AUTHOR: R. JAMES MAGUIRE
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ABSTRACT

Alkylphenol ethoxylates, in particular nonylphenol ethoxylates, are widely used nonionic surfactants that are discharged in high quantities to sewage treatment plants and directly to the environment in areas where there is no sewage or industrial waste treatment. This article reviews the treatability of nonylphenol ethoxylates and nonylphenol in sewage treatment plants and their persistence in aquatic environments. Nonylphenol ethoxylates can be biologically degraded in sewage treatment plants and in natural environments. Some of the degradation products, including nonylphenol, are more persistent than the parent surfactants and they are found in receiving waters of sewage treatment plants. Nonylphenol in particular is found at high concentrations in some sewage sludges that may be spread on agricultural lands. While some sewage treatment plants discharge significant amounts of nonylphenol ethoxylate degradation products in their final effluents and digested sludges compared to what enters the plant, others degrade nonylphenol ethoxylates more or less completely. The differences in treatment efficiency of such compounds and their degradation products among different sewage treatment plants have been attributed to the load of the surfactants in influent streams, plant design and operating conditions, and other factors such as temperature of treatment. The highest nonylphenol ethoxylate elimination rates were achieved in plants characterized by low sludge-loading rates and nitrifying conditions. In natural waters, it appears that parent nonylphenol ethoxylates are not persisent, but some degradation products may have moderate persistence, especially under anaerobic conditions. Recent results from mesocosm experiments indicate moderate persistence of nonylphenol in sediments, with half-lives of 28 to 104 days. Microbial acclimation to the chemicals is an important determinant of persistence vis-à-vis biodegradation. Sunlight photodegradation of such products is also likely important. Further research on the persistence in natural environments of the lower ethoxylate and carboxylate degradation products, as well as nonylphenol, is necessary. Based on the limited data available, nonylphenol and the lower ethoxylates and carboxylates are persistent in groundwater. They are also persistent in landfills under anaerobic conditions, but they do not appear to be persistent in soil under aerobic conditions. Recommendations are made for further research in order to more fully characterize the treatability of nonylphenol ethoxylates and their degradation products in sewage treatment plants and their persistence in the natural environment.

Key words: nonylphenol, ethoxylates, persistence, water, aquatic environment, review

INTRODUCTION

The Canadian Environmental Protection Act (CEPA), proclaimed June 30, 1988, authorizes the Ministers of Health and of the Environment to conduct research and collect information on a wide variety of substances that may contaminate the environment and cause adverse effects on human health or the environment (Government of Canada 1988). The term "substance" is defined in section 3 of CEPA and for the purposes of the Act includes chemicals in commerce, chemical contaminants in products or environmental media and complex mixtures of substances

in effluent streams and emissions. At the time the Act was proclaimed, the estimated 30,000 to 40,000 chemicals that were manufactured in, or imported into, Canada and hundreds of effluent streams and emissions were candidates for assessment of their health and environmental impacts under CEPA. It is not possible to assess simultaneously all the substances that may pose a threat to health or the environment. Therefore, it was necessary to select a manageable number that should be given priority for assessment, as required by subsection 12(1) of CEPA, which states:

> "The Ministers shall compile and may amend from time to time a list known as the Priority Substances List, and the List shall specify substances in respect of which the Ministers are satisfied priority should be given in assessing whether they are toxic or capable of becoming toxic."

Substances that appear on the Priority Substances List must be assessed to determine whether they are toxic according to the definition specified in section 11 of the Act, which states, in part:

> "... a substance is toxic if it is entering or may enter the environment in a quantity or concentration or under conditions
> (a) having or that may have an immediate or long-term harmful effect on the environment;
> (b) constituting or that may constitute a danger to the environment on which human life depends; or
> (c) constituting or that may constitute a danger in Canada to human life or health."

In preparing the CEPA Priority Substances List for the first time, the Ministers of the Environment and of Health gave consideration to recommendations from academia, industry, environmental public interest groups and provincial governments, as provided for in subsection 12(3) of CEPA. A substance was selected for the List if it met at least one of the following three criteria: (a) The substance causes or has the potential to cause adverse effects on human health or the environment. (b) The substance accumulates or could accumulate to significant concentrations in air, water, soil, sediment or tissue. (c) The substance is released or may be released into the environment in significant quantities or concentrations.

The first CEPA Priority Substances List, which appeared in the Canada Gazette in February 1989 (Canada Department of the Environment 1989), contained 44 substances, including organic compounds, metals, mixtures, effluents and emissions. Assessments of these substances were completed by February 1994. The Ministers of Environment and Health established a second Expert Advisory Panel in December 1994 to recommend a new list of priority substances for assessment under the Act. This Panel, drawn from major stakeholder groups, recommended a list of 25 substances (Ministers' Expert Advisory Panel 1995). The Ministers accepted this list and published the second Priority Substances List ("PSL2") in the Canada Gazette in December 1995 (Canada Department of the Environment and Department of National Health and Welfare 1995).

Nonylphenol (NP) and its ethoxylates (NPEs) are some of the "substances" on PSL2. The Ministers' Expert Advisory Panel (1995) made the following recommendation:

> "NPEs are discharged into the environment primarily from textile and pulp and paper production facilities. They are also used in coal processing, latex paints, grease and lubricating oils, pesticides and industrial detergents. Acute adverse effects have been reported in invertebrates, fish, mammals and algae. There are also concerns that these substances may interfere with endocrine function. An assessment is required to determine exposure levels

and the risk they may pose to the environment and human health in Canada."

This article reviews the persistence and fate of nonylphenol and nonylphenol ethoxylates, as well as other (intermediate) degradation products of the ethoxylates, primarily from an aquatic perspective. Some information is also provided on other closely related alkylphenols and alkylphenol ethoxylates. The information in this review will be combined with information on the analytical chemistry (Lee 1999), occurrence (Bennie 1999) and toxicity (Servos 1999) of such substances to produce the supporting document for the environmental assessment under CEPA. This information will be combined with data on the mammalian toxicity and exposure patterns of the chemicals (currently being prepared by the Department of Health) to provide environmental and human health risk assessments of nonylphenol and its ethoxylates under CEPA. Guidance for CEPA PSL environmental assessments is provided by Environment Canada (1997).

NOMENCLATURE

The predominant positional isomer of monoalkylphenols is the para isomer, which usually comprises $\geq$ 90% of industrial formulations, while the ortho isomer comprises $\leq$ 10%. In the United States, the U.S. Environmental Protection Agency and the Chemical Manufacturers Association Alkylphenols and Ethoxylates Panel have agreed that the commercial product that best represents "nonylphenol" is a chemical substance comprised of branched C_9-alkylphenols with Chemical Abstracts Service Registry Number 84852-15-3 (later called "4-NP, branched") (Hellyer 1991). Chemical Abstracts Service Registry numbers for a variety of alkylphenols, ethoxylates and other derivatives are given in Talmage (1994).

For convenience, abbreviations of the names of various chemicals will be used in this review.

AP — alkylphenol
NP — nonylphenol
OP — octylphenol
APE or APnEO — alkylphenol ethoxylate
NPE or NPnEO — nonylphenol ethoxylate
OPE or OPnEO — octylphenol ethoxylate
APEC or APnEC — alkylphenol carboxylate
NPEC or NPnEC — nonylphenol carboxylate
OPEC or OPnEC — octylphenol carboxylate

Structures of NPEs and associated degradation products are shown in Fig. 1. It should also be noted that halogenated (on the ring) derivatives of alkylphenol ethoxylates and carboxylates have been found in the effluents of some sewage treatment plants that employ chlorine for disinfection.

SYNTHESIS OF ALKYLPHENOLS

Alkylphenols of commercial importance are manufactured almost exclusively by catalyzed reaction of an olefin with phenol, cresols or xylenols (Reed 1978). The olefins used are all readily available from petrochemical operations. Nonylphenol (NP) is manufactured industrially by alkylating phenol with mixed isomeric nonenes (propylene trimer) in the presence of an acid catalyst. The product, consisting largely of a mixture of alkylphenols 4- substituted with various isomeric, branched-chain nonyl groups, is recovered by fractional distillation under reduced pressure. It is a viscous liquid possessing a slight phenolic odour. At low temperatures, nonylphenol sets to a clear glass-like solid without crystal formation (Reed 1978). 4-Octylphenol (4-(1,1,3,3-tetramethylbutyl)phenol) is made by alkylating phenol with diisobutylene followed by

vacuum distillation. 4-Octylphenol can be condensed with formaldehyde to give oil-soluble phenol resins, which are used in the manufacturer of surface coating compositions, brake and clutch linings, and in the production of special printing inks. 4-Octylphenol is used for the manufacture of nonionic surfactants by condensation with ethylene oxide using a basic catalyst. As a rubber chemical, it is a useful antiflex cracking agent, fungistat and plasticizer. 4-Octylphenol sulfide is used in vulcanizing synthetic rubbers (Reed 1978).

PRODUCTION OF OTHER CHEMICALS FROM ALKYLPHENOLS AND THEIR GENERAL USE

By far the most important industrial reaction of nonylphenol is etherification, whereby condensation with ethylene oxide using a basic catalyst yields nonionic surfactants of the nonylphenol ethoxylate type (NPEs). Low condensates with 4 to 5 ethylene oxide residues per molecule of nonylphenol are used as oil-soluble detergents and emulsifiers and can be sulfonated or phosphorylated to give anionic detergents, lubricants and antisatic agents. The 8 and 9 mol ethoxylates form the basis of high performance detergents, especially for textile scouring, but they have been replaced by straight-chain C_{12}-C_{14} alcohol ethoxylates in some household detergents in some countries because of concerns about their persistence (see below). Higher ethoxylates, the 13 to 15 mol derivatives, in conjunction with an oil-soluble anionic surfactant, are excellent emulsifiers for a wide range of solvents and agricultural pesticides (Reed 1978). Alkylphenol ethoxylates have been used in cleaning products and industrial processing for more than 40 years (Talmage 1994). It should be noted that ethylene oxide (another PSL2 chemical) may be present in NPE formulations at concentrations below 10 mg/L (Talmage 1994).

