Toxic Chemical “Nonylphenol”
A Barrier to Safe Drinking Water
ABOUT TOXICS LINK
Toxics Link is an Indian environmental research and advocacy organization set up in 1996, engaged in disseminating information to help strengthen the campaign against toxics pollution, provide cleaner alternatives and bring together groups and people affected by this problem. Toxics Link’s Mission Statement - “Working together for environmental justice and freedom from toxics. We have taken upon ourselves to collect and share both information about the sources and the dangers of poisons in our environment and bodies, and information about clean and sustainable alternatives for India and the rest of the world.” Toxics Link has unique expertise in areas of hazardous, medical and municipal wastes, international waste trade, and the emerging issues of pesticides, Persistent Organic Pollutants (POPs), hazardous heavy metal contamination etc. from the environment and public health point of view. We have successfully implemented various best practices and have brought in policy changes in the aforementioned areas apart from creating awareness among several stakeholder groups.

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Toxic Chemical "Nonylphenol": A Barrier to Safe Drinking Water
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Toxic Chemical "Nonylphenol": A Barrier to Safe Drinking Water
Nonylphenol (NP), an endocrine disrupting chemical is largely used in the production of nonylphenol ethoxylates (NPEOs). NPEOs are extensively used as surfactants and in other industrial applications as well as in day-to-day consumer products. Generally, NPEOs break down to NPs in the natural environment and enter into the ecosystem. NPs further enter the food chain, where they bioaccumulate and can pose serious environmental and health risks. Research studies across the globe have confirmed environmental and health impacts associated with NPs and NPEOs.

The previous study conducted by Toxics Link in 2019 revealed that NP is widely being used in detergents and the highest concentration was found to be 11.92% wt. Further the water samples collected from various rivers in that study also confirmed the presence of high NP concentration. In this context to evaluate the possible contamination of NP in drinking water, Toxics Link conducted a detailed assessment of drinking water samples in the present study. Fifteen drinking water samples were collected from different parts of India and sent to Shriram Institute of Industrial Research, New Delhi for analysis.

NP was observed in all the analyzed samples with concentrations ranging from 29.1–80.5 µg/L and the highest concentration was found in the borewell water collected from Bathinda, Punjab (80.5 µg/L). High concentrations were even detected in the drinking water samples collected after treatment at the point of use (i.e., filtration or RO treatment before drinking). Therefore, drinking water can be a major route of human exposure to NPs. Moreover, unlike other countries, India does not have specific standards for NPs in drinking and surface waters.

This study identifies the risks of continued usage of NP and recommends development of an action plan to phase out the chemical from the country as soon as possible. The chemical can be prohibited from use in products including detergents as suitable alternatives are widely available. The study also highlights the need to revise the Bureau of Indian Standards (BIS) testing protocols for analyzing specific phenolic compounds and come up with specific standards for NP and NPEOs in water.
Drinking water can be a major route of human exposure to nonylphenol. Unlike other countries, India does not have specific standards for nonylphenol in drinking and surface waters.
Introduction

1.1 Nonylphenol and Nonylphenol Ethoxylates

Nonylphenols (NPs) are a family of closely related phenolic compounds ($C_{15}H_{24}O$) (Fig. 1). NP is used as formulant in pesticides, lubricating oil additive, catalyst in epoxy resins curing, at industrial laundries and in the production of nonylphenol ethoxylates (NPEOs) for consumer products e.g., surfactants, detergents, wetting agents, dispersants, defoamers, deinkers, antistatic agents. In the form of tris(4-nonylphenyl) phosphite, NP can be used as an antioxidant in the stabilization of rubber, vinyl polymers, polyolefins, and styrenics.

Fig. 1 Molecular structure of nonylphenol

As shown in Fig. 2, NPEOs can have varying length of the hydrophilic ethoxylates (EO), which confers different properties to the molecule. After being used as detergents, emulsifiers, dispersants and humidifiers, about 60% of NPEOs will enter the environment and then get degraded by microorganisms and ultraviolet (UV) light. NPEOs ultimately degrade to NPs, that can enter different environmental matrices such as water, soil, etc.

