.7                 |
| DL2           | 2.6                       | 0.0049                          | 0.2                | 0.0                   | 4.1                             | 0.8                 |
| DR4           | 2.8                       | 0.0407                          | 22.0               | 4.8                   | 223.4                           | 46.5                |
| DR5           | 3.7                       | 0.0187                          | 11.6               | 2.5                   | 54.8                            | 11.4                |
| DR6           | 4.4                       | 0.0090                          | 377.2              | 82.4                  | 10.7                            | 2.2                 |
| DL3           | 4.8                       | 0.0050                          | 0.7                | 0.2                   | 6.4                             | 1.3                 |
| DR7           | 4.8                       | 0.0118                          | 4.9                | 1.1                   | 71.8                            | 14.9                |
| Total input   | —                         | 0.1810                          | 458.0              | 100.0                 | 480.9                           | 100.0               |
| <b>Output</b> |                           |                                 |                    |                       |                                 |                     |
| Site 2        | 5.6                       | 0.1755                          | 828.2              | 180.8                 | 664.1                           | 138.1               |

\*T-NPCs: NP + NP $n$ EOs ( $n = 1-15$ ) + NP $m$ ECs ( $m = 1-10$ ).

\*\*Mass flow ratio: Individual input / Total input.

each place, and the time of flow was not considered for the sampling of river waters. These factors might cause differences in the mass flows of Cl<sup>-</sup>. Although this matter was considered, it can be concluded that the mass flow of T-NPCs in Output was higher than that in Input.

Figure 4 shows the mass flow of each nonylphenolic compound in Input (DR6), Input (Others) and Output. The mass flows of NP, NP1EO, NP2EO, and NP3EO in Input were 11.7, 24.3, 78.3, and 53.1 mM/day, and the corresponding mass flows of Output were 106.7, 167.6, 154.0, and 84.0 mM/day, respectively. The ratios of Output to Input in the mass flows of these compounds were 9.1, 6.9, 2.0, and 1.6. Input of the other nonylphenolic compounds agreed well with Output. Moreover, the mass flows of NP $n$ EOs ( $n = 2-15$ ) at DR6 were predominant in Input.

## 4. Discussion

### 4.1 Sources of nonylphenolic compounds in the Kamo River

According to the mass balance study, the mass flow of nonylphenolic compounds at DR6 contributed significantly to the increase in those compounds at Site 2 in the Kamo River. However, the inflow waters at DR1, DR4, DR5, and DR7, which mainly consisted of domestic wastewater, also contributed to Input by 8.4% in total. Because an industry-level self-regulation has banned the household use of NP $n$ EOs from 1998 in Japan, it was suggested that a small but non-negligible amount of the pollutants was contributed by the use of some products that contained NP $n$ EOs, such as imported detergents, cosmetics, and spreading agents for pesticides.<sup>(3)</sup>



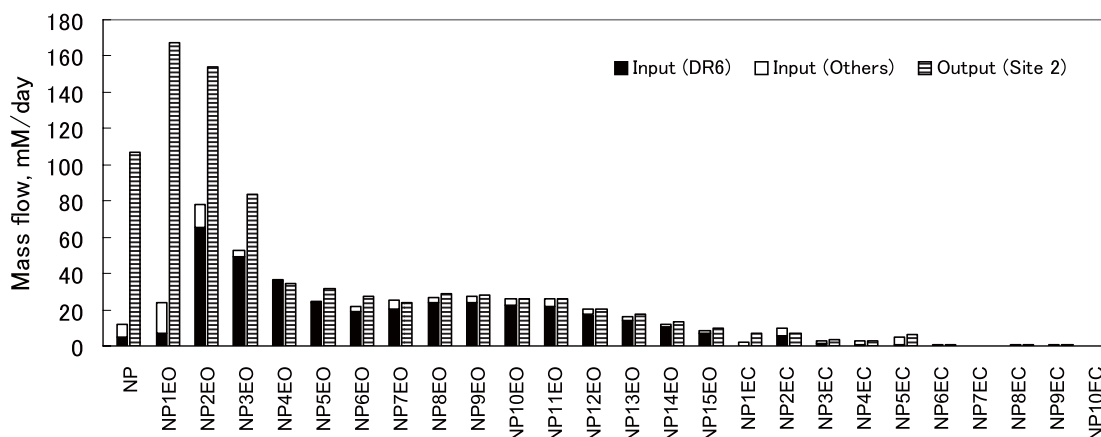


Fig. 4. Mass flow of nonylphenolic compounds in Input and Output.