The production of tris-4-nonylphenol phosphite as an antioxidant for rubber and the manufacture of lube oil additives account for most of the remaining nonylphenol market (Reed 1978). Nonylphenol has been found in extracts of food grade poly(vinyl chloride) (PVC), probably derived from the use of tris(nonylphenyl) phosphite as a pre-stabilizer during polymer drying (Gilbert et al. 1982). In a study of chemicals that could be leached from various types of tubing, Junk et al. (1974) found (but did not quantify) p-nonylphenol in PVC tubing for processed milk and “Food and Drug Administration — U.S. Department of Agriculture PVC”, as well as p-dodecylphenol in “FDA-USDA PVC”.

In the United States in 1980 there were 2.4×10^6 tons of surfactants of all types produced (68% anionic, 25% nonionic, 6% cationic and 0.5% amphoteric). Ethoxylated alkylphenols were produced in the amount 1.57×10^5 tons, which was 26% of all nonionic surfactants, and nonylphenol ethoxylates accounted for 73.6% of the 1980 production of alkylphenol ethoxylates (Cahn and Lynn 1983). Total consumption of alkylphenol ethoxylates in the Federal Republic of Germany was about 18,500 tonnes in 1984 and about 4900 tonnes in 1990 (Poremski 1991).

USES OF NONYLPHENOL AND NONYLPHENOL ETHOXYLATES IN CANADA

Nonylphenol itself has been used in aminocarb (4-dimethylamino-3-methylphenyl-N-methylcarbamate) insecticide sprays against the spruce budworm (Choristoneura fumiferana Clem.) in eastern Canada (National Research Council of Canada 1982). A typical formulation (“1.8D oil soluble concentrate”) consisted of (by weight) 19.5% aminocarb, 30% diluent 585 (the fraction of No. 2 fuel oil that distills at or below 585°F) and 50.5% nonylphenol. In the field, additional diluent 585 was usually added to make a spray formulation containing 70 g of aminocarb and 182 g of nonylphenol in 1-1.5 L, and the formulation was typically sprayed at 1-1.5 L/ha. This formulation was superseded in 1981 by an aminocarb formulation that did not contain nonylphenol. In the United States and possibly elsewhere, nonylphenol has been used in admixture with diisobutyl phthalate for marking fuel oil for taxation purposes (Reed 1978). It is not known if nonylphenol is used for this purpose in Canada.

In Canada, the total supply of nonylphenol in 1989 was estimated as 5.5 kilotonnes (3.7 kilotonnes from domestic production and 1.8 kilotonnes imported) (Camford Information Services 1990). Exports were estimated to be 1.0 kilotonnes and domestic demand was estimated to be 4.5 kilotonnes (1.0 kilotonnes in ethoxylated textile specialities, 1.6 kilotonnes in ethoxylated pulp mill specialties, 0.5 kilotonnes of miscellaneous ethoxylates, 0.5 kilotonnes for trinonylphenyl phosphite and 0.9 kilotonnes miscellaneous, including pesticides and lube oil). Nonylphenol ethoxylates (average n = 5) have been shown to be effective against apple powdery mildew in the United Kingdom (Bent et al. 1977) when sprayed at 3.5%, but no information is available on their use as pesticides in Canada (as opposed to their use as "inert" adjuvants in pesticide formulations). The use of NPEs as "inerts" in insecticidal formulations was recently reviewed by Narayanan et al. (1997).

Metcalfe et al. (1996) reviewed NPEs and their use in Canada. They identified 11 sectors which use NPEs as detergents, emulsifiers, wetting agents and dispersing agents. Five sectors are believed to be responsible for the bulk of NPE environmental discharges (pulp and paper manufacturing, petroleum production, household/industrial/institutional cleaning, textile manufacturing [see IEC International Environmental Consultants Ltd. 1982; Chen 1989] and leather manufacturing). Minor uses of NPEs are in the building and construction, paint and protective coating, metal processing, plastic and elastomer manufacturing, and food and beverage sectors. NPEs are also used as spermicides in contraceptive foams, jellies and creams; although small, this use is important because of direct human contact. For example, nonoxynol-9 (nonylphenoxypoly-ethoxyethanol) is a nonionic surfactant commonly used in commercial vaginal spermicidal formulations (Abrutyn et al. 1982).

SOME REGULATORY INITIATIVES IN OTHER JURISDICTIONS

Alkylphenols and their ethoxylates, in particular nonylphenol and ethoxylates, are high volume industrial chemicals that are discharged to the environment in significant quantities. Some of the degradation products of alkylphenol ethoxylates are more lipophilic than the parent compounds and demonstrate toxic effects to aquatic organisms. Consequently, there have been regulatory and voluntary initiatives to phase out NPE use from various products in North America and Europe. For example, concerns about the persistence and toxicity of degradation products of NPEs led to voluntary elimination of NPE surfactants from many uses in Europe and agreements by the Oslo and Paris Commissions (OSPAR) that NPE would be phased out of domestic cleaning products by 1995 and out of industrial cleaning products by 2000 (PARCOM Recommendation 92/8 1992). The Oslo and Paris Conventions for the Prevention of Marine Pollution Working Group on Diffuse Sources (1996) noted that a preliminary environmental risk assessment for NP, based on measured environmental concentrations (PEC) and a calculated predicted no effect concentration (PNEC), revealed that the PEC/PNEC quotient in river water and coastal sea water generally lies around or above 1, indicating the potential that ecotoxicological effects may occur. That organization is currently performing a full risk assessment and it noted that the significance of estrogenic effects of NP, octylphenol and their derivatives on aquatic biota and wildlife remains to be determined. In the United States, the U.S. Environmental Protection Agency (EPA) Testing Priority Committee in 1987 formally nominated nonylphenol as a candidate for rule-making under the Toxic Substances Control Act (TSCA). In 1988, the U.S. EPA proceeded with delisting 2-nonylphenol from the TSCA Public Inventory since it was no longer manufactured (Hellyer 1991). The U.S. EPA has required testing of NPEs and NP for persistence, fate and toxicity by the U.S. Chemical Manufacturers Association Alkylphenols and Ethoxylates Panel.

The CMA APE panel has also undertaken some voluntary studies, notably of occurrence of NPEs and NP in thirty U.S. rivers.

Part of the determination of the hazard that such chemicals pose to the Canadian environment is an estimation of their environmental persistence. The rest of this article reviews the environmental persistence of nonylphenol and its ethoxylates.

PERSISTENCE

The main focus of this review is on the aquatic persistence of nonylphenol (NP) and its ethoxylates (NPEs), although some relevant data on the persistence in other media, and the persistence of some other alkylphenols and their ethoxylates, are also reviewed. The persistence of NP and NPEs are reviewed in laboratory tests, sewage treatment plants and the natural environment. Earlier reviews of environmental aspects of alkylphenols and alkylphenol ethoxylates are provided by Beak Consultants Ltd. (1987), the Proceedings of the Seminar on Nonylphenol Ethoxylates and Nonylphenol in Saltsjöbaden, Sweden (1991), Holt et al. (1992), U.K. Department of the Environment (1993), Talmage (1994), Balson and Felix (1995), Nimrod and Benson (1996), Metcalfe et al. (1996), Dickey (1997), U.K. Environment Agency (1997), World Wildlife Fund Canada (1997), Thiele et al. (1997), Staples et al. (1998) and Lee (1998).

With regard to the behaviour of a chemical in the environment, it should be noted that there are many factors which influence its persistence, including its physical and chemical properties and ecosystem-specific properties such as (for aquatic ecosystems) the nature and concentration of microbial populations, the nature and concentration of dissolved and suspended material, temperature, degree of insolation, etc. In general, important physical, chemical and biological removal mechanisms for chemicals in aquatic ecosystems are (i) volatilization and adsorption to suspended solids and sediment, (ii) chemical and photochemical degradation or transformation, and (iii) uptake and transformation by microorganisms, respectively. The importance of such pathways for specific chemicals depends upon the chemical and the ecosystem. A more detailed description of the way in which physical-chemical properties and ecosystem-specific properties determine the fate of chemicals has been given by Howard (1989).

SOME PROPERTIES AND IMPLICATIONS WITH RESPECT TO ENVIRONMENTAL PATHWAYS

Some physical and chemical properties that have a bearing on the environmental persistence of NP and OP are shown in Table 1 and will be referred to in the appropriate sections that follow. It should be noted, for example, that the pK_a (negative logarithm of the acid dissociation constant) of NP is 10.7 (Romano 1991) which indicates that in most natural waters virtually all NP is present in the undissociated form.

Ahel and Giger (1993a) determined aqueous solubilities (at 20.5°C) for NP and NPnEO (n = 1-5) to be in the range 3-9 mg/L and for OP and OPnEO (n = 1-4) to be in the range 8-25 mg/L. They also determined solubilities as a function of temperature between 2°C and 25°C; over this temperature range there was only a modest variation in solubilities. Ahel and Giger (1993b) determined the following log K_{ow} values by a high performance liquid chromatographic (HPLC) method: OP (4.12), NP (4.48) and NP1EO (4.17), NP2EO (4.21) and NP3EO (4.20). Estimates of log K_{ow} values for higher oligomers were also made by two methods, which were not in agreement. McLeese et al. (1981) determined a value of 4.2 for the log K_{ow} of NP by HPLC.

Bidleman and Renberg (1985) estimated the vapour pressure of NP by a gas chromatographic method. Six major resolvable components were estimated to have vapour pressures in the range 0.06-0.17 Pa at 25°C.

ANALYTICAL METHODS FOR NP, NPES AND OTHER NONIONIC SURFACTANTS

Early methods of analysis of surfactants, including nonionic surfactants such as the NPEs, have been reviewed by Talmage (1994). These include the cobalt thiocyanate active substances (CTAS) method (in which NPnEO [n >5] form a blue complex with the ammonium cobaltothio-cyanate reagent), the bismuth iodide active substances (BIAS) method (in which Dragendorff reagent, a preparation containing barium tetraiodo-bismuthate, forms a precipitate with polyoxyethylene compounds by interaction with the ethoxylate oxygen atoms) and the Wickbold modification of the BIAS method (involving removal of particulates by filtration, sublation into ethyl acetate using a stream of nitrogen presaturated with ethyl acetate, removal of cationic surfactants with cation exchange resin, precipitation of nonionic surfactants by barium bismuth iodide reagent and measurement of the bismuth content of the precipitate by potentiometric titration with pyrrolidine dithiocarbamate solution). These methods were generally developed for parent surfactants, and not their low molecular weight degradation products, and they have been almost entirely supplanted by more modern methods of gas and liquid chromatography (see review of Lee 1998) with much greater specificity and sensitivity.