Fig. 2 Molecular structure of nonylphenol ethoxylate
A market survey agency has projected the global NPEO market size to reach US$ 516.7 million by 2026, at a CAGR of 3.3% during 2021-2026 while another survey is expecting it to reach US$ 928.89 million by 2027. There is a decreasing trend of NPEO demand in Europe, as it has been listed in list-A priority hazardous substances by Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). However, global demand has been increasing due to acceptance by various industries like oil & gas recovery, industrial and institutional cleaning, pest control products, polymers and metal industries. Some of the top manufacturers of NP are Clariant AG (Switzerland), DOW Chemicals, Huntsman (U.S.), India Glycols (India), ENI (Italy), Sasol (S. Africa), SABIC (Saudi Arabia), CMFC (Taiwan), Daqing Zhonglan (China), etc.

1.2 Environmental fate of nonylphenol and its ethoxylates

NP and NPEOs are not produced naturally, and their presence in the environment are as a consequence of anthropogenic emissions. Wastewater treatment, landfill and sewage sludge recycling have been found to be the three major contributors of NP and NPEOs in the environment. There are also studies which show the leaching of NPs from plastic bottles to water.

Although NPEOs undergo fast primary biodegradation, it leads to the formation of more toxic and persistent metabolites, such as NP, NPEOs, namely, nonylphenol monoethoxylate (NPEO1), nonylphenol diethoxylate (NPEO2), nonylphenoxy acetic acid and nonylphenoxyethoxy acetic acid, which are accumulated in the environment. NPs and other metabolites of NPEO also accumulate in the high organic content containing environmental compartments such as sewage sludge and river sediments. NPEO metabolites are ubiquitous in the environment because of their wide use patterns and the lack of adequate wastewater treatment. These compounds have been detected in air, water, sediment, soil and biota at varying concentrations in different regions of the world.
1.3 Toxicity of nonylphenol and its ethoxylates

The toxicity of NP-related compound was first observed in a study by Dodds and Lawson in 1938. Later a number of studies have confirmed the endocrine disrupting compound (EDC) property of NP and found NP affecting the hormonal system of several organisms. Moreover some toxicity studies have also confirmed the lethal impacts of NPs on fish and other aquatic organisms even at low concentrations. The impacts of NP on the aquatic environment include feminization of aquatic organisms, decrease in male fertility and lower survival rate of juveniles. Though less toxic than NP, NPEOs are also highly toxic and degrade to more environmentally persistent NPs.

As an EDC, NP is reported to have adverse effects on the central nervous system, reproductive and immune systems. The chemical can also interfere with the critical steps during the development of the brain. Continuous exposure to NP can decrease the efficiency of microorganisms to eliminate this substance. One of the most common effects of NP on plants is general growth inhibition, characterized by reduced biomass and length and reduction in germinative capacity.

Non-occupational exposure to NPs and NPEOs can occur through a variety of exposure routes such as inhalation of air, ingestion of food and indoor dust and by drinking contaminated water. NPs present in plastic containers and wrappings can also migrate into foods and drinking water. Other routes of human exposure include contact with personal care products and detergents. NPs have been detected in human breast milk, blood, and urine. A summary of toxicity impacts of NP on biota is provided in the Annexure.

Therefore, the use of NP and NPEOs has been restricted in the European Union. Moreover, NPEOs are being replaced by other surfactants, mainly alcohol ethoxylates, in most European, Canadian, and Japanese markets.
1.4 Nonylphenol in water

There are several studies reporting the presence of NPs in surface water, river sediments and near wastewater treatment plants.

1.4.1 Surface water

Mao et al., observed that several factors, such as temperature, flow rate, and biodegradation, affect the degradation and accumulation of NP in surface water.24 The maximum levels of NP in the dissolved and suspended particulate phases were observed during the winter periods while a significant decrease was observed during spring and autumn periods; thus, highlighting that temperature is a key factor affecting the seasonal variation of NP in water. According to the classification by Bartoni,25 surface waters with NP content less than 1 μg/L were considered as poorly contaminated, 1–10 μg/L as contaminated, and greater than 10 μg/L as highly contaminated.

Global studies

Zhang et al., (2009) reported NP concentrations ranging from 75.2 to 1520 ng/L in Jialu River near Zhengzhou city, China26 and the concentrations were mainly governed by the annual discharge of 726 kg NP from urban zone to the river.