Input (others) denotes the sum of nonylphenolic compounds in the water at Site 1, DR1–5, DR7, and DL1–3. Although Inputs of NP $n$ EOs ( $n = 4–15$ ) agreed well with Output, those of NP, NP1EO, NP2EO, and NP3EO were much lower than those of Output.

#### 4.2 Oligomer pattern

The oligomer pattern of nonylphenolic compounds in the factory effluent shown in Fig. 2 was similar to that of NP $n$ EOs frequently used for industrial purposes, which has a peak at around NP9EO. This indicates that the wastewater of the factory was not or poorly treated. The oligomer pattern at DR6 seemed to be shifted to NP $n$ EOs with short EO chains as compared with that of the factory effluent. This phenomenon might be attributed to the microbiological transformation of NP $n$ EOs under aerobic conditions.<sup>(20,21)</sup> On the other hand, the oligomer pattern at Site 2 had a peak at NP1EO and was distinctly different from the pattern at DR6. It is concluded that the oligomer pattern of nonylphenolic compounds at Site 2 was not attributable to only the dilution effect of the inflow water at DR6.

#### 4.3 Mass balance of nonylphenolic compounds

Ahel *et al.* performed a mass balance study of NP, NP $n$ EOs ( $n = 1–20$ ), and NP $m$ ECs ( $m = 1–2$ ) in the Glatt River in Switzerland.<sup>(10)</sup> They found that the mass flow of total nonylphenolic compounds in Output (the amount at the downstream of the river) decreased by 24% compared to that in Input (the amount at the uppermost stream of the river and in the secondary effluents from nine STPs located in the river basin). The component ratio of NP $m$ ECs ( $m = 1–2$ ) to total nonylphenolic compounds was 51% in Input and was increased to 85% in Output. These findings suggested that some part of NP $n$ EOs with longer EO chains was transformed into NP1EC and NP2EC in the river.

In contrast, NP1EC and NP2EC concentrations were not considerably increased at Site 2 in our survey. This difference could be attributable to the fact that the microbiological transformation to NP $m$ ECs from their precursors has been accelerated in the Glatt River, because their investigation was conducted during the warm season and the surveyed length of the river was long (35 km). Regarding the temperature effects on the microbiological transformation of nonylphenolic compounds, it was reported that the ultimate biodegradation rate of NP is accelerated more by warm temperature than by the cold condition in water, sediment, activated sludge, and soil,<sup>(22–25)</sup> low temperature decreased the shortening velocity of the EO chain of NP $n$ EOs.<sup>(20,21)</sup>

As described in §3.4, the mass flow of nonylphenolic compounds in Output was 1.8 times higher than that in Input in our survey. In comparison with the mass flow of Cl<sup>-</sup>, a most conserved substance, the mass flows of nonylphenolic compounds in Output were much higher than those in Input. Moreover, the mass flows of NP $n$ EOs with short EO chains were high.

In general, river sediment contains a higher proportion of hydrophobic compounds such as NP, NP1EO, and NP2EO than the other nonylphenolic compounds.<sup>(10,26)</sup> In our previous study, we also detected high seasonal average concentrations of NP (5,200 µg/kg dw), NP1EO (3,600 µg/kg dw), and NP2EO (630 µg/kg dw) in river sediments at Site 2.<sup>(19)</sup> Moreover, the concentration ratios on a molar basis of these three compounds to T-NPCs were 54.5% for NP, 36.3% for NP1EO, and 5.8% for NP2EO.

Düring *et al.* showed that a part of the NP initially adsorbed to the soil was released to the water layer under the given experimental conditions.<sup>(27)</sup> It was suggested that the excesses in the mass flows of NP, NP1EO, and NP2EO at Site 2 originated from river sediments by the sediment-water partitioning and the disturbance of sediments. A preliminary experiment supports this suggestion as shown in §4.4.

#### 4.4 Elution of nonylphenolic compounds from sediment

To know the possibility of the elution of nonylphenolic compounds from river sediment, we conducted a simple experiment. The sediment was collected at the Kamo River near by DR6 in September 2004 and stored at -20°C until use. Approximately 20 g of the wet sediment was placed in a 100-ml glass centrifuge test tube, and centrifuged at 3,000 rpm for 10 min. The supernatant was discarded, and the residue was placed into a 500-ml glass bottle. Then, 200 ml of pure water was poured into the bottle. The mixture in the bottle was transferred to four glass centrifuged tubes within a minute, and these tubes were centrifuged at 3,000 rpm for 10 min. The supernatant and the residue in each tube were combined to make a water sample and a residue sample, respectively. This whole procedure was performed in duplicate.

