# Alkylphenol Ethoxylates in the Environment[1]

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**A comprehensive monitoring study, sponsored by the Chemical Manufacturers Association and designed in cooperation with the Environmental Protection Agency (EPA), measured the levels of nonylphenol (NP) and its ethoxylates (NPE) in 30 rivers. The sites, all receiving municipal or industrial wastewater, were selected at random from EPA's United States river reach database by a statistical procedure. Water column and bottom sediment samples were collected along a perpendicular transect at each site. All samples were assayed for NP and $NPE_1$, and the higher ethoxylates ($NPE_2$ to $NPE_{17}$) were determined in the water samples. Analysis was by high-performance liquid chromatography (HPLC) with fluorescence detection of microgram quantities of NPE obtained by extractive steam distillation (NP and $NPE_1$) or a dual-column extraction procedure ($NPE_2$ to $NPE_{17}$). Sample collection and analytical procedures were validated according to rigorous EPA guidelines, and quality assurance standards were met throughout the study. NP and NPE concentrations in river water were mostly (60 to 75% of the samples) below their detection limits (about 0.1 ppb for NP, $NPE_1$, and $NPE_2$; 1.6 ppb for $NPE_{3-17}$). The highest levels found were about 1 ppb for NP, $NPE_1$, and $NPE_2$, 15 ppb for $NPE_{3-17}$. A majority of sediment samples contained detectable amounts of NP and $NPE_1$, ranging up to 3000 ppb for NP and 170 ppb for $NPE_1$. Sediment interstitial water concentrations of NP were estimated to be similar to concentrations in the water column.**

KEY WORDS: Alkylphenol, Chemical Manufacturers Association, environment, ethoxylate, nonylphenol, quality assurance, riverwater, wastewater, sediment.

Alkylphenol ethoxylates (APE) have been widely used in industrial processing and in household and institutional cleaning products for more than forty years. They remain one of the largest volume groups of surfactants; production in the United States (U.S.) exceeded 450 million pounds in 1990 (1). The major APE surfactants are the nonylphenol ethoxylates (NPE). They have attracted a great deal of attention and created controversy because of potential adverse environmental effects. The highly branched nonyl group and the phenol ring of nonylphenol, which comprise the hydrophobic portion of NPE, have been shown in many studies to have only low to moderate biodegradability (2). A number of studies have reported increased amounts of short-chain ethoxylates, which are demonstrably more acutely toxic to aquatic organisms than longer-chain ethoxylates (2 and Oak Ridge National Laboratory, manuscript in preparation).

Detection of nonylphenol and its lower ethoxylates in treated wastewater sludges, river waters and sediments in Europe led to their removal from cleaning products (3,4) and to the publication of a Chemical Hazard Information Profile by the U.S. Environmental Protection Agency (5). Such concerns prompted the U.S. producers of nonylphenol and NPE to organize a research effort under sponsorship of the Chemical Manufacturers Association's Panel on Alkylphenol and Ethoxylates beginning in 1987. The first of a series of research studies initiated by the APE Panel is described here. It is a comprehensive analytical monitoring effort of thirty river sites for trace levels of NP and NPE. The sites were selected, based on random selection criteria, from the U.S. EPA river reach database. A large number of sites were chosen by randomization procedures to allow the survey results to be projected across the entire U.S. with a high degree of confidence. The environmental exposure profile of NP and NPE that emerged will be used in future papers to calculate quantitative risk assessments.

To ensure the reliability of the results, EPA guidelines for quality assurance were followed throughout the analytical method validation, sample collection and handling, and analysis phases of the project.

## EXPERIMENTAL PROCEDURES

*Method validation.* Each aspect of the analytical procedures (6), including chromatography by HPLC/fluorescence detection, was validated for precision and accuracy before sample collection began. They included:

*(i) Determination of method detection limits (MDL) of NP and NPE in water and sediment.* Method detection limits were determined for NP, $NPE_1$, $NPE_2$, and $NPE_{3-17}$ by a U.S. Environmental Protection Agency-approved methodology for determination of detection limits (7). The MDL studies consisted of spiking seven replicates at a level within a factor of 10 of the estimated MDL and extracting and analyzing the samples. In this manner, the effect of sample container, extraction method, extract concentration, background concentration, and analytical techniques on the MDL could be determined. Four unspiked water samples were also analyzed to determine the blank levels.

*(ii) Extraction and analysis of NP and $NPE_1$.* The extractive steam distillation method (8,9) was employed on water and sediment for isolation of NP and $NPE_1$. A standard NP-NPE blend (6) was used, after its purity was confirmed, for spiking lab water (deionized, Milli-Q System) and clean sandy soil (surrogate for river sediment). Table 1 summarizes the results of the recovery experiments. Table 2 gives the method detection limits calculated from the blank and spiking data (7) according to the formula in the table title.

*(iii) Extraction and analysis of $NPE_{2-17}$.* The dual-column method (5) was used for isolating $NPE_{2-17}$ from water. To obtain consistently low method blanks and high

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**TABLE 1**

**Validation of Nonylphenol Ethoxylate Analytical Methods**

| Spike dose µg/L | NP (conc. found, µg/L) | % Recovery | % Recovery (corrected for Blank) | SD | $NPE_1$ (conc. found, µg/L) | % Recovery | % Recovery (corrected for Blank) | SD |
|---|---|---|---|---|---|---|---|---|
| Blank[a] | 0.07 | | | 0.015 | 0.03 | | | 0.03 |
| 0.03 | 0.06 | 209 | 0 | 0.016 | 0.03 | 114 | 0 | 0.022 |
| 0.15 | 0.14 | 96 | 55 | 0.016 | 0.12 | 80 | 64 | 0.022 |
| 0.30 | 0.24 | 80 | 57 | 0.032 | 0.22 | 75 | 65 | 0.035 |
| Blank[b] | 0.07 | | | 0.018 | 0.02 | | | 0.03 |
| 0.09 | 0.13 | 142 | 64 | 0.028 | 0.10 | 106 | 72 | 0.019 |
| 0.18 | 0.17 | 96 | 57 | 0.021 | 0.17 | 93 | 76 | 0.028 |
| 0.30 | 0.25 | 82 | 59 | 0.030 | 0.25 | 86 | 76 | 0.034 |
| Blank (9)[c] | 0.28[d] | | | | | | | |
| 2.82 (5) | 2.67 | 91 | 84 | 0.31 | | | | |
| 5.64 (5) | 4.84 | 85 | 80 | 0.38 | | | | |
| 9.40 (3) | 8.92 | 90 | 91 | 0.38 | | | | |

[a] Steam extractive distillation method for NP and $NPE_1$; water (Milli-Q) (5 replicates at each dose level).