DEGRADATION TESTS IN THE LABORATORY

The issue of the biodegradability of NPEs is complicated by the necessity, from a toxicological and ecotoxicological point of view, to determine the persistence of any intermediate or final products of metabolism or abiotic degradation. It is clear from the literature that some chemicals produced in the degradation of NPEs are more persistent than the parent compounds.

Although there are some conflicting reports in the literature, in general, NPEs and NP are not readily biodegradable using standard test methods. However, it is also clear that substantial biodegradation will occur after a period of acclimation. Branching of the nonyl group in NP and NPEs retards biodegradation, as does increase in length of the ethoxylate chain, and alkylphenols and alkylphenol ethoxylates are more persistent than alkylbenzene sulfonates and alcohol ethoxylates (e.g., Patterson et al. 1967, 1968, 1970; Davis and Gloyna 1969; Sturm 1973; Kravetz et al. 1984, 1991; Dorn et al. 1993; Strujis and Stoltenkamp 1994; Ahel et al. 1994a; Salanitro et al. 1995; Salanitro and Diaz 1995). Results from some representative studies that illustrate the above statements are described below. It should also be noted that the use of high concentrations of chemicals in tests of their biodegradability may give an artifactually high persistence if the chemical poisons the test organisms. This possibility has been suggested to account for some differences in results for the biodegradability of NPEs (e.g., U.K. Environment Agency 1997).

Patterson et al. (1968) showed that NP9EO in laboratory biodegradation tests (with dried activated sludge medium reconstituted) at neutral pH showed a half-life of 6 weeks at an initial concentration of 5 mg/L.

Davis and Gloyna (1969) noted that a branched chain NPnEO, with an average of 9.5 ethylene oxide units, was 37% degraded in 12 days in a river die-away test (analysis by Warburg respirometry), while a straight chain alkylbenzene sulfonate was 95% degraded in 12 days. In other work cited, a linear alkane sulfonate was 100% degraded in 5 days in a river die-away test, while a NPnEO was only 54% degraded in 30 days. They observed that algae plus associated bacteria contributed to a small extent in the degradation of surface active agents (including NPE 9.5) commonly found in household detergents at that time. Most of the degradation was attributed to bacteria and other microorganisms found in wastewater environments.

Sturm (1973) developed a screening test consisting of the Thompson-Duthie CO_2 test (scaled down from 20 to 6 L) and a biochemical oxygen demand test performed

with acclimated sewage-derived microorganisms. This work was concerned exclusively with the application of the CO_2 production method to the problem of nonionic surfactant degradation and showed very little % theoretical CO_2 production with a branched NP8EO molecule.

Rudling and Solyom (1974) determined the biodegradability of branched chain NPnEO, where n = 8, 10, 14, 16 and 30, according to a screening procedure recommended by the Organization for Economic Cooperation and Development (OECD) and also in a study conducted in a laboratory-scale activated sludge system operated with presettled sewage under treatment plant conditions. Typical test concentrations were 5 mg/L (and the presettled sewage had about 0.5 mg/L of nonionic surfactants). Gas chromatographic analysis of NP8EO, NP10EO and NP14EO samples incubated at 20°C for 4 days showed that primary degradation was > 90%. The major product was NP2EO. Analysis of the NP8EO, NP10EO and NP14EO samples incubated for 28 days at 20°C in the OECD screening test showed that about 50% of the NP2EO derivative had degraded, while at 15°C no degradation was observed. In the activated sludge test, > 80% degradation was observed for all NPE compounds tested in 10 days. Chromatographic analyses of these test systems indicated that disappearance of starting material was not simply due to adsorption to activated sludge and no NP2EO was found.

Kravetz et al. (1984) studied the ultimate and primary biodegradability of an alcohol ethoxylate ("AE 25-9") and NP9EO under conditions that simulated a sewage treatment plant under winter conditions. Primary biodegradation of NP9EO was found to decrease more with temperature than did that of AE 25-9. In addition, at low temperature NP9EO effluents foamed considerably while AE 25-9 effluents did not. NP9EO biodegraded to CO_2 much less extensively than AE 25-9 at all temperatures studied.

Neufahrt et al. (1987) showed that "biosimulators" with an activated sludge feature provided > 95% primary degradation of NPE. Concentrations in the influent were 13 mg/L and 1-1.5, 6-7 and 9-12 μL, respectively, for NPE, NP, NP1EO and NP2EO, and concentrations of NPE, NP, NP1EO and NP2EO in the outflow were on average 460, 0.5, 5 and 20 μg/L, respectively.

Kravetz et al. (1991) showed that branching in the alkyl chain has a considerable retarding effect on biodegradation in continuous flow-through activated sludge tests that simulate actual waste treatment. NP9EO was not readily biodegradable by the OECD biological oxygen demand (BOD) test. They also found low biodegradability in a test (OECD modification of the Sturm test) for ultimate biodegradation via CO_2 evolution (30% over 28 days). These tests were at 25°C. At 8°C biodegradation was slowed considerably.

Maki et al. (1994) isolated an alkylphenol ethoxylate-degrading bacterium from activated sludge in a Japanese sewage treatment plant by enrichment culture and tested it on a NP9.5EO formulation. NP2EO was the predominant product, although intermediates with a high degree of ethoxylation were observed. NP2EC was also found in the culture broth (relative amounts not stated). Degradation of the nonyl moiety was not observed.

Struijs and Stoltenkamp (1994) reviewed the development of screening biodegradability tests for surfactants and concluded that a positive result in a "ready biodegradability test" can safely be extrapolated to aerobic environments in regions where domestic waste water is processed by sewage treatment plants. Their results indicated that NP10EO and iso-octylphenol ethoxylate (10EO) did not show ready biodegradability in dissolved organic carbon (DOC) die-away, manometric respirometry and closed bottle tests.

Ahel et al. (1994a) studied the aerobic transformation of NPnEO (n = 1-3) by mixed bacterial cultures using a shake-flask technique. Initial concentrations were in the range

0.5-2.5 mg/L. Transformation was almost complete in 6-23 days, but was slower in a mineral medium where the NPnEO were the only carbon source. NPnEC were the major metabolites. Autochthonous bacterial cultures from river water and a secondary sewage effluent also transformed NPnEO (n = 1-3) fairly efficiently, with the transformation rate depending strongly on temperature. The use of microbes acclimated to NPnEO was conducive to faster biodegradation rates. Nevertheless, bacteria from a relatively pristine source (a forest soil) could effect biotransformation, albeit more slowly. The authors concluded that such compounds could not be regarded as truly persistent compounds under aerobic conditions. It is also important to note that NPnEO (n = 1-3) transformation was strongly dependent upon temperature, suggesting that their degradation in the aquatic environment during winter could be retarded significantly. The authors used gas chromatography-mass spectrometry (GC-MS) to check the hypothesis of APnEO biotransformation via oxidation of the alkyl chain, but no metabolites were found which contained carboxylate groups in the alkyl side chain, nor was transformation of the aromatic ring found. The conclusion of this work was that short-chain NPnEO can readily be biotransformed in aerobic environments such as secondary sewage treatment and natural waters chronically polluted with surfactants, and that NPnEC are more persistent than NPnEO (n = 1-3).

Salanitro et al. (1995) developed an automated pressure transducer system to evaluate the ready and ultimate biodegradability of surfactants in 28 days at low concentrations. This test indicated that NP9EO was not readily biodegradable (using the criterion % theoretical CO_2 [$ThCO_2$] > 60%, e.g., Balson and Felix 1995).

Kveštak and Ahel (1995) studied the biotransformation of NPnEO (n = 1-16) under laboratory conditions by using a static die-away method (aerobic conditions). Mixed bacterial cultures from the brackish water layer of the Krka River estuary, Croatia, exhibited a significantly greater ability to transform NPnEO than those from the saline water layer. The biodegradation rates (assuming first-order kinetics) showed a strong temperature dependence. The elimination of higher NPnEOs was followed by a significant formation of the short-chain NPnEOs (n = 1-4). The main lipophilic intermediate formed during the experiments was NP2EO, which accumulated quickly in the medium and was only slowly degraded. Because the experiment was performed under aerobic conditions, NP was not observed. The authors suggested that likely end-products were carboxylates.

Corti et al. (1995) studied the aerobic biodegradation of (pure) 4-(1-nonyl)phenol by a yeast (Candida maltosa) strain isolated from an aerobic sludge sample from a treatment plant that received effluents from a textile plant. The yeast was able to utilize 4-(1-nonyl)phenol as a sole carbon and energy source and there was evidence of attack on the alkyl chain, with the production of 4-acetylphenol. Evidence came from nuclear magnetic resonance (NMR) analyses and the co-elution of the most prominent transformation peak in the gas chromatogram of an extract of the incubation mixture with a sample of authentic 4-acetylphenol.

Salanitro and Diaz (1995) tested the anaerobic degradability of NP9EO (5-50 mg C/g solids/L medium) to methane in an automated pressure transducer serum bottle assay system at 35°C over periods of up to 50 days. At 50 mg/L, degradation was 30-40% theoretical methane (TM). However, it was readily metabolized (70%) to methane at 10 mg C/g solids/L medium, indicating the possibility that higher concentrations were inhibitory to methanogenesis. The authors noted that typical concentrations of NPnEO in sludges in the United States and Europe were up to 2.2 mg/g, perhaps indicating a range of 0.5-2 mg CTAS/g (CTAS [cobalt thiocyanate active substances]). Consequently, they suggested that more appropriate environmental concentrations for testing anaerobic biodegradability of surfactants may be in the range

0.5-10 mg/g digester solids (ca. 0.3-5 mg C/g), rather than the 50-100 mg C/g/L levels recommended previously.

Frassinetti et al. (1996) isolated and characterized three different Gram negative bacteria which can degrade NP9EO (primary degradation) by using it as the sole energy and carbon source in axenic cultures. The source was activated sludge from a tannery wastewater treatment plant. The isolates were identified as a strain of Pseudomonas putida strain Fus1B1, Pseudomonas sp. strain SscB2 and Xanthomonas sp. strain SscB3.

Cady (1996) studied the inherent biodegradability of ^{14}C-NPnEO (n = 1-14) (uniformly ring-labelled) by activated sludge in a laboratory test similar to the U.S. EPA modified semi-continuous activated sludge (SCAS) test. Mineralization of the ^{14}C-NPE to $^{14}CO_2$ was about 9% of the applied dose during a 30-day steady state phase. A further 23% of sludge-incorporated ^{14}C activity was released as $^{14}CO_2$ during the die-away phase. There was extensive degradation to highly polar intermediates, which were not identified. A large portion of the radioactivity in the supernatant was too polar to be extracted from the (acidic) aqueous phase with methylene chloride (but 60% was still recovered). No products were identified in the supernatant.