Duong et al., (2010) reported higher levels of NP in surface water samples collected from 8 south-east Asian countries (Korea, Laos, Cambodia, Vietnam, China, Indonesia, Thailand and Malaysia) compared to those reported in European countries, America and Japan.27

Jie et al., (2017) observed NP concentrations ranging from 0.174 to 3.411 μg/L in Xiangjiang river.28 Cherniaev et al., (2017) monitored 4-NP in Amur Bay (Japan/East Sea) and reported concentrations as high as 1.24 μg/L.29 They suggested that although the concentrations are not high enough to cause disruption of the endocrine system of marine organisms, it is considered as poorly contaminated surface water due to anthropogenic activities.

Araujo et al., (2018) monitored the presence of 4-NP in Guandu river in the state of Rio de Janeiro, Brazil.30 The study detected 4-NP in 12 out of 19 samples, within a range of 1.73–2.32 μg/L.

According to the classification by Bartoni, surface waters with NP content less than 1 μg/L were considered as poorly contaminated, 1–10 μg/L as contaminated, and greater than 10 μg/L as highly contaminated.

According to a study conducted by Salomon et al., (2019), NP and NPEO concentrations in surface water around the industrial area of Taiyuan city, China ranged from 99.3 to 113.4 μg/L and 38 to 743 μg/L respectively. On the other hand, the concentrations in groundwaters ranged from 25.5 to 166.4 μg/L and 24.2 to 275.8 μg/L for NP and NPEOs, respectively.31
Indian studies

Selvaraj et al., (2014) observed the presence of NP in Kaveri, Vellar and Tamraparni rivers and the concentrations ranged from ND to 2200 ng/L, which are quite high as compared to the prescribed standard for phenolic compounds (1000 ng/L) in drinking water in India. In a study conducted by Gautam et al., (2015), 4-NP concentrations varied between 12.4–16.29 μg/L in water samples drawn from river Ganga and river Varuna at 3 different sites that are either witness high anthropogenic activities or located near a city wastewater treatment efflux point.

Raju et al., (2018) conducted a study on surface water and sediment samples from the marine environment of Chennai. In this study, NP ranged from 1.22 to 7.24 μg/L in water and 3.31 to 30.96 μg/kg in sediments. They suggested that domestic and industrial waste water as well as surface runoff could be possible sources of NP in the aquatic environment.

All the above studies clearly highlight that discharge of inadequately/untreated domestic and industrial wastewater are the major NP sources in the aquatic environment.

1.4.2 Nonylphenol and its ethoxylates in drinking water: A health challenge

NP detection in rivers and lakes has raised serious concerns on the level of contamination in surface waters in India. Further, there is every possibility that the drinking water may have also been contaminated with NP and NPEOs and needs to be investigated. Regulations are in place for general phenolic compounds in drinking water but based on the harmful impacts, now globally, governments are coming up with standards on NPs in drinking water as well. Some of the research studies as given below have reported significant amounts of NP contamination in drinking water.

Chen et al., (2013) monitored NP concentrations in water samples collected from 11 water treatment plants (WTPs), including conventional WTPs and WTPs with advanced treatment units in different regions of Taiwan. Mean NP concentration in raw water ranged from 118 to 361 ng/L and decreased to 68–234 ng/L in treated water. Similarly, Dai et al. (2019) reported maximum NP concentration of 980 ng/L in Taiwanese drinking water samples. Both these...
studies demonstrated the necessity to upgrade conventional water treatment processes for substantial removal of EDCs such as NPs.

Li et al., (2010) analyzed NP in bottled and tap waters and observed NP concentrations ranging from 108 to 298 ng/L, while the maximum concentration in tap water was 1987 ng/L. Amiridou and Voutsa (2011) observed NP in bottled water purchased from the market at a median concentration of 7.9 ng/L. These studies emphasize the need to study the migration of chemicals from bottles during long storage time especially under poor storage conditions.

1.5. National and international regulations on nonylphenol in water

1.5.1 Global regulations

In Japan, NP is designated as one of the parameters in the environmental quality standards for water pollution.

US water quality criteria states that freshwater aquatic life and their uses should not be affected if the 1-h average NP concentration does not exceed 28 µg/L more than once every 3 years on the average (chronic criterion). The acute criterion states that the 4-d average NP concentration does not exceed 6.6 µg/L more than once every 3 years on the average.