[b] Steam extractive distillation method for NP and $NPE_1$; sediment (sandy soil) (4 replicates at each dose level).

[c] Dual-column extraction method for $NPE_{2-17}$; water (Milli-Q) (number of replicates given in parentheses).

[d] This number represents µg/L of the total of $NPE_{2-17}$.

**TABLE 2**

**Method Detection Limits**

| Species in medium | Blank, µg/L (4 replicates) | Spike, µg/L (6 to 8 replicates) | SD | MDL[a] (µg/L) |
|---|---|---|---|---|
| NP in water | 0.057 | 0.15 | 0.016 | 0.107 |
| NP in sediment | 0.07 | 0.18, 0.30 | 0.026 | 2.93 |
| NP-1EO in water | 0.017 | 0.15 | 0.016 | 0.067 |
| NP-1EO in sediment | 0.02 | 0.18, 0.30 | 0.031 | 2.26 |
| NP-2EO in water | 0.0 | 0.15 | 0.02 | 0.063 |
| NP-3-17EO in water | 0.11 | 4.55 | 0.47 | 1.58 |

[a] Method detection limit = SD × $t$ + Blank where $t$ = Student's $t$ for 7 replicates, 99% confidence limit = 3.143.

spike recoveries, some new modifications were necessary. These included washing the ion-exchange resin with high-purity methanol prior to use and nitric acid scouring and silanizing of all glassware between runs. The standard NPE blend in lab water was used for determining spike recoveries and method detection limits. Tables 1 and 2 summarize the results. $NPE_2$ was quantitated separately from the aggregate $NPE_{3-17}$.

*(iv) Storage stability of samples.* A set of spiked river water samples (water collected from the Colorado River in Austin, Texas, at Redbud Trail Bridge) were preserved with or without 1% formalin, then stored at 4°C. Sandy soil was used as a surrogate for river sediment. Spiked soil samples were kept frozen at −15°C to −20°C without formalin. Table 3 lists the results of the 4-wk preservation study. After 2 wk, there was a clear deterioration of both water and sediment samples. The use of formalin appeared to protect sample integrity during storage.

These results were used to design a sampling protocol, which specified river water samples to be formalin-treated and to be extracted within 2 wk of collection. The extracts were analyzed by HPLC as soon as possible, usually within one day. The maximum holding time was 14 days. Prior to analysis the extracts were stored in the freezer.

*Site selection procedures.* The river reach file maintained by the U.S. EPA was used to design a statistically valid sampling plan. It was considered an appropriate source for selection of sampling sites because most major U.S. rivers are included, the rivers are divided into discrete reaches defined by branch points, and the file is conducive to random sampling. There are over 68,000 entries in the file. Because a key objective of the study was to identify river reaches most likely to contain measurable concentrations of NP and NPE, the sites were selected from those reaches with known effluent discharges, either from wastewater treatment plants or industries expected to be using NPE. After excluding reaches without effluents, nonflowing sites, lakes and estuaries, and sites without proper flow records, 5,000 reaches remained. These remaining reaches were divided into three categories: i) having identified industrial wastewater effluents; ii) having a biologically treated wastewater effluent with less than the medium dilution factor (*i.e.,* small rivers); and iii) having one or more treated effluents with greater than the medium dilution factor (*i.e.,* large rivers).

A table of binomial tail probabilities (not shown) was prepared to calculate the number of samples needed to support the hypothesis that if no "high concentration"

**TABLE 3**

**Sample Preservation Studies**

| Time (wk) | NP (Blank, μg/L) | Recovery, %, uncorrected (spike = 0.3 μg/L) | $NPE_1$ (Blank, μg/L) | Recovery, %, uncorrected (spike = 0.3 μg/L) |
|---|---|---|---|---|
| NP and $NPE_1$ in river water; no preservative added; stored at 4°C | | | | |
| 0 | 0.048 | 72 | 0.015 | 63 |
| 1 | 0.040 | 80 | 0.014 | 75 |
| 2 | 0.010 | 71 | 0.01 | 71 |
| 3 | 0.021 | 45 | 0.034 | 32 |
| 4 | 0.020 | 69 | 0.005 | 66 |
| NP and $NPE_1$ in river water; formalin, 1%, added; stored at 4°C | | | | |
| 0 | 0.035 | 67 | 0.008 | 70 |
| 1 | 0.060 | 72 | 0.02 | 74 |
| 2 | 0.030 | 79 | 0.02 | 72 |
| 3 | 0.030 | 57 | 0.01 | 65 |
| 4 | 0.020 | 62 | 0.01 | 65 |
| NP and $NPE_1$ in sediment; no preservative added; stored at −15°C | | | | |
| 0 | 0.10 | 95 | 0.05 | 92 |
| 1 | 0.06 | 97 | 0.01 | 97 |
| 2 | 0.098 | 104 | 0.111 | 99 |
| 3 | 0.07 | 42 | 0.013 | 25 |
| 4 | n.d.[a] | 36 | n.d. | 31 |

| Time (wk) | $NPE_2$ (Blank, μg/L) | Recovery, %, uncorrected (spike = 0.3 μg/L) | $NPE_{3-17}$ (Blank, μg/L) | Recovery, %, uncorrected (spike = 9.1 μg/L) |
|---|---|---|---|---|
| $NPE_2$ and $NPE_{3-17}$ in river water; no preservative added; stored at 4°C | | | | |
| 0 | | 102 | | 67 |
| 1 | | 125 | | 78 |
| 2 | | 96 | | 68 |
| 3 | | 43 | | 45 |
| 4 | | 37 | | 20 |
| $NPE_2$ and $NPE_{3-17}$ in river water; formalin, 1%, added; stored at 4°C | | | | |
| 0 | 0.13 | 99 | 0.47 | 75 |
| 1 | n.d.[a] | 114 | 2.13 | 77 |
| 2 | 0.09 | 78 | 0.13 | 72 |
| 3 | 0.09 | 62 | 0.04 | 64 |
| 4 | 0.09 | 57 | 0.85 | 56 |

