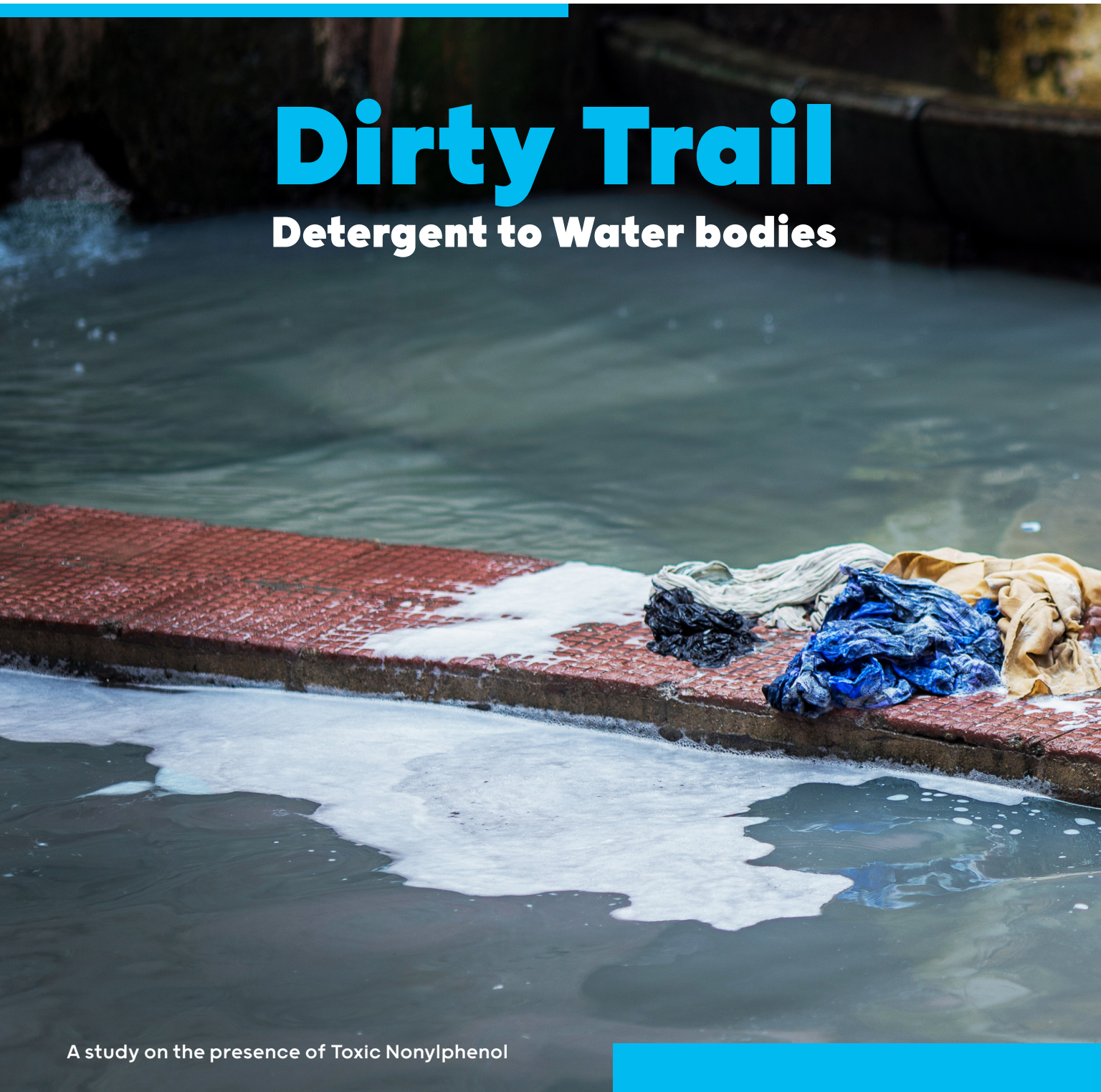
Toxics Link
for a toxics-free world

Dirty Trail

Detergent to Water bodies



A study on the presence of Toxic Nonylphenol

Toxics Link
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DIRTY TRAIL

DETERGENT TO WATER BODIES

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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 a 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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Abbreviations

APE	Alkylphenol Ethoxylates
µg	Microgram
bw	Body weight
CAS	Chemical Abstracts Service
EDCs	Endocrine Disrupting Chemical
EU	European Union
FMCG	Fast Moving Consumer Goods
Kg	Kilogram
L	Liter
LOAELs	Lowest Observed Adverse Effect Levels
ml	Milliliter
ng	Nanogram
NHFPC	National Health and Family Planning Commission
NOAELs	No Observed Adverse Effect Levels
NP	Nonylphenol
NPE	Nonylphenol ethoxylates
ppb	Parts per billion
ppm	Parts per million
SDWA	Safe Drinking Water Act
TDI	Tolerable Daily Intake
UNEP	United Nations Environment Programme
US EPA	The United States Environmental Protection Agency
WFD	Water Framework Directive