NP is on Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) list of dangerous substances and the Water Framework Directives list of priority hazardous substances.

The water quality standard for NP in EU is 0.3 µg/L (this value is the Environmental quality standard (EQS) expressed as an annual average value (i.e., AA-EQS) in inland surface water. Here, “inland surface water” means the rivers and lakes and related artificial or heavily modified water bodies.)

New US EPA regulation directs companies to report their annual quantities of 13 NPEOs to EPA every year. Under this regulation, information will be made public under the US right-to-know law starting in 2020. Although, EPA has not curtailed the use of NPEOs, retailers such as Walmart and Target have told their suppliers to eliminate NPEOs, among a handful of other substances, from household and personal care products they sell.
NP and its ethoxylates have been added to the list of toxic substances in the Schedule I of the Canadian Environmental Protection Act, 1999. Canada has set NP standard at 1.0 µg/L in freshwater.

1.5.2 Indian regulations

The Bureau of Indian Standards (BIS) has set standards for phenols (phenolic compounds expressed as phenols) in drinking water (0.001 mg/L) and surface water (5 mg/L). The methods of sampling and test for phenols are given in IS 3025 (Part 43): 1992 (Reaffirmed 2003). However, there are no specific standards for NPs or NPEOs in drinking water and surface water or regulations on its use in surfactants and other consumer products.

The Bureau of Indian Standards (BIS) has set standards for phenols (phenolic compounds expressed as phenols) in **drinking water (0.001 mg/L) and surface water (5 mg/L)**. The methods of sampling and test for phenols are given in IS 3025 (Part 43): 1992 (Reaffirmed 2003).
UNICEF data said the estimated economic burden of waterborne diseases is approximately US$600 million as chemicals contaminate the water in 1.96 million homes.45
Toxic Chemical “Nonylphenol”: A Barrier to Safe Drinking Water

2.1 Rationale of the study

Considering the harmful impact of NP and global actions on the chemical, in 2019 Toxics Link had carried out a detailed assessment of the presence of nonylphenol in twelve detergent samples collected from the Delhi market and in twelve river water samples collected from different part of the country. That study reported the presence of NP in detergents from 0.82% to as high as 11.92 wt%. Further, water samples collected from various rivers in that study also showed high NP concentrations. NP concentrations in the river water samples ranged from 9.2 – 41.3 mg/L. Highest concentration was detected in Bandi River (41.3 mg/L) in Pali, Rajasthan which is a known textile hub of the country indicating excessive use of NP in textile industries.

Water safety and quality are fundamental to human development and well-being. Through the United Nations Sustainable Development Goal (SDG) 6, i.e., Clean Water and Sanitation, countries across the world have resolved to achieve universal and equitable access to safe and affordable drinking water for all by 2030. More than 50% of the population has no access to safe drinking water and about 200,000 people die every year for lack of access to safe water. UNICEF data said that the estimated economic burden of waterborne diseases is approximately US$600 million as chemicals contaminate the water in 196 million homes. A 2015 study on the quality of drinking water in public utilities revealed that even those using water purifiers had exceeded permissible pH limits and were contaminated with E Coli. Therefore, drinking water safety has received considerable interest in recent times. As NP is widely present in detergents and river waters, there is a high possibility that the drinking water is also contaminated with NP and its EOs.

Therefore, in continuation with the previous study, Toxics Link has come up with the present report on the presence of NPs in drinking water samples collected from various geographical regions of the country. Although BIS has set standards for phenolic compounds in drinking water in India, there is no specific standard for nonylphenol and its ethoxylates in drinking water.

2019 Toxics Link study on nonylphenol can be accessed online at the following url: http://toxicslink.org/Publication/nonylphenoldirty-trail-detergent-to-water-bodies
2.2 Objectives of the study

To detect the presence of nonylphenol in drinking water samples collected from various regions of the country
To highlight the possible environment and health impacts associated with nonylphenol
To highlight the need for stringent regulation in place for nonylphenol in drinking water

2.3 Sampling and analysis

2.3.1 Sampling

Fifteen drinking water samples were collected from different parts of India with the help of partner NGOs. The source of 7 out of 15 samples was water supplied by local government bodies (i.e., surface water from lakes, rivers, etc.). The source of 4 samples collected from borewell was groundwater. One sample was a mixed water sample, i.e., the source was surface water mixed with groundwater. Remaining three water samples were also from local government supply but they were treated at point of use. Out of these three samples, two were simple filtered water samples and one was RO-treated sample.