[a]None detected.

sites were found in the survey, it can be stated with 95% confidence that no more than 10% of the universe of U.S. river reach sites with discharges will have "high" values. To achieve this level of confidence, the probability table indicated that 29 sites needed to be examined. If one "high" value were to emerge in these 29 sites, confidence would drop to 80%. Therefore, 30 sites plus a number of alternate sites were chosen for this monitoring project. Sites were selected from the three categories in the same proportion as the three categories occur in the constrained river reach file: 5 from category 1, 14 from category 2, and 11 from category 3. It should be emphasized that the reaches sampled represent a subset of locations where NP and NPE were considered most likely to occur. The results do not reflect the condition of all waters of the U.S. Rather, the results are intended to allow statistically valid characterization of the upper range of environmental NP concentrations in U.S. rivers.

The list of the sample sites and water quality parameters at each site are given in Table 4. Gaps in the site numbering sequences are due to rejection of sites because they did not meet the initial criteria, or because on-site inspection found the rivers to have sediment that could not be sampled.

*Sample collection.* A general description of the sampling procedures used at each of the 30 river sites sampled for the survey is given here. In-depth details are provided in the program protocols (10). At each site, the location of the pertinent industrial and municipal wastewater discharges was determined, and whenever possible, local officials were interviewed in advance to complete an information checklist.

Samples of river water and sediment were taken along a transect across the mainstream flow at 1/4, 1/2 and 3/4 of the distance across the river (Stations 1, 2, and 3, respectively) as measured from left to right while facing

TABLE 4

**River Sampling Locations and Water Quality Parameters**

| River name | State | Location | Temperature (°C) | Conductivity (μmhos/cm) | pH | DO (ppm) | TDS (mg/L) | TSS (mg/L) | DOC (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| Mohawk | NY | Utica | 10 | 350 | 7.8 | 7.7 | 210 | 3.8 | 2.5 |
| Chattahoochee | AL | West Point, GA | 10 | 70 | 7.0 | 7.8 | 40 | <3.0 | 2.3 |
| Chattooga | GA | Trion | 8 | 210 | 8.0 | 9.9 | 120 | <3.0 | 1.6 |
| Bernard Bayou | MS | Gulfport | 10 | >1990 | 7.9 | 9.6 | 870 | 18 | 6.9 |
| Red | AR | Index | 1 | 1200 | 8.1 | 13.8 | 4800 | 5.6 | 5.8 |
| Grand Calumet | IN | Gary | 17 | 490 | 7.4 | 7.8 | 600 | 30 | <1.0 |
| Dragoon Creek | WA | Deer Park | 13 | 260 | 8.2 | 7.4 | 140 | <3.0 | 1.7 |
| Brandywine Creek | PA | Coatsville | 9 | 250 | 8.4 | 12.4 | 200 | <3.0 | 2.4 |
| Fish Cr., W. Branch | NY | Camden | 8 | 90 | 7.4 | 10.7 | 78 | <3.0 | 7.3 |
| Great Egg Harbor | NJ | Berlin | 7 | 80 | 6.1 | 6.1 | 41 | 4.8 | 12 |
| Kennebec | ME | Waterville | 6 | 60 | 7.1 | 11.9 | 78 | <3.0 | 8.2 |
| Pecos | NM | Artesia | 22 | >1990 | 8.3 | 10.6 | 4900 | 13 | 6.8 |
| Palouse, S. Fork | WA | Colfax | 12 | 520 | 8.1 | 9.6 | 370 | <3.0 | — |
| Cuyahoga | OH | Mantua | 11 | 340 | 7.5 | 7.0 | 220 | <3.0 | 9.6 |
| Portneuf | ID | Pocatello | 14 | 680 | 7.7 | 6.1 | 480 | 190 | <1.0 |
| Perry Creek | GA | Arlington | 9 | 200 | 7.2 | 7.1 | 30 | <3.0 | 4.3 |
| Thames | CT | Uncasville | 11 | >1990 | 7.2 | 10.2 | 5000 | 3.8 | 1.0 |
| Catawba | NC | Morganton | 5 | 40 | 7.4 | 11.0 | 60 | <3.0 | <1.0 |
| Turkey Creek | LA | Winnsboro | 5 | 1190 | 7.7 | 7.6 | 560 | <3.0 | 3.2 |
| Delaware | NJ/PA | Croydon, PA | 8 | 150 | 7.4 | 9.2 | 220 | 5.6 | 3.8 |
| Shenandoah, N. Fork | VA | Mount Jackson | 5 | 240 | 8.8 | 12.9 | 160 | <3.0 | <1.0 |
| Tallahaga Creek | MS | Noxapater | 2 | 60 | 6.9 | — | 70 | <3.0 | 4.8 |
| South Anna | VA | Ashland | 4 | 70 | 7.5 | 12.8 | 70 | 19 | 2.1 |
| Potomac | MD | Brunswick | 5 | 260 | 8.6 | 13.7 | 160 | <3.0 | <1.0 |
| White | VT | Sharon | 7 | 140 | 8.1 | 12.1 | 110 | <3.0 | 14 |
| Youghiogheny | PA | McKeesport | 13 | 220 | 7.1 | 7.5 | 160 | <3.0 | 1.9 |
| St. Clair | MI | Marysville | 11 | 200 | 7.4 | 9.6 | 140 | <3.0 | <1.0 |
| Yellowstone | MT | Gardiner | 10 | 180 | 9.5 | 8.3 | 140 | <3.0 | <1.0 |
| Machias | ME | Machias | 13 | 1990 | 6.9 | 9.1 | 2200 | <3.0 | 14 |
| Muskegon | MI | Freemont | 11 | 390 | 8.0 | 7.2 | 230 | <3.0 | <2.0 |

upstream. Water was collected from 15 cm below the surface with pre-cleaned one-liter amber glass bottles. Additionally, one pre-cleaned 500-mL amber glass bottle was used to collect a sample at station 2 for total organic carbon (TOC), total dissolved solids (TDS) and total suspended solids (TSS). Measurements of the temperature, pH, conductivity, and dissolved oxygen (DO) were taken at station 2 at each of the sampling sites.