Williams et al. (1996) used the OECD method 301B (modified Sturm method) to demonstrate that the degradation of NP1EC and NP2EC exceeded 60% $ThCO_2$ after 28 days of incubation, but required more than 10 days to proceed from 10 to 60%. Consequently, the compounds would not be considered as readily biodegradable.

Serak and Zhixing (1997) determined the persistence of ^{14}C-NPE in an aerobic river die-away test in the dark at 20°C for 128 days (patterned after ASTM Standard Method E1279-89). After 128 days, 31-53% of the applied test substance was mineralized to $^{14}CO_2$. The organic-extractable radioactivity decreased from 74% at day 28 to 33% at day 128, and non-extractable radioactivity increased from 12% at day 28 to 46% at day 128. The general conclusion was that NPE could be depleted from the environment due to microbially mediated mineralization.

One facet of the degradation of NPEs that is only rarely considered is the persistence of polyethylene glycol (PEG) degradation products from the ethoxylate moiety of NPEs. A few studies have shown that the PEG residues are more persistent than the parent NPEs (Patterson et al. 1967; Tobin et al. 1976; Maki et al. 1994). For example, Tobin et al. (1976) showed that the polyethoxylate moiety of an alkyl ethoxylate surfactant (Dobanol 25-9) remained essentially undegraded long after the Wickbold analysis indicated removal of 95% of the parent compound.

There are very few studies of the persistence of NPEs or NP in soil, in the laboratory or in the natural environment. Hughes et al. (1996) studied the biodegradation of NP9EO in soil in laboratory biometer experiments and found 57% degradation in 64 days at room temperature, with evidence of aromatic ring destruction, indicating ultimate biodegradability. This test was based on a U.S. Food and Drug Administration test for aerobic degradation in soil which required 50% degradation for a compound to be considered biodegradable in soil; consequently, NP9EO was considered to be biodegradable in soil.

The general conclusion in this section is that although NPEs are not readily biodegradable, they can be biodegraded through a mechanism of stepwise loss of ethoxy groups to lower NPnEO congeners, followed by the production of NPnEC and NP, depending upon experimental conditions. The degradation pathway is shown in Fig. 1. The intermediate and final products of metabolism are more persistent than the parent NPEs, but there is no doubt that such chemicals will also be ultimately biodegraded. In agreement with such an assessment, the U.K. Environment Agency (1997) has estimated a half-life for biodegradation of NP in soil and surface waters of about 30 days.

There are relatively much fewer data on the biodegradability of alkylphenol ethoxylates other than NPEs; consequently, general conclusions cannot be made. Ball et al. (1989) studied the biotransformation of halogenated and nonhalogenated octylphenol polyethoxylate residues under aerobic and anaerobic conditions. Their results indicated that the ethoxy chain of OPEO and OPEC compounds was transformed aerobically to relatively stable OP2EO and OPnEC ($2 \leq n \leq 4$). Further transformation to unidentified products was possible after long adaptation times. However, anaerobic transformation was incomplete even after 190 days of adaptation. Biotransformation of halogenated OPnEO and OPnEC ($n > 2$) resulted predominantly in the formation of the halogenated aromatic compound XOP2EC, which was resistant to biotransformation under both the aerobic and anaerobic conditions studied. In contrast to that study, Williams et al. (1996) used the OECD method 301B (modified Sturm method) to demonstrate that OP1EC and OP2EC would be classified as readily biodegradable. Both compounds tested exceeded 60% theoretical CO_2 ($ThCO_2$) by day 28 and required 10 days or less to proceed from 10 to 60% $ThCO_2$.

DEGRADATION IN SEWAGE TREATMENT PLANTS

It has been noted that full-scale sewage treatment plants (STPs) can provide greater removal efficiencies of NPEs than bench-scale systems, which may be due a greater variety of microbial populations and nutrients in the former (Holt et al. 1992). In general, primary biodegradation of NPEs in STPs is readily achievable, but ultimate biodegradation is not. Substantial differences have been noted in efficiencies of treatment of NPEs and their degradation products among STPs, and such differences have been attributed to the load of NPEs in influent streams, STP design and operating conditions, and such factors as temperature of treatment. In some locations, more persistent products such as NP have been observed in STP final effluents and in receiving waters and this has caused concern, especially with regard to the toxicity of NP to aquatic organisms. (It should be noted that one of the most studied receiving waters, the Glatt River in Switzerland, has relatively low flow [3-8 m^3/s] by North American standards; consequently, STP effluent dilution is low compared to many other systems studied.) In addition, substantial concentrations of NP and other products are found in sludges from STPs. The practice of disposal of sludges at sea may reintroduce NP to aquatic environments. In addition, the leaching of NP and related chemicals from sludge disposal sites and the application of NP-containing sludges to agricultural land, is a matter of concern in that a potential aquatic contamination problem may become, at least partially, a terrestrial contamination problem. Results from some representative studies of NPE treatment in STPs that illustrate the above statements are described below.

Mann and Reid (1971) studied the biodegradation of various ethoxylates with a trickling filter STP in Preston, England, acclimated to inputs of the various detergents. (They used acclimated bacteria because of the suggestion that discrepancies in biodegradability results for NPEs might have been due to the failure to acclimate bacteria. Theywere able to employ acclimation trials by supplying the whole village with detergents.) Ethoxylates based on iso-octylphenol biodegraded in winter to an extent of about 20%. In summer, biodegradation was up to 80%. However, they considered that in general iso-octylphenol ethoxylates were not biodegradable, because effluents showed a considerable tendency to foam even in summer. They used two ethoxylates based on octylphenol (predominantly 1,1,3,3-tetramethylbutylphenol) — one with an average of 8-9 oxyethylene groups per mole (Shell Nonidet P40), and one with an average of 14-15 oxyethylene groups per mole (Shell Nonidet P100).

Stiff et al. (1973) assessed the degree of biodegradability of an octylphenol ethoxylate (Shell Nonidet 40, 8-9 ethoxylate groups per mole, predominantly 1,2,3,3-

tetramethylbutylphenol), as well as two alcohol ethoxylates, using small-scale "porous pot" activated sludge STPs. Nonidet P40 was 95% degraded at 15°C, but at lower temperatures the biodegradability was dependent upon concentration. At 5 mg/L, greater than 90% removal was achieved, but at 20 mg/L the degree of removal fluctuated between 40 and 95% at 11°C and between 20 and 80% at 8°C. The results of this work confirmed the importance of temperature in the biodegradation of Nonidet P40 found by Mann and Reid (1971).

Jones and Nickless (1978) analyzed the influent to, and effluent from, a STP downstream from Bath, England, for nonionic detergents. (Domestic consumption of detergents based on secondary alcohol ethoxylates was known to be fairly light in the area, and so low concentrations of polyethoxylated material were expected.) Their spectroscopic methods (ultraviolet, infrared and nuclear magnetic resonance) did not distinguish between secondary alcohol ethoxylates and alkylphenol ethoxylates. Estimated total concentrations were 700 μg/L for STP influent, 70 μg/L for STP effluent and 8 μg/L for river water (Avon River) downstream from the STP (distance not specified). The alkylphenol ethoxylates were more persistent than the secondary alcohol ethoxylates.

Among the earliest reports of degradation products of NPEs in STP effluents, Giger et al. (1981) and Stephanou and Giger (1982) found NP, NP1EO, NP2EO and NP3EO in secondary sewage effluents in Switzerland and in receiving waters (i.e., the River Glatt, which flows through a densely populated area east of Zurich). No quantitative data were presented, but the fact that such species were found, but not higher ethoxylates, indicates that they are more persistent than their higher homologues.

Reinhard et al. (1982) provided evidence that alkylphenol ethoxylates can be brominated to a slight extent during the chlorination stage of wastewater treatment and that the corresponding carboxylates can be produced in sewage treatment. Stephanou (1985) has also shown that brominated and chlorinated AP1EO and AP2EO and AP1EC could be produced from alkylphenol polyethoxylates during treated water chlorination. Such metabolites were found in secondary effluent samples from Swiss STPs (conventional mechanical-biological activated sludge plants).

Giger et al. (1984) concluded that the large amount of NP they found in anaerobically treated sewage sludge (mean 1 g/kg dry weight) originated from NPE and proposed the following pathway for its formation: during aerobic treatment of wastewater, the polyethoxylate chains of the NPE are shortened by microbial transformation. The resulting NP1EO and NP2EO appear to be less biodegradable. These metabolites are less water-soluble and they are partially removed from the water stream by adsorption onto sludge. When the sludge is stabilized, the NP1EO and NP2EO degrade further to NP, which accumulates in the digested sludge. It should be noted that NP can also be produced under aerobic conditions, albeit at lower concentrations.

Ahel and Giger (1985a) found 1000 mg/kg NP in anaerobically digested sludge and 467 μg/L NP in effluent from the anaerobic sludge digester, from the Glatt STP, Zürich, Switzerland. Earlier work had not detected NP in laboratory biodegradation experiments of NPEOs, but the finding of high NP levels in anaerobically stabilized sewage sludge in an earlier study (Giger et al. 1984) and in digester effluents (this study) indicated that formation of NP by anaerobic processes during wastewater and sludge treatment was occurring.

Ahel and Giger (1985b) studied the biodegradation of Marlophen 810 NP surfactant in a laboratory-scale continuously operated biodegradation apparatus according to the OECD-coupled units test for simulating aerobic sewage treatment. In the influent containing Marlophen 810, NPnEO oligomers with 1-17 ethoxy units were observed. In

the effluent from the apparatus only NPEO with less than four ethoxy groups were present. The authors stated that NPnEC were probably also present in the effluent, but no evidence was provided. Similar observations were made with regard to influent to, and effluent from, the Glatt STP, Zürich, Switzerland, and river water downstream from that STP. A comparison of the removal efficiencies of NPEO by five Swiss STPs showed that mechanical treatment (simple settling) had little effect on total NPEO concentrations, but that biological treatment (activated sludge treatment) reduced total NPEO from levels of 840-2250 μg/L to 40-370 μg/L. However, the lower NPEOs were more persistent. The authors also found (but did not provide evidence for) carboxylated NPEO species.