Fig. 3 Sampling locations
2.3.2 Extraction and Analysis

- The water samples were centrifuged for 5 min under 6000 rpm to remove the suspended solids, if any.
- The supernatant was then filtered by a 0.45 µm organic membrane. 50 ml of water was pipetted into a 125 ml separating funnel, then 0.5 mL of 1 mol/L HCl and 2.5 g NaCl were added, and shaken well.
- After that, 5 ml of dichloromethane was added, shaken for 2 minutes, kept for 20 minutes, and then the lower organic phase was collected, which was centrifuged at 5000 rpm for 10 min.
- Afterwards, the centrifuged upper water phase was moved back into the separating funnel, 5 ml of dichloromethane was added, and then the extraction and centrifugation processes were repeated.
- The centrifuged lower organic phase of two centrifugation processes was filtered to remove the floccules, then the filtrate was evaporated to dryness at 40 °C, the residue was dissolved with isopropanol, made to 2 ml, and filtered by 0.45 µm filtration membranes.
- Injected onto LC-MS/MS.
- NP concentrations were expressed in terms of NPEO (NPEO3 to NPEO15) in µg/L. The limit of quantification was 2 µg/L.

Through United Nations Sustainable Development Goal (SDG) 6, i.e., Clean Water and Sanitation, countries across the world have resolved to achieve universal and equitable access to safe and affordable drinking water for all by 2030.
In our previous study, NP concentrations in the river water samples ranged from 9.2 – 41.3 mg/L. Highest concentration was detected in Bandi River (41.3 mg/L) in Pali, Rajasthan which is a known textile hub of the country indicating excessive use of NP in textile industries.
Results and Discussion

3.1 Presence of nonylphenol in drinking water samples

There is little information concerning the levels of NP in drinking and supply waters in comparison with those in other environmental matrices. In this study, NP concentrations were expressed as NPEOs (NPEO3 to NPEO15), i.e., EOs with 3 to 15 chains were considered. The drinking water concentrations of NP at various sampling locations are given in Table 1. The concentration profiles of the drinking water samples collected across India are shown in Fig. 4.

Highest NP concentration was observed in the borewell water sampled from Bathinda (80.5 µg/L), while the lowest concentration was found in the government supply water from Indraprastha, New Delhi (29.1 µg/L).
Fig. 4 Nonylphenol concentration profile of drinking water samples
Table 1. Sampling locations and corresponding nonylphenol concentrations

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Sample ID</th>
<th>Location</th>
<th>Source</th>
<th>NP Concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WL1</td>
<td>Vaishali, Ghaziabad, Uttar Pradesh</td>
<td>Filtered water (government water supply treated at point of use)</td>
<td>61.5</td>
</tr>
<tr>
<td>2</td>
<td>WL2</td>
<td>Vaishali, Ghaziabad, Uttar Pradesh</td>
<td>Government water supply</td>
<td>46.5</td>
</tr>
<tr>
<td>3</td>
<td>WL3</td>
<td>Indraprastha, New Delhi</td>
<td>Government water supply</td>
<td>29.1</td>
</tr>
<tr>
<td>4</td>
<td>WL4</td>
<td>Balbeer Vihar, North west Delhi</td>
<td>Government water supply</td>
<td>48.9</td>
</tr>
<tr>
<td>5</td>
<td>WL5</td>
<td>Zuarinagar, Sancoe, South Goa</td>
<td>Filtered water (government water supply treated at point of use)</td>
<td>58.8</td>
</tr>
<tr>
<td>6</td>
<td>WL6</td>
<td>Kattampatty Panchayat, Annur Block, Coimbatore, Tamil Nadu</td>
<td>Groundwater</td>
<td>78.5</td>
</tr>
<tr>
<td>7</td>
<td>WL7</td>
<td>Project Phase I, Coimbatore Municipal Corporation, Tamil Nadu</td>
<td>Government water supply</td>
<td>76.4</td>
</tr>
<tr>
<td>8</td>
<td>WL8</td>
<td>Dausa city, Rajasthan</td>
<td>Mixed water (surface water + groundwater from government water supply)</td>
<td>42.3</td>
</tr>
<tr>
<td>9</td>
<td>WL9</td>
<td>Bapi village, Dausa rural, Rajasthan</td>
<td>Groundwater</td>
<td>61.1</td>
</tr>
<tr>
<td>10</td>
<td>WL10</td>
<td>Arjun Nagar, Bathinda, Punjab</td>
<td>Groundwater</td>
<td>80.5</td>
</tr>
<tr>
<td>11</td>
<td>WL11</td>
<td>Pratap Nagar, Bathinda, Punjab</td>
<td>RO water (government water supply treated at point of use)</td>
<td>61.1</td>
</tr>
<tr>
<td>12</td>
<td>WL12</td>
<td>KIIT University, Bhubaneswar, Odisha</td>
<td>Groundwater</td>
<td>54</td>
</tr>
<tr>
<td>13</td>
<td>WL13</td>
<td>Damana slum, Bhubaneswar, Odisha</td>
<td>Government water supply</td>
<td>40.9</td>
</tr>
<tr>
<td>14</td>
<td>WL14</td>
<td>Vashi, Navi Mumbai, Maharashtra</td>
<td>Government water supply</td>
<td>39</td>
</tr>
<tr>
<td>15</td>
<td>WL15</td>
<td>Gurugram, Haryana</td>
<td>Government water supply</td>
<td>51</td>
</tr>
</tbody>
</table>
NP was observed in all the analyzed samples with concentrations ranging from 29.1–80.5 µg/L.