Sediment samples were collected with a ponar sediment grab sampler ("dredge"). This dredge has an empty weight of 50 pounds, a sample volume of approximately 4 L and jaws designed to close on impact with the river bottom. At some river sampling sites, it was not possible to procure suitable sediment at the desired transect locations. Under these circumstances, sediment samples were taken wherever suitable sediments could be found along, or as near to the sampling transect as possible.

All samples were preserved in the field by storing them on ice. In addition, 10 mL of formalin was added to all the water samples, except for the TOC samples. Two of the water samples from station 2 at each site were spiked with 100 μL of standard nonylphenol ethoxylate blend stock solution. The samples were then shipped to the laboratory *via* Federal Express. The temperatures of the ice chests were measured in the laboratory upon arrival and ranged from −5°C to +8°C over the course of the survey.

The field sample collection program was carried out from late September through late December of 1989 to correspond with typical lowest flow conditions. Sites were sampled at a rate of two per week.

*Analytical results.* Data gathered from the 30 river reach sites includes, in addition to NP and NPE concentrations, the above-mentioned water quality parameters (Table 4). A total of 98 water samples, including 9 duplicates, were analyzed by the steam distillation method, as were 81 sediment samples. One-hundred-one water samples were analyzed *via* the dual column extraction method, including 12 duplicates. The individual values are not shown. For purposes of statistical analysis, each value was considered independently rather than as part of the set from a river. Examination of the duplicate (*i.e.,* taken at the same station) sample analyses, in which the measured concentrations often differed greatly, suggests that the rivers probably should be considered heterogeneous systems.

Sediment samples from the Mohawk River and the Grand Calumet River were used for gas chromatography/mass spectrometry (GC/MS) confirmatory analysis of nonylphenol. Presence of NP was verified in both sediments. Octylphenol was detected, but not quantitated, in the former.

*Quality control measures.* A high level of quality assurance was needed for this study because it involved the use of sensitive extraction and analytical procedures, and the analytes were unstable at trace concentrations (ppb range and below). The key measures used for quantitatively evaluating data quality were the following:

(i) Laboratory blank samples were used to indicate laboratory contamination. Quality control (QC) limit target was method detection limit (MDL) × 5. (ii) Field blank samples (laboratory reagent water carried to the field and returned with field samples) were used to assess sampling contamination. QC limit was 5 × MDL. (iii) Laboratory-spiked river water samples (river water samples to which an aliquot of the standard NPE blend was added) were used to determine the extent of analyte recovery from river water matrices. QC target was ≥70% recovery. (iv) Field-spiked river water samples were used to determine stability of analytes in river water matrices. Field spiking ampules (standard NPE blend in methanol) were also checked for stability. (v) Laboratory check samples (laboratory reagent water spiked with the standard NPE) were used to monitor analytical accuracy and bias. The quality objective of 30% relative standard deviation from the method validation study was used as the performance guideline. (vi) Duplicate samples were used for assessing variability of samples taken at the same spot and time. (vii) Replicate analyses of the same samples were used for assessing the random variability in the analytical procedures and measuring precision. (viii) Daily instrument calibration was performed and charted to monitor chromatograph detector response and lamp degradation.

Table 5 summarizes the quality assurance (QA)/QC analytical tests performed during the course of the river survey. Blank values measured for laboratory water remained satisfactorily low, with none outside the QC limit. Field blanks were nearly all within QC limits; two NP and one $NPE_2$ values were outside the limits. The intended one field blank per site was not quite achieved because three of 30 blank samples were lost.

The lab spike of lab water QC check sample recoveries of NP were better than recoveries seen during method validation (86% *vs.* 59%), while those of $NPE_{3-17}$ (77% *vs.* 85%), and $NPE_1$ (78% *vs.* 76%) were about the same. (Recoveries of $NPE_2$ were not determined during method validation.)

Spiked river water samples, both lab- and field-spiked, gave recoveries comparable to or somewhat higher than the reference data obtained during method validation. Recoveries of $NPE_2$ had more scatter than those of the

**TABLE 5**

**Quality Assurance/Quality Control Analyses**

| Parameter | Analyte/Method | No. samples | Concentration, μg/L mean ± SD | QC Limit (5 × MDL) | Number outside QC limit |
|---|---|---|---|---|---|
| Laboratory blank (lab water) | NP/Steam distillation | 19 | 0.005 ± 0.010 | 0.55 | 0 |
| | $NPE_1$/Steam dist. | 19 | 0 | 0.35 | 0 |
| | $NPE_2$/Dual column | 21 | 0.008 ± 0.017 | 0.30 | 0 |
| | $NPE_{2-17}$/Dual col. | 21 | 0.16 ± 0.24 | 8.0 | 0 |
| Field blank (lab water) | NP/Steam dist. | 28 | 0.113 ± 0.21 | 0.55 | 2 |
| | $NPE_1$/Steam dist. | 28 | 0.025 ± 0.073 | 0.35 | 0 |
| | $NPE_2$/Dual col. | 29 | 0.022 ± 0.065 | 0.30 | 1 |
| | $NPE_{2-17}$/Dual col. | 29 | 0.24 ± 0.36 | 8.0 | 0 |
| | NP in sediment | 5 | 0.25 ± 0.51 μg/kg | 14.7 μg/kg | 0 |
| | $NPE_1$ in sediment | 5 | 0.61 ± 0.75 μg/kg | 11.3 μg/kg | 0 |
| | | | Recovery, % Mean ± SD | QC limit (Val. Rec. ± 30%)[a] | |
| Lab QC Check (lab water) | NP/Steam dist. | 19 | 86 ± 21 | 59 ± 30 | 6 |
| | $NPE_1$/Steam dist. | 19 | 78 ± 27 | 76 ± 30 | 5 |
| | $NPE_2$/Dual col. | 18 | 62 ± 31 | [b] | — |
| | $NPE_{3-17}$/Dual col. | 18 | 77 ± 22 | 85 ± 30 | 3 |
| Field spike (river water) | NP/Steam dist. | 28 | 63 ± 26 | 59 ± 30 | 5 |
| | $NPE_1$/Steam dist. | 28 | 68 ± 24 | 76 ± 30 | 4 |
| | $NPE_2$/Dual col. | 27 | 64 ± 42 | [b] | — |
| | $NPE_{3-17}$/Dual col. | 27 | 86 ± 32 | 85 ± 30 | 6 |
| Lab spike (river water) | NP/Steam dist. | 13 | 91 ± 26 | 59 ± 30 | 6 |
| | $NPE_1$/Steam dist. | 13 | 90 ± 20 | 76 ± 30 | 2 |
| | $NPE_2$/Dual col. | 11 | 70 ± 58 | [b] | — |
| | $NPE_{3-17}$/Dual col. | 11 | 87 ± 27 | 85 ± 30 | 2 |
| Field spike ampules (std. NPE in MeOH) | NP/Steam dist. | 17 | 90 ± 11 | | |
| | $NPE_1$/Steam dist. | 17 | 99 ± 12 | | |
| | $NPE_{2-17}$/Dual col. | 20 | 102 ± 6 | | |
| | | | Mean relative % difference | QC Limit (±30%) | |
| Field duplicates (river water) | NP/Steam dist. | 9 | 52 | 30 | 7 |
| | $NPE_1$/Steam dist. | 9 | 23 | 30 | 2 |
| | $NPE_{2-17}$/Dual col. | 12 | 35 | 30 | 6 |