Brown et al. (1986) applied an optimized bismuth iodide active substance (BIAS) procedure in a monitoring study to determine the removal of nonionic surfactants in an activated sludge plant. The results showed that typically 1-2 mg/L of alkylphenol ethoxylate (expressed as NPE with an average of 9-10 ethoxylate units) was present in Hochdahl (Düsseldorf, Germany) raw/settled sewage. The removal of this surfactant in the complete treatment averaged > 90% in this activated sludge treatment plant. Brown et al. (1987) later applied the optimized BIAS procedure in a monitoring study to determine the removal of nonionic surfactants in a trickling filter plant (at Hösel-Dickelsbach, Germany) under winter (March) and summer (September) conditions. There was no temperature effect for methylene blue active substances (MBAS — for cationic surfactants) removal (88-89% removal in March and September). However, the BIAS removal (for nonionic surfactants) was lower (81±3%) in March than in September (88±1%). The mean removal of alkylphenol ethoxylates was 70% in March and 75% in September. It should be noted that concentrations of alkylphenol ethoxylates determined by high performance liquid chromatography (HPLC) are not strictly comparable with those obtained from BIAS analyses because the latter do not determine NPnEO with $n < 6$.

Giger et al. (1986) demonstrated the presence of NPnEO (n = 3-20) in raw and primary sewage effluents of STPs in Switzerland at concentrations of 400-2200 μg/L, corresponding to 3-10% of the total dissolved organic carbon. The surfactant molecules themselves were eliminated efficiently, generally more than 90% by activated sludge treatment. Biologically treated sewage effluents contained NP, NP1EO and NP2EO at concentrations of 10-100 nmol/L. The carboxylated derivatives showed increased abundances after activated sludge treatment (200-3000 nmol/L).

Giger et al. (1987) analyzed effluents and sludges from 13 Swiss STPs for NPEs, NP1EO, NP2EO, NP1EC, NP2EC and NP. Parent NPEs were efficiently removed by the activated sludge treatment. APnEO (n = 3-20) concentrations in influents were in the range 400-2200 μg/L, and the bulk of these APEO were NPEO, with smaller amounts of 2-nonyl-, 4-decyl-and 4-octylphenol polyethoxylates. Poisson distributions generally centered at AP(9-10)EO were found in surfactants used in laundry detergents in Switzerland. AP(1-2)EO were very minor constituents (less than 1%) and there was no NP. Raw wastewaters and primary effluents, however, typically contained bimodal NPnEO oligomer distributions, with one maximum at n = 1 or 2, and the second maximum at about n = 7, and NP was present in substantial concentrations. Aerobic and anaerobic biotransformation processes occurring in the sewers and during mechanical treatment (i.e., settling) were thought responsible. The secondary effluent of plants, operating at low-loading, nitrifying conditions or high-loading non-nitrifying conditions, showed a pronounced skewing of the distribution towards one maximum at n = 1 to 2. Comparisons of concentrations in primary and secondary effluents of four STPs showed that NPnEO (n = 3-20) were substantially removed in the secondary effluents, NP1EO and NP2EO concentrations declined or increased, NP concentrations

decreased, while NP1EC and NP2EC concentrations always increased. A more detailed examination of the Uster STP (which had tertiary treatment) showed the same trends, and showed considerable buildup of NP in activated sludge and (most dramatically) in digested sludge. There was also some production of NP1EO and NP2EO in digested sludge.

Ahel et al. (1987) determined NP1EC and NP2EC in influents and effluents of mechanical-biological STPs and in the River Glatt in Switzerland. High concentrations of NP1EC and NP2EC were observed in secondary sewage effluents (71-330 μg/L), whereas untreated sewage and primary effluents contained much lower levels (<1-17 μg/L). Considerable concentrations of NPnEC (2-116 μg/L) were found in the Glatt River. The sums of concentrations of NP1EC and NP2EC were higher in the Glatt River than sums of concentrations of NP, NP1EO and NP2EO, and [NP2EC] > [NP1EC], as was the case for STP effluents. The total [NPEC] was up to 1.9% of the DOC in the river. No compounds were detected in which a methyl group of the branched chain was carboxylated, as had earlier been suggested by others. NPEOs were more abundant in untreated sewage and primary effluents than the NPEC. The situation was reversed in the secondary effluent. This means that the typical metabolites of NPEs under aerobic-activated sludge treatment in the STPs examined were NPEC, whereas the concentration of NP1EO and NP2EO in secondary effluents was usually lower than in untreated sewage and in the primary effluents. Thus biotransformation of NP1EO and NP2EO during secondary treatment via carboxylation into the corresponding NPECs can be inferred. It should be noted that NPECs are less lipophilic than NPEOs.

Marcomini et al. (1988a) determined dissolved and particulate NP, NP1EO and NP2EO in raw sewage, primary effluent, secondary effluent, and primary and secondary sludge of the Glatt STP, Zürich, Switzerland, on two consecutive days in May 1986. There was substantial accumulation of NP (especially), NP1EO and NP2EO in anaerobically digested sludge. NP1EO and NP2EO were poorly removed in the secondary effluent.

Brunner et al. (1988) determined fluxes of NP, NP1EO and NP2EO through sewage and sludge treatment at 29 Swiss STPs. Sludges stabilized by aerobic treatment contained less NP than those treated anaerobically. About 50% of the NPnEO in sewage was transformed to NP and accumulated in the digested sludge. Both NP1EO and NP2EO were partially degraded during aerobic and anaerobic sewage and sludge treatment and were precursors for NP in sludge. The fact that the load of NP1EO and NP2EO in the raw sludge could be higher than in the raw sewage implies that NPnEO produce NP1EO and NP2EO when they are degraded during aerobic wastewater treatment. NPECs were not determined in this work.

An environmental assessment of the Canadian textile industry in 1985-86 (Chen 1989), including a detailed examination of the effluents of 10 mills producing a variety of fabrics, showed that secondary (biological) treatment was up to 90% effective in reducing parent nonionic surfactant concentrations, as determined by the CTAS technique. However, concentrations of degradation products were not determined.

Kubeck and Naylor (1990) noted that exposure of NPE to oxygen during the course of extraction could cause degradation, with production of abnormally high levels of lower NPEO oligomers. This phenomenon may have caused experimental artifacts in studies in which proper preservation procedures were not employed. These authors showed that in a STP in High Point, N.C., U.S.A., the efficiency of removal of all NPEs (n = 1-18) was γ 90%.

Giger and Ahel (1991) estimated for the Zürich-Glatt STP that 60-65% of all nonylphenolic compounds (i.e., compounds still having the alkylbenzene moiety) which

enter sewage treatment are released into the environment, 38-42% being discharged via secondary effluents and 21-23% via digested sewage sludge.

Clark et al. (1991) analyzed effluents from three publicly owned treatment works (POTWs) in New Jersey. POTW-A was located in a rural area with no known industrial contributor of waste. POTW-B had 73% (by volume) domestic waste and 27% industrial waste (pharmaceutical, yeast, paper processing and chemical manufacturing). POTW-C had 82% (by volume) domestic waste and 18% industrial waste (from 300 industries, mostly textile and dye manufacturers). POTW-B was about three times larger than POTW-A and POTW-C was about three times larger than POTW-B. OP, NP, NP2EO, NP3EO, NP4EO and NP5EO were generally found at < 15 μg/L. NP2EO was found at 120 μg/L and 75 μg/L in effluent from POTW-C. NP5EO was also found at concentrations as high as 25 μg/L in effluent from POTW-C.

Birch (1991) used a porous pot activated sludge reactor to demonstrate the effects of temperature and sludge retention time on the efficiency of degradation of a number of chemicals, including NPnEO (identity not given) (concentration determined by bismuth iodide active substance [BIAS], and thus only parent compound). Primary degradation was extensive at 15°C and 11°C, but at 7°C, high levels of the parent surfactant were found in plants operating at sludge retention times (SRT) of 2, 4 and 6 days. According to the author, the results suggested a critical SRT of about 6 days at 11-15°C, and the results were consistent with the variation in the biodegradability of these nonionic surfactants observed by a number of workers during the winter months.

Zoller (1992) noted that there was very high use of NPEs in Israel and claimed that the removal efficiencies of nonionic detergents by Israeli STPs was about 69-81%. He later claimed 97% removal by combined activated sludge/soil aquifer treatment, but noted that a residual 25 μg/L of “hard” nonionic surfactant was cause for concern, because it was reclaimed and then used for irrigation (Zoller 1994).

Naylor (1992) found high removal efficiencies of NPE by seven U.S. wastewater treatment plants using biological treatment. Removal was > 92% in all except one plant, where removal was 84%. In two North Carolina plants, the effluent showed no skewing of NPE oligomer distribution and no enhancement of NP or NP1EO levels. In a Midwestern U.S. STP, the anaerobic sludge had only 10 mg/kg NP dry weight, compared to values as high as 0.1% in Switzerland reported earlier. This work and later work (Naylor 1995) indicated that digested sludge in some U.S. STPs is not a major sink for NP.

Ahel et al. (1994b) studied the behaviour of NPnEO in several fullscale mechanical-biological STPs in the Glatt Valley, Switzerland. Untreated sewage and primary effluents contained considerable amounts of surfactant-derived nonylphenolic compounds (3.0-9.6% of the DOC). Parent NPnEO (n = 3-20) were efficiently eliminated during biological treatment (average of 72%). However, the overall rate of biodegradation was limited due to the formation of biorefractory metabolites, including NP, NP1EO and NP2EO, and NPnEC. As expected, the highest elimination rates were achieved in the STPs characterized by low sludge-loading rates and nitrifying conditions. They estimated that at least 60-65% of all nonylphenol compounds that have entered sewage treatment were released into the environment (either in secondary effluent or sludge). Approximately 19% of all nonylphenolic compounds introduced to STPs was released to the environment in the form of NPEC, 11% in the form of NP1EO and NP2EO, 25% in the form of NP and 8% as untransformed NPnEO. Almost all of the released NPnEO and NPEC, as well as most of the NP1EO and NP2EO, were discharged into natural receiving waters via secondary effluents, which were responsible for 60% of the total input of nonylphenolic compounds into the environment. In contrast, most NP (>90%) was disposed to the environment via

digested sewage sludge, representing about 40% of the total load. The authors noted that from an ecotoxicological point of view, the most critical alkylphenolic constituent was NP, which originated predominantly during anaerobic sludge treatment. Only a minor portion of NP reached receiving waters directly via secondary effluents. The sludge-bound NP, which is often disposed to the environment through application of sludge onto soil, can reach natural waters through runoff and leaching. It should also be noted that the practice of disposal of sludges at sea can also introduce NP to aquatic environments.