The highest concentration was observed in the borewell water sampled from Bathinda (80.5 µg/L), while the lowest concentration was found in the government supply water from Indraprastha, New Delhi (29.1 µg/L).

NP concentrations ranged from 29.1–76.4 µg/L (mean ± stdev; 47.4 ± 14.7 µg/L) in water from surface water sources.

The concentration range was 54–80.5 µg/L (68.5 ± 13 µg/L) in groundwater samples from borewells.

NP concentrations in the surface water samples treated at source (filtered and RO-treated) ranged from 58.8–61.5 µg/L. NP concentrations in the two simple filtered water samples were 61.5 µg/L (WL1) and 58.8 µg/L (WL5).

NP in the only mixed water sample from Rajasthan was found to be 42 µg/L.

3.2 Source apportionment

NP detected in household water supplied by the local government water supply agencies may indicate that the water treatment facilities in those regions are incapable of removing these compounds and need to be upgraded.

There is no study monitoring the concentrations of NP and NPEOs in drinking water in India. However, some studies were conducted in other countries to determine NP concentrations in drinking water. NP concentrations from the present study were compared to those global studies. A comparison of NPs in raw and drinking water (water after treatment in water treatment plants) in the Area of Chongqing, China demonstrated that NPEOs with greater EO units are more easily removed by the water treatment processes. NP concentrations in the present study were found to be much higher than that study (ND–0.3 µg/L). Mean NP concentrations (0.07–0.2 µg/L) in finished waters, i.e., after treatment in water treatment units in Taiwan were also found to be much lower than the present study. Thus, the results clearly indicate the extensive use of NPs in India and the lack of NP removal in existing water treatment facilities in India.

One of the possible other sources may be leaching of NP from household pipes. NP concentrations were detected in tap water from households using PVC pipes. However, the concentrations were found to be strongly affected by contact time of water with the pipes and ambient temperature. Additional studies are warranted to assess the potential leakage of NP from household pipes.
In our earlier study, the presence of NP in river water has been mainly attributed to the use of NPEOs in detergents. Previous studies have also highlighted that the occurrence of NP and NPEOs in aquatic environments is mainly correlated with the effluent discharge from sewage treatment plants treating wastewaters from industrialized/urban areas and with other related anthropogenic activities such as storm water discharges and run-offs.47

High NP concentrations in borewell samples clearly implied NP contamination in groundwater. NP was detected in groundwater up to 0.9 µg/L in two agricultural areas of Spain.49,50 Other studies have also reported NP concentrations in groundwater up to 3.85 µg/L.51,52,53 NP levels in the irrigation districts of China ranged from 0.2–0.4 µg/L. NP levels from the present study were also found to be much higher than those reported in earlier studies. NP contamination in groundwater have been mainly associated to landfill leachate, water from agricultural land, or seepage of septic tanks and sewer systems.51 Long-term irrigation with reclaimed water can lead to infiltration and migration of NP in groundwater and is also one of the possible sources.54