[a]Recoveries obtained during method validation. [b]Recoveries of $NPE_2$ not determined during method validation.

other analytes, suggesting a greater sensitivity to matrix variability.

Another indication that water matrix variability influences analytical recoveries is given by the results from duplicate sample analysis. Mean relative percent differences for nine NP, nine $NPE_1$, and 12 $NPE_{2-17}$ duplicate analyses were 52%, 23% and 35%, respectively. A large portion of the duplicates were outside the target QC limit of ±30%. Stability of NPE carried to the field and back to the lab in methanol solution was essentially 100%.

## RESULTS AND DISCUSSION

*Water quality of the rivers.* Water quality parameter measurements on the rivers (Table 4) indicate that all were well aerated, containing from 6.1 ppm to over 13 ppm DO. The pH ranged from 6.1 (Great Egg Harbor, Berlin, NJ) to 9.5 (Yellowstone, Gardiner, MT). Conductivity varied from low to brackish; three of the high salt streams were estuarine (Thames, Uncasville, CT; Machias, Machias, ME; and Bernard Bayou, Gulfport, MS). TDS closely correlated to conductivity, hence salinity, ranging from 40 to 5000 ppm. DOC ranged from <1 to 14 ppm and TSS ranged from <3 to 190 ppm. Water quality thus varied from excellent to conditions where the water was heavily laden with dissolved organics and suspended solids.

*Nonylphenol species in the rivers.* A summary of the concentration of nonylphenol species measured in the river samples is given in Table 6; organic carbon levels in the sediments are included. Ranges of values, averages, percent of values below method detection limits and upper limits for the lowest 95% of the samples and the number of river reaches with all samples below MDL are shown. (Averages were calculated by using values less than MDL as MDL/2.)

Most water samples had concentrations below the detection limits; average concentrations were just above MDL's. The lowest 95% of values were in the lower half of the concentration ranges, *i.e.,* only the highest 5% of observations were in the upper half of the ranges.

NP and $NPE_1$ were detected more frequently and at higher concentrations in sediments than in the waters, as would be expected from their low water solubility. This fact is a validation of the initial assumption that the river reaches in the survey were likely to have been exposed to NP species. Organic matter in the sediments provides matrices for sorbing hydrophobic materials and releasing them only slowly and incompletely (11). Thus sediments can provide an integrated record of past chemical exposures in a waterway.

Sediment samples contained a higher frequency of detectable levels of NP and $NPE_1$ than the water samples and all but two samples had measurable organic carbon levels. NP levels ranged from below the MDL to 2,900 μg/kg. Approximately 95% of the samples contained less than 635 μg/kg. $NPE_1$ had a maximum level of 175 μg/kg and 95% of the samples were 100 μg/kg or less.

Distribution of the NP species concentrations among the water and sediment samples is shown graphically in Figures 1, 2 and 3. The rapid decrease of frequency of occurrence with increasing concentration is similar for all of the analytes in water. A similar but less abrupt decrease is also observed for the sediments, and there is a scattering of NP measurements across a broader range of concentration.

*Profiles of the river reaches.* Nearly three-fourths (22/30) of the rivers had no detectable water concentrations of one or more NP species at all sampling stations. Seventeen of the 30 had no NP, 17 no $NPE_1$, 12 no $NPE_2$ and 19 had no $NPE_{3-17}$. A total of 20 rivers had no or only marginal (≤MDL) levels of any of the NP species. Six of the rivers had no NP in their sediments and 7 rivers had no $NPE_1$.

Another way of viewing the sediments as depositories of earlier contamination is to consider those sites with measurable sediment concentrations of NP but none in the water column. Twelve and 9 of the sites contained detectable levels of NP and $NPE_1$, respectively, in the sediments but not in the water. Only two sites had NP in the water but not in the sediments, and those levels found were of marginal significance (Chattahoochee, West Point, GA and Catawba, Morganton, NC).

Two rivers (Grand Calumet, Gary, IN and Great Egg Harbor) accounted for 19 of the 28 "highest 5%" sediment values. Three other sites (Mohawk, Utica, NY; Delaware, Croydon, PA; and Bernard Bayou) had measurable levels of all the NP species.

To summarize for both sediment and water, five river sites had relatively high concentrations of NP species, 12 had measurable but lesser contamination levels of one or more NP species, and 13 were virtually devoid of contamination.