The concentrations of nonylphenolic compounds in the water sample and the residue sample were determined according to the methods described in our previous study.<sup>(19)</sup> Figure 5 shows the average concentrations of nonylphenolic compounds in the samples. The average concentrations of NP, NP1EO, NP2EO, and NP3EO in two residue samples were 31,000, 2,000, 860, and 240 µg/kg dw, respectively. The average concentrations of NP, NP1EO, NP2EO, and NP3EO in two water samples were 18, 1.6, 0.76, and 0.18 µg/L, respectively.

These results suggest that NP and nonylphenolic compounds with short EO chains might be supplied from the sediment to the river water even by the slight disturbance of the sediment. NP concentration was the maximum among the nonylphenolic compounds in the water sample, and 3.1 µg/L of NP2EC was also detected in the sample. According to this result, the mass flow of NP2EC in Output must be higher than those in Input. However, the apparent excess of mass flow was not observed (Fig. 4). At this moment, the reason of this matter is not clear. Further investigation is required concerning the transport of nonylphenolic compounds in the sediment-water system.

## 5. Conclusion

In our previous study, seasonal changes in nonylphenolic compounds in the water and sediment were investigated in the Kamo River whose water and sediment had been found to be polluted with NP. A river section in which nonylphenolic compounds increased considerably was identified, and in a subsequent survey, we found that the major pollution source was a rubber product manufacturing factory. In this paper, a mass balance study of nonylphenolic compounds in this river section was