Di Corcia et al. (1994) provided evidence for the production of NPnEC, where n = 3-10, in effluents from an Italian secondary treatment STP. Total NPEC (NP1-3EC and NP>3EC) concentrations in effluents were up to 145 μg/L.

Field and Reed (1996) found in a study of the occurrence of NPnEC in effluents that in 14 paper mill effluents NP2EC was the dominant oligomer. The average proportions of NPECs in paper mill effluents were NP1EC (16%), NP2EC (72%), NP3EC (10%) and NP4EC (2%), which gives an indication of relative stabilities. The authors noted that typically, industrial wastewater treatment is characterized by higher temperatures, increased hydraulic residence times and greater degrees of acclimation than that of municipal STPs. Because municipal STPs operate at ambient temperatures, more seasonal variation in effluent composition could be expected from municipal STPs than from industrial effluents. They also noted that the concentrations of NPECs in the Fox River and other U.S. rivers are approximately a factor of 10 lower than those reported for the Glatt River in Switzerland, presumably due to dilution. The Glatt is a smaller river with a discharge of 3-8 m^3/s, as compared to the Fox River, Wisc., U.S.A., with a discharge of 41 m^3/s.

Paxéus and Schröder (1996) found removal efficiencies for NP9EO of > 90% (primary degradation) in two small Swedish STPs. NP removal was < 10% in one plant and 38% in another. Sludges contained 20-26 mg NP/kg dry weight of sludge.

Weeks et al. (1996), in discussing environmental aspects of NPEs and NP, noted that, in contrast to the results of Ahel et al. (1994c) in Switzerland that showed NPnEC to predominate over the NPE oligomers and NP itself, studies in the United States had found levels of NP1EC and NP2EC that are about the same as NP, NP1EO and NP2EO. They also noted cases in the U.S. in which treatment of NPEs in wastewater was quite efficient, with little residue remaining in sludge.

Mackay et al. (1997) found that levels of NPEO and OPEO up to 450 μg/L in the influent to two tertiary STPs in Australia were reduced below detection levels (5 μg/L) in the effluents, but no details were given of the tertiary treatment processes.

Fytianos et al. (1997) found the efficiency of removal (defined as biodegradation plus adsorption to sludge) of NPEs from sewage from the secondary STP of Thessaloniki, Greece, to be 92-97% over a 6-month period.

Lee et al. (1998) determined concentrations of NP1EC and OP1EC in influents, primary effluents and final effluents of some Canadian STPs. For NP1EC, concentrations in influents were in the range 0.9-8.3 μg/L (n = 5, mean = 3.6 ± 3.3 μg/L, median = 1.6 μg/L), concentrations in primary effluents were in the range 2.4-17.7 μg/L (n = 10, mean = 6.2 ± 4.7 μg/L, median = 4.2 μg/L), and concentrations in final effluents were in the range 3.2-703 μg/L (n = 10, mean = 82.9 ± 218.1 μg/L, median = 13.9 μg/L). NP2EC concentrations were estimated, not determined, but there was a general similar trend of production in the STPs. The same was true of OP1EC and OP2EC.

Lee and Peart (1998) determined the occurrence and elimination of NPnEO and metabolites in municipal wastewater and effluents from a Canadian STP using primary and secondary treatment. Twenty-four hour composite raw sewage, primary effluent

and final effluent samples were collected monthly over one year in 1997-98. Compounds determined were NPnEO (n = 1-17), NP and NPnEC (n = 1 and 2). While about 85% of the total alkylphenolic compounds in raw sewage are ethoxylates, the major component (nearly 80%) in the final effluent was in the form of carboxylic acids. During the study period, the median total alkylphenolic compound concentrations in raw sewage and final effluent were 526 and 248 nmol/L, respectively, indicating an overall elimination rate of 53%. The estimated median daily discharge of nonylphenolic compounds to the aquatic environment was 20 moles. These data suggested that conventional sewage treatment is ineffective in the removal of surfactant-derived metabolites. The overall elimination rate of 53% was similar to the mean elimination rate of 59% for all nonylphenolic compounds observed by Ahel et al. (1994b) for 11 STPs in Switzerland.

The Water Technology International Corporation (1998b) studied the degradation of NPnEO (n = 3-17) in two Canadian STPs in 1997. STP A was monitored for 2 weeks and STP B (the same STP studied by Lee and Peart 1998) for only 2 days. STP A is a conventional activated sludge secondary treatment plant, including nitrification, followed by tertiary treatment and UV disinfection. STP B employs a conventional non-nitrifying activated sludge process and disinfection by chlorination in the months of May to October only. It should also be noted that STP A receives a high load of NPnEO because of significant textile industry discharges. In this study, total AP was the sum of NP, NP1EO, NP2EO, NP(3-17)EO, NP1EC, NP2EC, OP, OP1EC and OP2EC. For STP A, the total alkylphenolic compounds mass loading rate in the treated effluent plus sludge releases was substantially lower than the average influent mass loading of 44 kg/d. With average discharge loadings of 1.2 kg/d and 6.4 kg/d in the final effluent and digested sludge, respectively, there was a net destruction efficiency of 83%. Of the total average discharge (final effluent plus sludge), 84% of the total alkylphenolic compounds were in the sludge. Of the total alkylphenolic compounds in the sludge, 75% was NP, 22% was APEO and 2% was APEC. Of the total alkylphenolic compounds in the final effluent, 75% was APEC, 21% was APEO and 3% was NP. For STP B, the total alkylphenolic compound mass loading rate in the treated effluent plus sludge releases was also substantially lower than the influent mass loading of 40.4 kg/d. With discharge loadings of 5.6 kg/d and 5.9 kg/d in the final effluent and digested sludge, respectively, there was a net destruction efficiency of 72%. Of the total discharge (final effluent plus sludge), 51% of the total alkylphenolic compounds were in the sludge. Of the total alkylphenolic compounds in the sludge, 56% was NP, 37% was APEO and 4% was APEC. Of the total alkylphenolic compounds in the final effluent, 69% was APEC, 29% was APEO and 2% was NP.

The general conclusion in this section is that there can be a wide range in treatment efficiencies of NPEs in the course of wastewater treatment. Primary biodegradation as measured by loss of surfactant properties or determination of parent compound is facile. However, the biodegradation mechanism, involving loss of ethoxy groups, the production of NP1EO and NP2EO and their carboxylate derivatives NP1EC and NP2EC, and the final product, NP, does produce chemicals which are more persistent than the parent NPEs and which are not completely degraded during sewage treatment. NP (in particular) and NP1EO and NP2EO are more lipophilic than the parent NPEs and tend to accumulate in sludges, while NPnECs are generally found in the final effluents, sometimes at much higher concentrations than other nonylphenolic compounds. NP, NP1EO and NP2EO can also be found in such effluents and have also been found in receiving waters. There is also evidence for the halogenation of some of these products in STPs that use chlorine for disinfection (see also later sections). Some STPs discharge significant amounts of NPE degradation

products in their final effluents and digested sludges compared to what enters the STP plant. Others degrade NPEs very efficiently. The differences in treatment efficiency of NPEs and their degradation products among STPs, have been attributed to the load of NPEs in influent streams, STP design and operating conditions, and such factors as temperature of treatment (e.g., the efficiency of NPE treatment in trickling filter STPs is significantly reduced in the winter compared to the summer). Birch (1991) and Watkinson and Holt (1991) have noted that a critical control parameter for the treatment of NPEs in STPs with activated sludge plants is the sludge retention time (SRT). This parameter dictates the necessary growth rate for the competent organisms within the total microbial population. When the growth rate of the organisms is less than the SRT the competent organisms are washed out of the system and little treatment of the specific substance takes place. The growth rate of organisms is influenced by temperature and thus a combination of decreasing SRT and decreasing temperature makes the biodegrading system less effective. Watkinson and Holt (1991) noted that the normal range of SRTs for activated sludge plants would appear to be in the range 6-20 days. Ahel et al. (1994b) noted that the highest NPE elimination rates were achieved in the STPs characterized by low sludge-loading rates and nitrifying conditions, and this was confirmed in a limited study of two Canadian STPs (Water Technology International Corporation 1998). It should also be noted that there may be substantial differences in treatment efficiencies of NPE between dedicated industrial wastewater treatment facilities and municipal STPs. Field and Reed (1996) have noted that industrial wastewater treatment can be characterized by higher temperatures, increased hydraulic residence times and greater degrees of acclimation than that of municipal STPs. Because municipal STPs operate at ambient temperatures, more seasonal variation in effluent composition could be expected from municipal STPs than from industrial effluents.

DEGRADATION AND PERSISTENCE IN AQUATIC ECOSYSTEMS

There are relatively few studies of the persistence and fate of NPEs and NP in aquatic ecosystems compared to the number of studies on biodegradation in STPs. Some of these studies are described below.

Using methods that only assessed primary biodegradation, Schöberl and Mann (1976) found that NP9EO was degraded by 33-36% at 20-23°C in freshwater over 50 days, and by 95% in sea water over 25 days. At 3-4°C, degradation was about 37% in freshwater over 50 days, and only 15% in sea water over 50 days.

Yoshimura (1986) studied the biological degradation of NP9EO in river water/sediment mixtures and observed more than 98% degradation of NP9EO in a standing water phase in 5 days and in a stirred water phase in 10 days. NP1EO, NP2EO and NP3EO were found at 5 and 10 days, at low concentrations (< 0.4 mg/L, compared to an initial NP9EO concentration of about 20 mg/L). Some unidentified related chemicals remained after 30 days of incubation in water. NP1EC and NP2EC were identified as intermediates and were much less toxic than NP to fish in an acute test.

Ekelund et al. (1993) studied the biodegradation of NP in sea water and sediment, using ^{14}C ring-labeled NP at 11 μg/L. Degradation in the absence of sediment was very slow during the first 3-4 weeks, but increased after 28 days, indicating the need for microbial acclimation. There was 50% degradation by 58 days. The authors contended that for minimally polluted environments, the first phase of their laboratory results would be representative and would indicate some persistence. In the presence of sediment, there was no lag time for degradation, with 40% degradation in 58 days under aerobic conditions (20% under anaerobic conditions). Overall, these results would indicate some persistence in water and sediment.