**TABLE 6**

**Summary of Nonylphenolic Concentrations in Rivers**

| Analyte | Range, μg/L[a] | Average | Highest value in lowest 95% | Percent below MDL | Number of rivers with all samples below MDL |
|---|---|---|---|---|---|
| Water | | | | | |
| Nonylphenol | <0.11–0.64 | 0.12 | 0.35 | 70 | 17[b] |
| $NPE_1$ | <0.06–0.60 | 0.09 | 0.31 | 67 | 17 |
| $NPE_2$ | <0.07–1.2 | 0.10 | 0.46 | 58 | 12 |
| $NPE_{3-17}$ | <1.6–14.9 | 2.0 | 6.6 | 76 | 19 |
| Sediment | | | | | |
| Nonylphenol | <2.9–2960 | 162 | 580 | 28 | 6[c] |
| $NPE_1$ | <2.3–175 | 18.1 | 89 | 44 | 7 |
| Total organic carbon | <0.01–4.4 wt% | 0.86 | 2.8 | 2 | 0 |

[a]Minimum values = MDL's from Table 2. [b]Number of rivers of 30. [c]Number of rivers of 29.

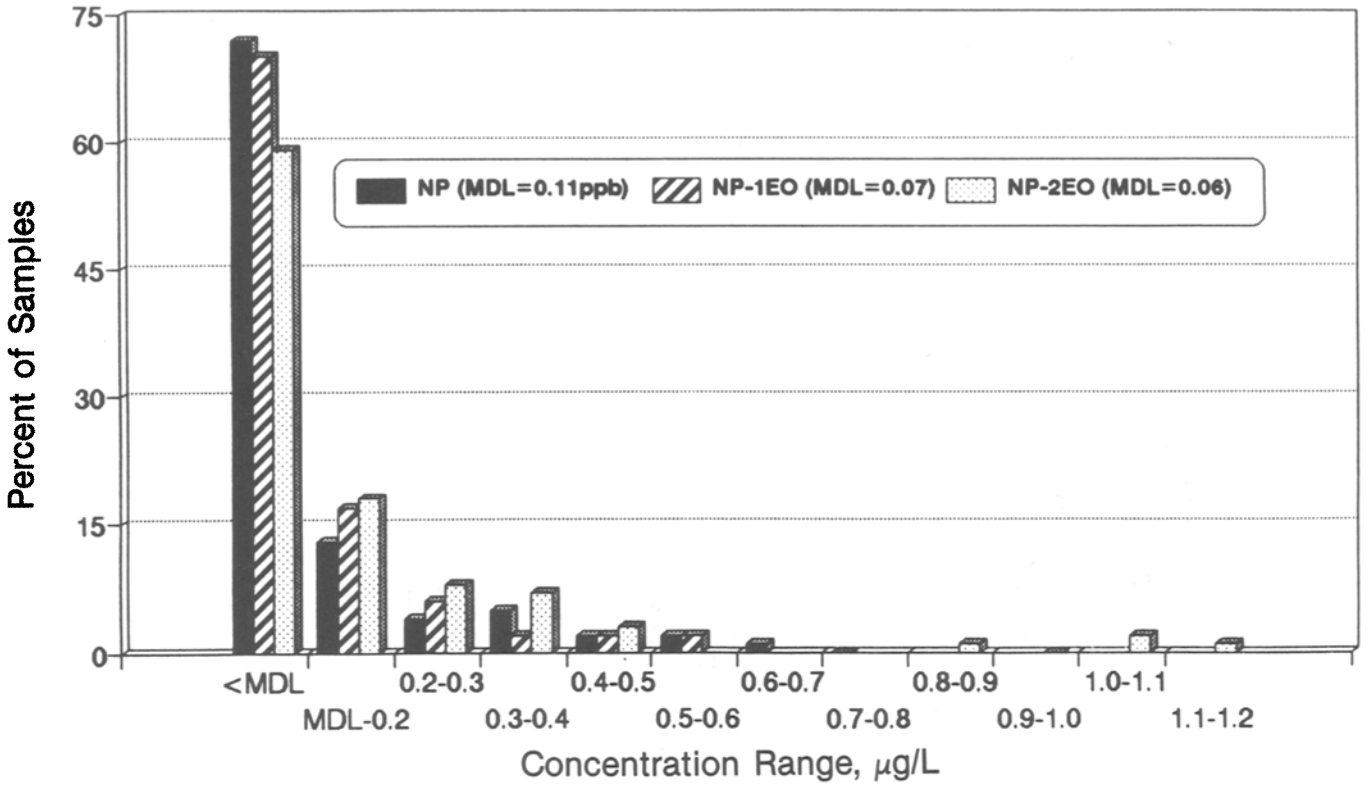


**FIG. 1. NP, $NPE_1$, and $NPE_2$ levels in river water.**

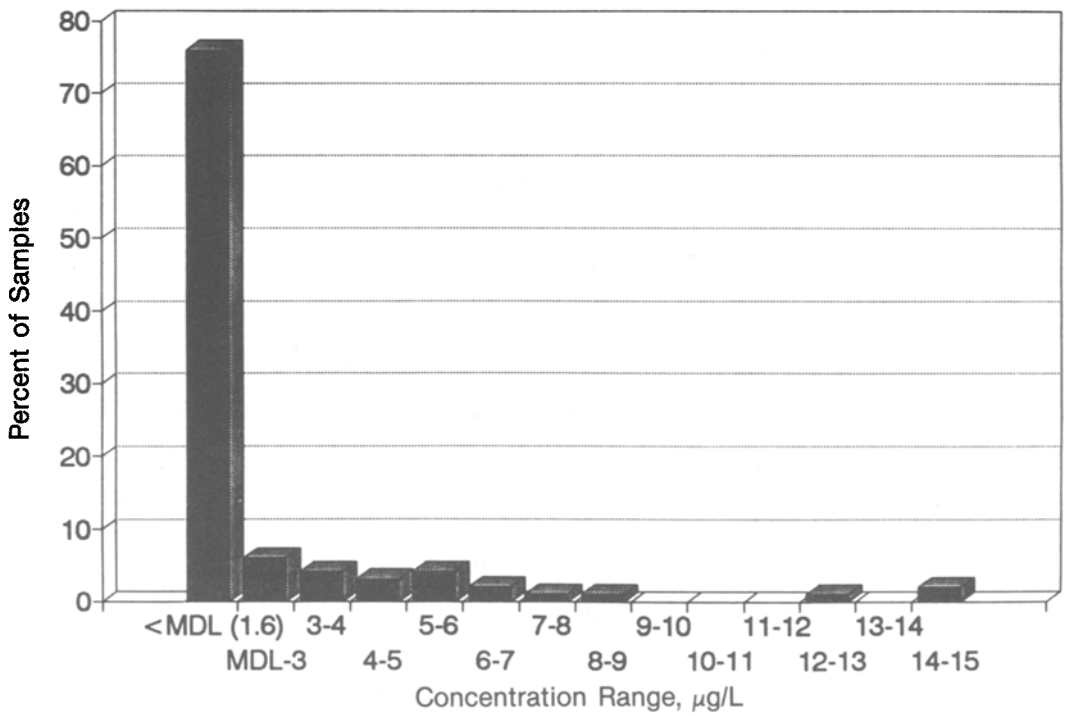


**FIG. 2. $NPE_{3-17}$ levels in river water.**

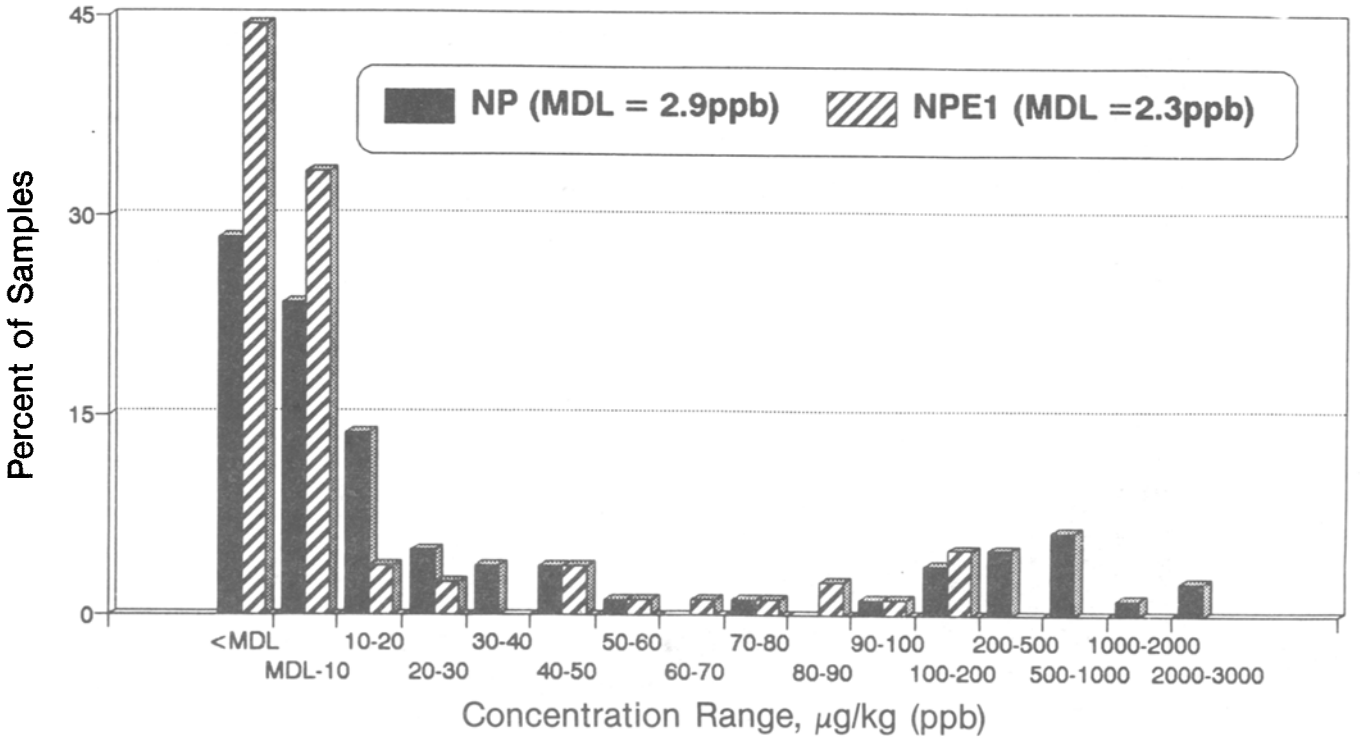


**FIG. 3. NP and $NPE_1$ levels in river sediment.**

This work did not attempt to assay for NP ether carboxylates, transient intermediates in the degradation of NPE. They can form in large amounts under conditions of poorly operating wastewater treatment plants (11), and are much less toxic than the short-chain ethoxylates (12).

*Calculated sediment interstitial water concentrations based on organic content and NP level in sediment.* Sediments may act as a sink for hydrophobic analytes in river water. The extent of partitioning to sediment is a function of the chemical's sediment/water partition coefficient and the organic content of the sediment. This partitioning relationship is approximated by the equation:

$$C_w = C_{sed}/(K_{oc} \times F_{oc}) \quad [1]$$