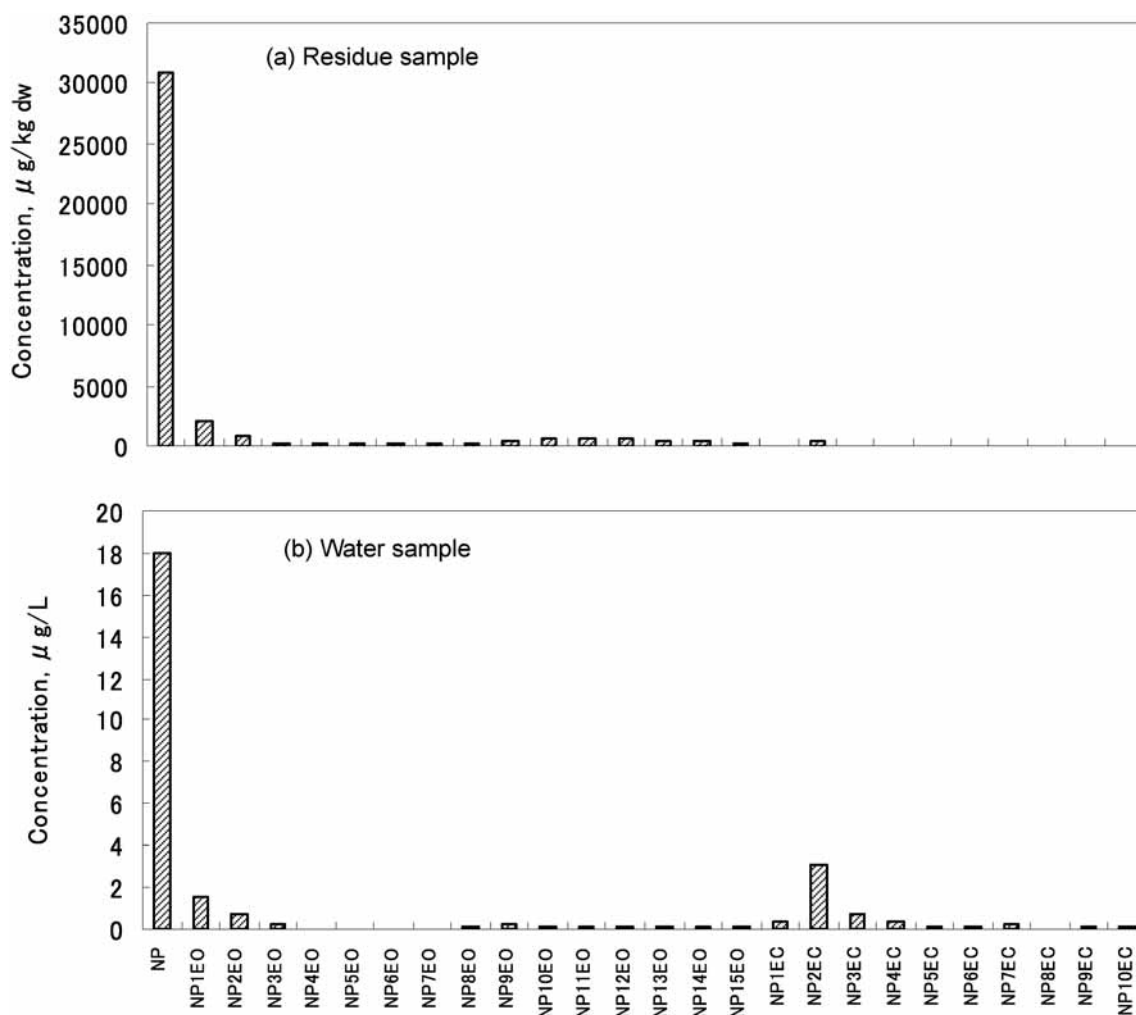


Fig. 5. Elution of nonylphenolic compounds from (a) the residue sample to (b) the water sample.

carried out to clarify the contribution of this pollution source to the river pollution. The results are summarized as follows.

- (1) T-NPCs concentrations in the water at the upstream (Site 1) and the downstream (Site 2) of the river were 4.6 and 54.6 nM/L, respectively. Those in the waters at the outlets of 10 inflow channels ranged from 0.4 to 487.1 nM/L. In particular, the T-NPCs concentration at DR6 was the highest and approximately ninefold higher than that at Site 2.
- (2) The oligomer pattern of nonylphenolic compounds in the drainage water at DR6 seemed to be shifted to NP $n$ EOs with short EO chains as compared with that in the effluent of the factory which locates at the upstream of DR6.
- (3) The mass flows of T-NPCs in Input and Output were 458.0 and 828.8 mM/day, respectively. The latter was 1.8-fold higher than the former. Moreover, the mass flow at DR6 comprised 82.4% of Input.
- (4) In comparison with the mass balance of Cl<sup>-</sup>, a conserved substance in the water environment, the mass flow of T-NPCs in Output was still higher than that in Input. This phenomenon could be attributed to the high mass flows of NP and NP $n$ EOs ( $n = 1-3$ ) in Output. It was suggested that these compounds might originate from the sediment to the river water by the disturbance of the sediment and the sediment-water partitioning.