Three samples collected in the present study were treated at point of use. NP detection in the treated water samples were also found to be high, clearly demonstrating that installed household treatment units were not capable of removing NPs. Therefore, studies must be carried out to evaluate the performance of household RO and filtration systems in removing NPs and other emerging contaminants.
3.3 Necessity of revising BIS testing protocols

The present analytical method for phenols in water and wastewater as prescribed by BIS is based on the spectrophotometric technique with the absorbance measured at a fixed wavelength of 460 nm. However, the spectrophotometric determination of a mixture of phenolic compounds, especially complicated structures such as alkylphenols (e.g., NP and NPEOs) is a very complex problem in analytical chemistry due to spectral interferences. This may result in the underestimation of phenolic concentrations in the samples. Davi and Gudi (1999) underlined that most of the phenolic compounds found in river water were not detected by condensation with BIS prescribed 4-aminoantipyrine. Therefore, this method is not suitable for determining total phenol concentration. Moreover, it is necessary to determine phenolic compounds using chromatographic techniques such as, LC/MS/MS used in the present study to determine the nature and type of each phenolic compound. The present analytical method measuring total phenol concentration in water may not be able to estimate NPs and their EOs. Hence, BIS should revise the testing protocols for analyzing specific phenolic compounds and come up with specific standards for NP and NPEOs in water.

Some of the important observations coming out of the present study are:

- Nonylphenol was detected in all the drinking water samples, irrespective of the source, in high concentrations compared to previous studies carried out globally.
- High concentrations were even detected in the drinking water samples collected after treatment at the point of use.
- Unlike other countries, India does not have specific standards for nonylphenols in drinking and surface waters.
- There is a possibility that the complete removal of nonylphenols does not take place in the existing water treatment plants in India and the treatment units need to be upgraded.
3.4 Conclusions

In the present study, NP was found to be high in drinking water samples from different sources collected from different regions of India. Therefore, drinking water can be a major route of human exposure to NPs. Even the treatment systems, such as RO (as in Pratap Nagar, Bathinda, Punjab) and simple filtration were not capable of removing NPs. NPEO detection can be directly attributed to its high presence in detergents. However, apart from detergents, there can be other possible sources of NP contamination in the surface and ground water samples. Nevertheless, the detection of NP in drinking water raises serious concerns on the level of NP contamination in India.

Recently, India has come up with the drinking water quality, testing, monitoring and surveillance framework that is a part of the government’s flagship Nal se Jal scheme, under which drinking water connection will be provided to each and every rural household by 2024. This framework, developed by the National Jal Jeevan Mission in partnership with Indian Council of Medical Research, WQIMS will have an automated data flow of water sample test results, which can help in assuring the safe supply of drinking water. This initiative of the government can be a key to solving India’s clean water problem if the framework includes emerging contaminants, including NPs as well.
It is necessary to **monitor the presence of NP and NPEOs** in drinking water as well to bring about a possible revision of drinking water standard at par with the **global standard specific to NP and NPEOs**.
Toxic Chemical “Nonylphenol”: A Barrier to Safe Drinking Water

As NP and NPEOs are toxic chemicals of high concern, concerted actions have been initiated globally to restrict the application of these chemicals in products as far as possible to minimize their adverse impacts on the environment and human health. However, there is a lack of awareness in India and hardly any intervention has been made to restrict the use of this chemical, except for the prohibition of NP in cosmetics. Therefore, a road map is necessary to phase out the chemical in the country. In terms of environmental risk, alcohol ethoxylates seem to present a clear advantage over NPEOs, mainly owing to biodegradability issues. Specifically, alcohol ethoxylates are found to biodegrade more readily than NPEOs in the environment. However, while substituting an NPEOs with an alcohol ethoxylate, it is important to look at the toxicity of the specific chemicals under consideration, as toxicity may vary substantially depending on the alkyl chain lengths, chain branching and the degree of ethoxylation. Although alcohol ethoxylates in general have been identified as suitable alternatives to NPEOs, they are not currently applicable to all uses. For some specific uses, either no suitable alternative has been identified or significant issues arise over the environmental impacts of the alternative.