where $C_w$ = interstitial aqueous concentration of the analyte, $C_{sed}$ = sediment concentration of the analyte, $F_{oc}$ = organic fraction of the sediment, $K_{oc}$ = partition coefficient of the analyte between the sediment and water. An increase in $C_w$ will lead to higher $C_{sed}$ values. Conversely, analytes will desorb when $C_w$ is lowered. Thus, high analyte loadings on sediment can raise the concentration in the interstitial water by desorption to the equilibrium value. It is this interstitial water value that often correlates with exposure of the analyte to benthic organisms rather than $C_{sed}$ (13,14).

Interstitial water concentrations of NP, $C_w$, were calculated from the $C_{sed}$ values by using the value $K_{oc} = 3825$. This constant is the average of nonylphenol partition coefficients measured on three soils (15). The calculated values, clustered into concentration ranges, are shown graphically in Figure 4 and are compared to those of NP in the water column.

Qualitatively the distributions of NP are similar, confirming that the NP levels in sediments correlate with total organic carbon and the assumed discharge pattern. The large majority of samples were below detection limits for both water zones, and the maximum concentrations in the two zones were within a factor of two of each other. This is excellent agreement, considering the heterogeneity of the sediments and the assumption that $K_{oc}$ is constant. We can therefore state with confidence that, despite relatively much higher NP levels in sediment (a typical pattern for hydrophobic materials), exposure of aquatic organisms dwelling in the sediments is not substantially different from those in the water column.