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### References

- 1 Ahel, M., Giger, W. and Koch, M. (1994): Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment — I. Occurrence and transformation in sewage treatment. *Water Res.* **28**: 1131–1142.
- 2 Barber, L.B., Brown, G.K. and Zaugg, S.D. (2000): Potential endocrine disrupting organic chemicals in treated municipal wastewater and river water. *ACS Symp. Ser. (Am. Chem. Soc.)* **747**: 97–123.
- 3 Ministry of the Environment of Japan (2005): *FY2004 Edition of Chemical Substance Fact Sheets*. pp. 315–318. (in Japanese).
- 4 Ying, G.G., Williams, B. and Kookana, R. (2002): Environmental fate of alkylphenols and alkylphenol ethoxylates — a review. *Environ. Int.* **28**: 215–226.
- 5 Renner, R. (1997): European bans on surfactant trigger transatlantic debate. *Environ. Sci. Technol.* **31**: 316A–320A.
- 6 Giger, W., Brunner, P.H. and Schaffner, C. (1984): 4-Nonylphenol in sewage sludge: accumulation of toxic metabolites from nonionic surfactants. *Science* **225**: 623–625.
- 7 Tanaka, H., Sato, C., Komori, K., Yakou, Y., Tamamoto, H., Miyamoto, N. and Higashitani, T. (2003): Occurrence of endocrine disruptors in sewage and their behavior in sewage treatment plants in Japan. *Environ. Sci.* **10**: 1–24.
- 8 Lee, H.-B. and Peart, T.E. (1998): Occurrence and elimination of nonylphenol ethoxylates and metabolites in municipal wastewater and effluents. *Water Qual. Res. J. Canada* **33**: 389–402.
- 9 Fujita, M., Ike, M., Mori, K., Kaku, H., Sakaguchi, Y., Asano, M., Maki, H. and Nishihara, T. (2000): Behaviour of nonylphenol ethoxylates in sewage treatment plants in Japan – biotransformation and ecotoxicity. *Water Sci. Technol.* **42**: 23–30.
- 10 Ahel, M., Giger, W. and Schaffner, C. (1994): Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment — II. Occurrence and transformation in rivers. *Water Res.* **28**: 1143–1152.
- 11 Yoshimura, K. (1986): Biodegradation and fish toxicity of nonionic surfactants. *J. Am. Oil Chem. Soc.* **63**: 1590–1596.
- 12 Jobling, S., Sheahan, D., Osborne, J.A., Matthiessen, P. and Sumpter, J.P. (1996): Inhibition of testicular growth in rainbow trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals. *Environ. Toxicol. Chem.* **15**: 194–202.
- 13 Gray, M.A. and Metcalfe, C.D. (1997): Induction of testis-ova in Japanese medaka (*Oryzias latipes*) exposed to *p*-nonylphenol. *Environ. Toxicol. Chem.* **16**: 1082–1086.
- 14 Tabata, A., Kashiwada, S., Ohnishi, Y., Ishikawa, H., Miyamoto, N., Itoh, M. and Magara, Y. (2001): Estrogenic influences of estradiol-17 $\beta$ , *p*-nonylphenol and bis-phenol-A on Japanese medaka (*Oryzias latipes*) at detected environmental concentrations. *Water Sci. Technol.* **43**: 109–116.
- 15 Patrolecco, L., Capri, S., De Angelis, S., Pagnotta, R., Polesello, S. and Valsecchi, S. (2006): Partition of nonylphenol and related compounds among different aquatic compartments in Tiber River (central Italy). *Water Air Soil Poll.* **172**: 151–166.
- 16 Isobe, T., Nishiyama, H., Nakashima, A. and Takada, H. (2001): Distribution and behavior of nonylphenol, octylphenol, and nonylphenol monoethoxylate in Tokyo Metropolitan area: Their association with aquatic particles and sedimentary distributions. *Environ. Sci. Technol.* **35**: 1041–1049.
- 17 Isobe, T. and Takada, H. (2004): Determination of degradation products of alkylphenol polyethoxylates in municipal wastewaters and rivers in Tokyo, Japan. *Environ. Toxicol. Chem.* **23**: 599–605.
- 18 Tsuda, T., Takino, A., Kojima, M., Harada, H., Muraki, K. and Tsuji, M. (2000): 4-Nonylphenols and 4-*tert*-octylphenol in water and fish from rivers flowing into Lake Biwa. *Chemosphere* **41**: 757–762.

- 19 Motegi, M., Nojiri, K., Hosono, S. and Kawamura, K. (2007): Seasonal changes in nonylphenol ethoxylates and their metabolites in water and sediment of urban river polluted by nonylphenol. *Environ. Sci.* **14**: 109–128.
- 20 Manzano, M.A., Perales, J.A., Sales, D. and Quiroga, J.M. (1999): The effect of temperature on the biodegradation of a nonylphenol polyethoxylate in river water. *Water Res.* **33**: 2593–2600.
- 21 Maruyama, K., Yuan, M. and Otsuki, A. (2000): Seasonal changes in ethylene oxide chain length of poly (oxyethylene) alkylphenyl ether nonionic surfactants in three main rivers in Tokyo. *Environ. Sci. Technol.* **34**: 343–348.
- 22 Topp, E. and Starratt, A. (2000): Rapid mineralization of the endocrine-disrupting chemical 4-nonylphenol in soil. *Environ. Toxicol. Chem.* **19**: 313–318.
- 23 Ekelund, R., Granmo, Å., Magnusson, K., Berggren, M. and Bergman, Å. (1993): Biodegradation of 4-nonylphenol in seawater and sediment. *Environ. Poll.* **79**: 59–61.
- 24 Tanghe, T., Devriese, G. and Verstraete, W. (1998): Nonylphenol degradation in lab scale activated sludge units is temperature dependent. *Water Res.* **32**: 2889–2896.
- 25 Chang, B.V., Yu, C.H. and Yuan, S.Y. (2004): Degradation of nonylphenol by anaerobic microorganisms from river sediment. *Chemosphere* **55**: 493–500.
- 26 Rice, C.P., Schmitz-Afonso, I., Loyo-Rosales, J.E., Link, E., Thoma, R., Fay, L., Altfater, D. and Camp, M.J., (2003): Alkylphenol and alkylphenol- ethoxylates in carp, water, and sediment from the Cuyahoga River, Ohio. *Environ. Sci. Technol.* **37**: 3747–3754.
- 27 Düring, R.-A., Krahe, S. and Gäth, S. (2002): Sorption behavior of nonylphenol in terrestrial soils. *Environ. Sci. Technol.* **36**: 4052–4057.