Kveštak et al. (1994) determined the input and distribution of APnEO in a stratified estuary, the Krka River estuary in Croatia. Partitioning of the lower ethoxylated forms to suspended solids was observed in the sewage and in the estuarine water. The oligomer distribution centred at n = 6-7 (N.B. the sewage in this case from the city of Šibenik was untreated). The extent of biodegradation appeared to be slower than for freshwater systems, but there were no kinetics derived, just a comparison of profiles with distance from shore and at different times of the year.

Ahel et al. (1994c) studied the behaviour of NPnEO and their metabolites in the Glatt River, Switzerland. The majority of nonylphenolic compounds in the Glatt River were in the form of persistent metabolites (relative to NPEs), the most abundant being the NPEC. Biotransformation appeared to be the predominant mechanism determining the fate of nonylphenolic compounds. The Glatt River, a tributary to the Rhine River, is small, with a discharge rate of 3-9 m^3/s. In the lower reaches of the Glatt River, up to 20% of the water is treated wastewater. The most abundant compounds in river water were NP1EC and NP2EC, followed by NP1EO and NP2EO. NP was significantly less abundant and NPnEO (n = 3-20) even less. The ratios of the specific degradation products of NPnEO in the river water were similar to those in secondary effluents from the various STPs in the valley. In the most polluted part of the river 0.4-1% of the total DOC was in the form of nonylphenolic compounds. The authors estimated the degree of biological transformation of the various species in a 35-km reach of the river to be 24%, with a net accumulation of NP1EC and NP2EC. They also indicated that NP was found in various Swiss rivers at concentrations up to 100 μg/L. In sediments, NP was a predominant species.

Ahel et al. (1994d) determined the kinetics of photochemical degradation of OP, NP and NP1EO in natural waters. For NP, a photolysis (disappearance) half-life of 10-15 hours in surface water was observed (OP half-life about the same). Photolysis at 20-25 cm depth in lake water (dissolved organic carbon concentration 4 mg/L) was 1.5 times slower. Photochemical degradation of NP1EO in sunlight was much slower, but not quantified. Thus, sunlight photolysis could be a significant degradation pathway for NP in shallow waters. Sherrard et al. (1996) studied the degradation of NP(8-9)EO using heterogeneous photocatalysis with TiO_2. Identified intermediates suggested that the ethylene oxide chain was more susceptible to degradation than aliphatic or aromatic moieties. After 96 hours of irradiation, the most abundant oligomer shifted from n = 9 to n = 6-7. The isomer peak pattern within each homologue was unchanged, suggesting little degradation of the aliphatic or aromatic moiety occurred, and from this it was inferred that only cleavage of ethylene oxide units, particularly the terminal units, had occurred. The gas chromatograms of the aqueous phase taken after 172 and 250 hours of irradiation showed almost total disappearance of the original homologous series, with only a small group of early eluting peaks remaining.

Ahel et al. (1996) studied the behaviour of various relatively persistent NPnEO metabolites during infiltration of river water to groundwater in the Glatt River and Sitter River, Switzerland. In general, NP1EO, NP2EO and NP were more efficiently removed during infiltration, but not NP1EC and NP2EC. Lower temperatures strongly reduced NP adsorption to soil material in the aquifer. In one case water 130 m from the Glatt River at a pumping station had total nonylphenolic compound concentrations of up to 7 μg/L. Elimination efficiencies were in the order NP2EO > NP1EO > NP > NP1EC = NP2EC.

Maki et al. (1996) studied the biodegradation of NP(9.5)EO by bacteria from river water in Japan and concluded that NP1EC was the most probable ultimate biodegradation product of NPE under aerobic conditions.

Quiroga et al. (1996) studied the biodegradation of NP15EO in river water using the "river die-away test" at concentrations of 1.5, 3 and 7 mg/L. Primary biodegradation

was 85-90% and by day 6 of 17 days nearly all the homologues with n > 2 had disappeared. Carboxylates were not determined.

Heinis et al. (1998) studied the persistence and distribution of NP in littoral enclosures following repeated applications in a mesotrophic pond in Minnesota, U.S.A. NP partitioned to enclosure wall material (polyolefin plastic), macrophytes and sediment within 2 days of subsurface application of the chemical to water. Nominal aqueous concentrations tested were in the range 0-300 μg/L, and actual concentrations were determined. The sediment was the primary sink for NP 440 days after the initial application, with a concentration of about 2 mg/kg at the 300 μg/L treatment. Mean sediment DT_{50} and DT_{95} (DT: dissipation time) values were 66 (range 28-104) and 401 (range 354-448) days, respectively, for the 30 and 300 μg/L treatments and indicated a long persistence for NP. Macrophytes accumulated maximal concentrations of NP of 11.5 and 139 mg/kg within 2 days after the application period at the 30 and 300 μg/L treatment levels, respectively, and corresponding mean DT_{50} and DT_{95} estimates were 10 and 189 days, respectively.

As mentioned above, NP itself (not NPEs) had been used from the mid-1970s to 1981 in aminocarb insecticide sprays against the spruce budworm in eastern Canada, and there have been a few studies of its distribution, dissipation and persistence after aerial sprays. Ernst et al. (1980) monitored NP in surface water (using a bottle for collection at the surface in order to get as much of the surface slick as possible) of Britt Brook Lake, New Brunswick, that was in a forest sprayed with an aminocarb formulation containing NP. There was a 400 m buffer between the sprayed area and the lake. The NP concentration was as high as 12 μg/L 1 hour after the spray and declined to < 1 μg/L between 10 and 66 hours after the spray. In laboratory experiments they found substantial loss of NP from exposure tanks over 24-48 hours, which may have been due to volatilization (aided by aeration) and/or adsorption to container walls. Holmes and Kingsbury (1980) determined the persistence of NP sprayed on water at 0.47 L/ha, simulating a forest spray. They found no residues of NP in flowing or standing water after 3 days. Sundaram et al. (1980) determined residues of NP in spruce foliage, forest soil, stream water and sediment after its aerial application at 0.47 L/ha. Residues in white spruce foliage were the highest 1 hour after spraying (18.9 mg/kg) and decreased by 40% in the next 2 hours. Only 3% remained after 30 days and no detectable levels (< 0.20 mg/kg) were found after 62 days. No residues were detected in any forest soil sample collected after spraying. NP residues were about 9 μg/L in the stream water 1 hour after application (except one sample contaminated by a surface slick, yielding a concentration of 1100 μg/L) and declined by 50% in the next two hours. Only trace amounts (< 2 μg/L) were detected after 5 days. Residues at trace levels (< 0.1 mg/kg) were detected in only one sediment sample taken 4 hours after spraying. Sundaram and Szeto (1981) determined the persistence of NP in natural water and sediment. In water-only experiments at 16°C, the half-life for dissipation of NP from open containers was 2.5 d, which they ascribed to volatilization (the possibility of adsorption to container walls was not discussed) and the half-life in closed containers was 16 days. They showed that NP was adsorbed to sediments in test containers. The importance of microbial degradation was shown by the fact that NP concentrations in sediment were reduced to 20% after 70 days, but it persisted unchanged in autoclaved sediment over 70 days. These studies indicate that NP is not persistent in water or sediment, but rigorous mass balances in the test systems were not attempted. It is possible that some of the losses of NP were due to physical redistribution rather than degradation. The inference that volatilization of NP may have been a route of dissipation in some of these studies contradicts the prediction that volatilization from water would not be significant as indicated by the low

Henry's Law constant for NP (11.02 Pa m^3/mol, U.K. Environment Agency 1997). However, it is possible that NP sprayed on the surface of water may volatilize more quickly than NP in subsurface water as introduced by the usual means, i.e., in STP effluents. For example, it has been shown for some aerially applied pesticides such as fenitrothion and deltamethrin that volatilization from the surface of sprayed water is much faster than volatilization from subsurface water (Maguire 1991).

The general conclusion in this section is, as expected from the studies of degradation in STPs, that primary biodegradation of NPEs is faster than ultimate degradation of more persistent products such as NP1EO, NP2EO, NP1EC, NP2EC and NP. Microbial acclimation to such chemicals is required for optimal degradation efficiencies. Sunlight photodegradation of such products is also expected to be important. In aquatic ecosystems, it appears that parent NPEs are not persistent, but some degradation products may have moderate persistence, especially under anaerobic conditions. (It should be noted that the U.K. Environment Agency [1997] estimated a half-life for biodegradation in surface water of about 30 days.) The recent results of Heinis et al. (1998) indicate that NP can be moderately persistent in sediments. There is a need for mass balance studies that take into account the relative importance of biodegradation and sunlight photodegradation, as well as adsorption to suspended solids and bed sediment, aerobic and anaerobic conditions, and temperature effects. To the extent that NPEs are used in aerially applied pesticide formulations, there is a need to determine their atmospheric chemistry, photochemistry and fate.

DEGRADATION AND PERSISTENCE OF NPES, NP AND RELATED CHEMICALS IN OTHER MEDIA

There are relatively few studies on the persistence of APEs and AP in media other than aquatic ecosystems. Several studies on their persistence in groundwater and soil are described below.

In groundwater, there is only limited opportunity for biodegradation compared to surface water, and consequently chemicals such as NP and other alkylphenols may persist much longer. Reinhard et al. (1984) found OP and OP1EO in two landfill leachate plumes, which indicates some stability. Barber et al. (1988) found NP in sewage-contaminated groundwater in Massachusetts, U.S.A., with a possible residence time of 30 years. In some areas septic systems may be a significant source of APEs to groundwater (Rudel et al. 1998). Fujita et al. (1996) evaluated two different types of dissolved organic carbon characteristics, aggregate and specific trace organic characteristics, as possible indicators of wastewater origin in considerations of groundwater recharge. The identification and monitoring of trace organic compounds such as ethylenediamine tetraacetic acid (EDTA) and APECs are useful because these compounds can be unequivocally related to authropogenic sources. They noted that the alkyl group of APECs may be carboxylated. (They had earlier found carboxyalkylphenoxy ethoxy carboxylates and their brominated analogs in low μg/L concentrations in tertiary treated wastewater effluents in Orange County, Calif., U.S.A., Ding et al. [1996].) Many of the APECs they found were brominated; bromination of the aromatic ring can occur during chlorine disinfection in the presence of bromide. In this study, total APECs were in the low μg/L range. APECs persist in groundwater at site M21 in Orange County, Calif., U.S.A. after 1-2 months travel time, and preliminary results indicated that these compounds may persist even after 2-3 years of residence time in the groundwater. However, brominated APECs were not detected in the groundwater. Fujita and Reinhard (1997) studied the aerobic biological transformation of OP1EC (single isomer: 4-(1,1,3,3)-tetramethylbutylphenoxyacetic acid) and its brominated analog BrOP1EC by groundwater enrichment cultures. The metabolite

2,4,4-trimethyl1-2-pentanol was found in stoichiometric quantities in OP1EC-metabolizing cultures, representing the intact alkyl side chain as a tertiary alcohol. BrOP1EC was transformed by the OP1EC-utilizing cultures only if OP1EC was simultaneously metabolized, suggesting a cometabolic transformation mechanism. Brominated octylphenol and (tentatively) 2-amino-3-bromo-5-(1,1,3,3-tetramethylbutyl)phenol were identified as products. They noted that APECs can persist in treated wastewater at low μg/L levels even after granular activated carbon contact or reverse osmosis, and that they have also been detected in finished drinking water.