Recommendations

As NP and NPEOs are toxic chemicals of high concern, concerted actions have been initiated globally to restrict the application of these chemicals in products as far as possible to minimize their adverse impacts on the environment and human health. However, there is a lack of awareness in India and hardly any intervention has been made to restrict the use of this chemical, except for the prohibition of NP in cosmetics. Therefore, a road map is necessary to phase out the chemical in the country. In terms of environmental risk, alcohol ethoxylates seem to present a clear advantage over NPEOs, mainly owing to biodegradability issues. Specifically, alcohol ethoxylates are found to biodegrade more readily than NPEOs in the environment. However, while substituting an NPEOs with an alcohol ethoxylate, it is important to look at the toxicity of the specific chemicals under consideration, as toxicity may vary substantially depending on the alkyl chain lengths, chain branching and the degree of ethoxylation. Although alcohol ethoxylates in general have been identified as suitable alternatives to NPEOs, they are not currently applicable to all uses. For some specific uses, either no suitable alternative has been identified or significant issues arise over the environmental impacts of the alternative.
Some of the suggested recommendations are:

- To ban the use of NP in detergents, one of the major sources of environmental contamination
- More attention should be paid to carry out epidemiological studies and obtain toxicological data to assess the possible impacts of NP and NPEOs on human health and environment
- To create an inventory of the usage of NP and NPEOs in different sectors in the country
- To carry out substantial research studies on the presence of NP and its EOs in water bodies and develop policy to reduce the presence of these chemicals in the environment
- To revise industrial effluent standards to prevent the release of NP to the environment
- To promulgate suitable regulations in the country to phase out NP and its EOs in consumer products
- To initiate legal action against corporations for practicing double standards based on the polluter pay principle
- To bring standards on NP and NPEOs in drinking water and in food to protect human health and the environment
- To monitor the presence of NP and NPEOs in drinking water as well to bring about a possible revision of drinking water standard at par with the global standard specific to NP and NPEOs
- Upgradation of existing water treatment and wastewater treatment technologies for the removal of NPs and other emerging contaminants
- Assessment and adoption of available safer alternatives to NP and NPEOs
References


Annexure

Toxicity impacts of nonylphenol on biota

<table>
<thead>
<tr>
<th>Study</th>
<th>Type of organism</th>
<th>Important Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lepretti et al. (2015)</td>
<td>Human epithelial intestinal cell lines</td>
<td>Exposure to 4-NP through diet may lead to local damage at the level of intestinal mucosa, with potentially negative consequences for intestinal homeostasis and functionality</td>
</tr>
<tr>
<td>Spagnoletti et al. (2015)</td>
<td>Human trophoblast cells</td>
<td>p-NP affect human placenta development at concentrations detected in human tissues and fluids</td>
</tr>
<tr>
<td>Zhang et al. (2016)</td>
<td>Wheat seedlings</td>
<td>NP adversely affected shoot length, root length, chlorophyll, lipid peroxidation, and enzymatic activities</td>
</tr>
<tr>
<td>Kazemi et al. (2016)</td>
<td>Rats</td>
<td>NP resulted in decrease in the weight of rat testes, decreased epididymal sperm motility and affected sperm morphology</td>
</tr>
</tbody>
</table>
| Xu et al. (2019)       | Xenopus laevis (Frog) | ◆ NP and NPEO decreased the total length of tadpoles  
◆ NP and 4-NP increased gut malformation and bent tails in tadpoles  
◆ NP showed the highest teratogenic potential |
| Kim et al. (2019)      | Crop plants (mung bean and rice) | ◆ In rice, shoot growth, chlorophyll content and root development were reduced by chronic exposure to nonylphenol at 2000 mg/kg  
◆ In mung bean, chlorophyll content and stomata size decreased by NP exposure  
◆ Necrosis of the leaves of mung bean was observed at 2000 mg/kg soil |
| Yang et al. (2020)     | Chlorella pyrenoidosa (Microalgae) | NP significantly inhibited algal growth, thereby causing oxidative stress |
| Li et al. (2020)       | Male Sprague-Dawley (SD) rats | NP led to reproductive system injury in SD rats by disturbing the balance of hormones secretion, inducing apoptosis of testis, etc. |