*The question of environmental persistence.* A key conclusion of this study is a demonstrated lack of significant NP or NPE accumulation in any compartment of the aquatic environment. Considering the large volumes of NPE entering the aquatic environment (1), the levels actually measured at sites most likely to contain substantial amounts are low. We consider this finding as definitive evidence for the high rates of NPE degradation by biological and probably other mechanisms, such as autoxidation. NPE in wastewater have been shown to undergo a high degree (approximately 95%) of removal during activated sludge treatment (6).

Our results contrast with previous reports of much higher levels of NP species in river water (8) and sediment (16): NP concentration up to 2 μ/L in the Glatt River near Zurich, Switzerland, $NPE_1$ up to 18 and $NPE_2$ up to 16 μg/L. The highest we found were 0.64, 0.6 and 1.2, respectively. Rhine River sediment levels were 900 μg/kg NP (below the 2960 we saw in the Grand Calumet River), 800 $NPE_1$ (our highest finding was 715) and 700 $NPE_2$

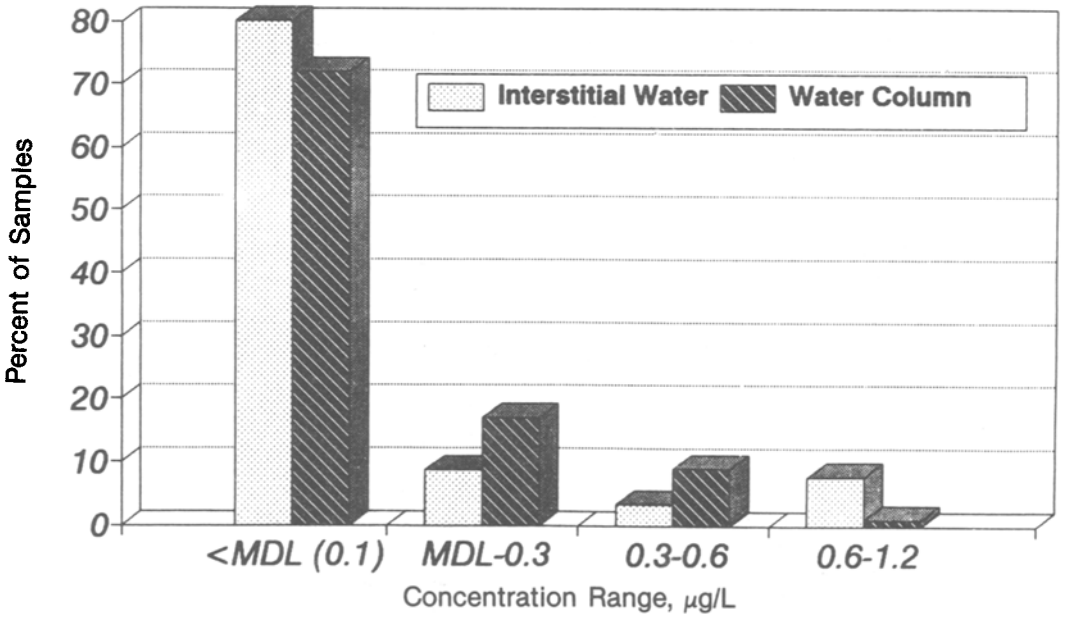


**FIG. 4. Water concentration range of nonylphenol.**

(we did not look for it in sediment). Our first report (6) highlighted the pitfalls that can occur in trace NPE analysis. Difficulties with earlier trace analytical methods and absence of strict quality assurance procedures (6,8, 9,17) raise serious questions about the validity of reports of hazardous NPE environmental concentrations.

The present work, conducted under rigorous quality assurance standards, provides a high degree of confidence in its results. Future reports from the APE Panel will combine these results with aquatic toxicity and bioaccumulation studies, still in progress, to determine quantitatively the environmental risk of APE surfactants.

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## REFERENCES

1. *Synthetic Organic Chemicals, United States Production and Sales, 1990,* USITC Publication 2470, December 1991, US International Trade Commission, Washington, DC.
2. Swisher, R.D., *Surfactant Biodegradation,* Marcel Dekker, New York, NY, 1987.
3. Marcomini, A., F. Filipuzzi and W. Giger, *Chemosphere 17*:853 (1988).
4. Thoumelin, G., *Environ. Technol. 12*:1037 (1991).
5. *Chemical Hazard Information Profile—Nonylphenol,* U.S. EPA, Office of Toxic Substances, Washington, DC, 1986.
6. Kubeck, E., and C.G. Naylor, *J. Am. Oil Chem. Soc. 67*:400 (1990).
7. *40 Code of Federal Regulations, Vol. 40, pt. 136, App. B.*, US Government Printing Office, Washington, DC, 1986.
8. Ahel, M., and W. Giger, *Anal. Chem. 57*:1577 (1985).
9. Ahel, M., and W. Giger, *Ibid. 57*:2584 (1985).
10. Radian Corporation, *Report to CMA Panel on Alkylphenols and Ethoxylates,* CMA, Washington, DC, 1990.
11. Ahel, M., W. Giger and M. Koch, *Commun. Eur. Communities (Rep.)*:414 (1986).
12. Yoshimura, K., *J. Am. Oil Chem. Soc. 63*:1590 (1986).
13. Adams, W.J., R.A. Kimerle and R.G. Mosher, *Aquatic Toxicology and Hazard Assessment: Seventh Symposium, ASTM STP 854,* American Society for Testing and Materials, Philadelphia, PA, 1984, pp. 429–453.
14. DiToro, D.M., *Briefing Report to the EPA Science Advisory Board on the Equilibrium Partitioning Approach to Generating Sediment Quality Criteria,* EPA 440/5-89-002, USEPA, Office of Water Regulations and Standards, Washington, DC, 1989.
15. *Report to CMA Panel on Alkylphenols and Ethoxylates, Study No. 90-041,* Roy F. Weston, Inc., Washington, DC, 1991.
16. Marcomini, A., and W. Giger, *Anal. Chem. 59*:1709 (1987).
17. Zoller, U., *Tenside Surfactants Deterg. 26*:394 (1989).

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