Trocmé et al. (1988) studied the toxicity (i.e., effects on CO_2 evolution and biomass adenosine triphosphate [ATP]) and persistence of NP during incubation in a compost-sandstone mixture. NP depressed CO_2 production significantly only at high concentrations (1000 mg/kg). Biomass ATP declined progressively after the fifth day. At 100 mg/kg, no toxic effects were detected. After a lag phase of 5 days at 25°C, NP disappeared readily upon incubation at 100 mg/kg (half-life about 15 days), but persisted at 1000 mg/kg (50% degradation by day 10, but no subsequent degradation for the duration of the 40 day test) and persistence increased under aseptic conditions. Volatilization was insignificant.

Marcomini et al. (1988b, 1989) studied the fate of NPEs and NP in sludge-amended soil and sludge-only landfills. In sludge-amended soil, the initial concentrations of NP, NP1EO and NP2EO were 4.7, 1.1 and 0.01 mg/kg dry weight. After 320 days, the concentrations were 0.5, 0.1 and 0.01 mg/kg dry weight, respectively. The kinetics appeared to be triphasic. Concentrations fell to 20% of initial concentrations within 3 weeks, followed by a slower decline for the next 9 weeks, with a plateau over the following 7 months. There was some measure of persistence over the entire 320-day period, with implications for carry-over from year to year. High concentrations were found in sludge-only landfills (up to 375 mg/kg dry weight for NP). Marcomini et al. (1991) further noted that the biodegradation of NP and NP1EO in two sludge-only landfills was much faster under aerobic conditions than under anaerobic conditions, where biodegradation was minimal over 15 years. In another article, Marcomini (1991) noted that in landfills under anaerobic conditions the persistence of NP, NP1EO and NP2EO is greatly increased and that they behave conservatively over a period of 30 years.

The Water Technology International Corporation (1998a) applied dewatered sewage biosolids from the Guelph, Ontario, STP at rates of 0, 8 (the maximum allowed under Ontario legislation), 20 and 40 tonne/ha to test plots, and monitored concentrations of NPEs and degradation products. Initial concentrations in the sludge were about 450 mg/kg NP, 15 mg/kg OP, no detected NP1EO, 10 mg/kg NP2EO, 350 mg/kg NP[3-17]EO and $\leq$ 15 mg/kg APEC. No products were identified at 8 t/ha after 121 days in the period July to October 1997.

Bokern et al. (1998) have demonstrated that 4-n-NP can be taken up from soils by some plants and can be metabolized to polar compounds.

Leenheer et al. (1991) addressed the question of the environmental occurrence of poly(ethylene glycol) (PEG) residues from nonionic surfactants. They claimed that there were conflicting reports in the literature about the biodegradability of the polyethoxylate chain, with reported half-lives in various aquatic systems of days to months. They found total PEG residues in the Mississippi River ranging from non-detectable to 145 μg/L. Crescenzi et al. (1997) recently showed the widespread occurrence of PEG residues in STP influents and effluents in Rome, Italy. Although they are fairly efficiently degraded in STPs, some PEG residues were found in effluents. The authors found PEG residues at ng/L concentrations in sea water 16 nautical miles from the Italian coast and in five groundwater samples collected at depths of 60-208 m.

Based on the limited data available, NP and the lower ethoxylates and carboxylates are persistent in groundwater. They are also persistent in landfills under anaerobic conditions, but they do not appear to be persistent in soil under aerobic conditions. (It should be noted that the U.K. Environment Agency [1997] estimated a half-life for biodegradation in soil of about 30 days.) There is a need for mass balance studies in soils that take into account the relative importance of biodegradation and other routes of degradation, as well as adsorption, the formation of unextractable residues, and the effects of temperature and aerobic and anaerobic conditions.

CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

APEs, in particular NPEs, are widely used nonionic surfactants that are discharged in high quantities to STPs and directly to the environment in areas where there is no sewage or industrial waste treatment. Although NPEs are not readily biodegradable, they can be biodegraded through a mechanism of stepwise loss of ethoxy groups to lower NPnEO congeners, followed by the production of NPnEC and NP, depending upon the conditions. The intermediate and final products of metabolism are more persistent than the parent NPEs, but there is no doubt that such chemicals will also be ultimately biodegraded. There is a wide range in treatment efficiencies of NPEs in the course of wastewater treatment. Primary biodegradation as measured by loss of surfactant properties or determination of parent compound is easily achieved. However, degradation products such as NP1EO and NP2EO and their carboxylate derivatives NP1EC and NP2EC, and the final product, NP, are more persistent than the parent NPEs and are not generally completely degraded during sewage treatment. NP (in particular) and NP1EO and NP2EO are more lipophilic than the parent NPEs and tend to accumulate in sludges, while NPnECs are generally found in the final effluents, sometimes at much higher concentrations than other nonylphenolic compounds. NP, NP1EO and NP2EO can also be found in such effluents and have also been found in receiving waters. There is also evidence for the halogenation of some of these products in STPs that use chlorine for disinfection. Some STPs discharge significant amounts of NPE degradation products in their final effluents and digested sludges compared to what enters the STP plant. Others degrade NPEs very efficiently. The differences in treatment efficiency of NPEs and their degradation products among STPs, have been attributed to the load of NPEs in influent streams, STP design and operating conditions, and such factors as temperature of treatment. The highest NPE elimination rates were achieved in the STPs characterized by low sludge-loading rates and nitrifying conditions. It should also be noted that there may be substantial differences in treatment efficiencies of NPE between dedicated industrial wastewater treatment facilities and municipal STPs. The U.K. Department of the Environment (1997) estimated that 37% of NPEs used in the United Kingdom entered receiving waters, 46% was applied to soils or was deposited in landfills, and 17% was destroyed through incineration or was biologically degraded.

In aquatic ecosystems, it appears that parent NPEs are not persistent, but some degradation products may have moderate persistence, especially under anaerobic conditions. Recent results from mesocosm experiments (Heinis et al. 1998) indicate moderate persistence of NP in sediments, with half-lives of 28-104 days. Microbial acclimation to the chemicals is an important determinant of persistence vis-à-vis biodegradation. Sunlight photodegradation of such products is also likely important. Further research on the persistence of the lower ethoxylates, carboxylates and NP is necessary. Based on the limited data available, NP and the lower ethoxylates and carboxylates are persistent in groundwater. They are also persistent in landfills under anaerobic conditions, but they do not appear to be persistent in soil under aerobic conditions.

In order to more fully characterize the treatability of NPEs and their degradation products in STPs and their persistence in the natural environment, there is a need for more research in the following areas:

* Efficiency of treatment by STPs with advanced tertiary treatment processes, e.g., ultraviolet oxidation, adsorption "polishing", etc.

* The production, treatability and persistence of halogenated derivatives of NPE degradation products.

* In aquatic environments, mass balance studies that take into account the relative importance of biodegradation and sunlight photodegradation, as well as adsorption to suspended solids and bed sediment, aerobic and anaerobic conditions and temperature effects. To the extent that NPEs are used in aerially applied pesticide formulations, there is a need to determine their atmospheric chemistry, photochemistry and fate.

* Because sludges containing high concentrations of NP and other related compounds may be spread on agricultural land, there is a need for mass balance studies in soils that take into account the relative importance of biodegradation and other routes of degradation, as well as adsorption, the formation of unextractable residues and the effects of temperature and aerobic and anaerobic conditions.

In addition, the persistence of polyethylene glycol residues from the degradation of APEs requires further research in order to assess the ecotoxicological implications.

ADDED MATERIAL

R. JAMES MAGUIRE

National Water Research Institute, Environment Canada, Canada Centre for Inland Waters, 867 Lakeshore Road, Burlington, Ontario L7R 4A6

Table 1. Properties of nonylphenol and 4-octylphenol(FN1)

Property/ Specification	Nonylphenol	Octylphenol
CAS Registry Number	84852-15-3	140-66-9
Molecular formula	$C_{15}H_{24}O$	$C_{14}H_{22}O$
Molecular weight	220.3	206.3
Melting point, °C	81-83	
Boiling point, °C (kPa)	295-320 (101.3)	280-302 (101.3)
Colour	Colourless to pale straw (liquid)	White (solid)
Specific gravity	0.953	0.922
pK_a	10.7(FN2)	
Vapour pressure	$(4.55 +/- 3.5) \times 10^{-3}$ Pa(FN2)	
Solubility, mg/L	5.4(FN3)	12.6(FN3)
Log K_{ow}	4.48(FN4), 4.2(FN5)	4.12(FN4)
Henry's Law constant ($Pa\ m^3$/mol)	11.02(FN6)	

FOOTNOTES

1 From Reed (1978) except where noted. Note that "nonylphenol" refers to a mixture of branched C_9-alkylphenols, while "octylphenol" refers to 4-(1,1,3,3-tetramethylbutyl)phenol. CAS refers to Chemical Abstracts Service. Other physical and chemical properties may be found in U.S. Environmental Protection Agency (1985).
2 Romano (1991).
3 Ahel and Giger (1993a).
4 Ahel and Giger (1993b).
5 McLeese et al. (1981).
6 U.K. Environment Agency (1997).

Fig. 1. Biological degradation pathway for nonylphenol ethoxylates. R — branched nonyl group; NPnEO — nonylphenol ethoxylates; NPnEC — nonylphenol carboxylates; NP — nonylphenol.

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