Executive Summary

Nonylphenol (NP), a xenobiotic and an Endocrine disrupting chemical is used largely in the production of Nonylphenol Ethoxylates (NPE). NPE is extensively used as a surfactant and in other industrial applications as well as in day to day consumer products. NPE generally breaks down to Nonylphenol in natural environmental conditions and enters into the ecosystem. NP further enters the food chain, where it bio-accumulates and can pose serious environmental and health risks. Research studies across the globe have confirmed environmental and health impacts associated with Nonylphenol.

Countries such as the USA, the EU and China have acknowledged the menace of this chemical and have put restrictions on its use in various industrial processes and have shifted towards safer alternatives. Nonylphenol's use has been completely phased out from detergent in these countries long time ago. Further many FMCG industries have also taken voluntary approach to prohibit the use of Nonylphenol in detergents. Though India has prohibited the use of NP in cosmetic products (2009), there is no regulation on its use in surfactants or other consumer products. Further, there is no public information available on the possible impacts of the chemical and to minimize the risks associated with it.

In this context to assess the possible contamination of the chemical in the environment, Toxics Link carried out a detailed assessment of the presence of Nonylphenol in detergent as well as in river water samples. The study was carried out in association with the Department of Chemical Engineering IIT, Guwahati. Twelve detergent samples were collected from the local market of Delhi and were sent to the lab for analysis as per the standard protocol. Further, twelve water samples were collected from rivers and lakes of India (Garh Ganga, Uttar Pradesh; Krishnan River, Andhra Pradesh; Hindon River, Uttar Pradesh; Tapti River, Gujarat; Bandi River, Rajasthan; Ambazari Lake, Nagpur and Mahanadi River, Odisha) and were sent to the lab for analysis of concentration of NP .

The present study has revealed that the chemical is widely being used in detergents and the highest concentration is found to be 11.92% wt. Further the water samples collected from various rivers have also confirmed the presence of high concentration of Nonylphenol. The highest concentration of chemical was detected in Bandi River (41.27 ppm) in Pali, Rajasthan which is a known textile hub of the country indicating excessive use of Nonylphenol in textile industries.

This study identifies the risks of continued usage of Nonylphenol 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 detergent as suitable alternatives are widely available.

CHAPTER 1

Introduction

1.1 About Nonylphenol

Nonylphenol (NP) is a phenolic substance synthesized through the alkylation process of phenols used in the industrial process and is the most extensively used member of Alkylphenol ethoxylates.

Nonylphenol is primarily used as a raw material in the production of Nonylphenol ethoxylates (NPEs) and NPE is a synthetic chemical belonging to a larger group of chemicals APEs (Alkylphenol ethoxylates) which is widely used as a surfactant, emulsifiers as well as in other household and industrial applications such as paints, paper, cosmetics, textiles and pesticides etc.[1] Due to its amphipathic property, cost effectiveness and high performance, it is considered as workhorse surfactant. Initially the chemical was largely used in the laundry products and was subsequently commercialized for other uses. The most commonly used compound of Nonylphenol is **4-Nonylphenol** which makes up over 90% of commercial production of Nonylphenol.[2]

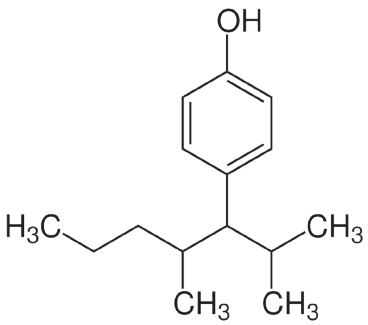


Figure 1 Chemical structure of 4- Nonylphenol

Table 1 Properties of Nonylphenol

Chemical formula	C15H24O
Molar mass	220.35 g/mol
Appearance	Light yellow viscous liquid with phenolic smell
Density	0.953
Melting point	−8 to 2 °C (18 to 36 °F; 265 to 275 K)
Boiling point	293 to 297 °C (559 to 567 °F; 566 to 570 K)
Solubility in water	6 mg/L (pH7)

1 Priority Substances List Assessment Report: Nonylphenol and its Ethoxylates , Environment Canada, Health Canada April 2001

2 Subha Raju, Madhumathi Sivamurugan, KarunaGunasagaran, ThirunavukkarasuSubramani and MunuswamyNatesan Preliminary studies on the occurrence of nonylphenol in the marine environments, Chennai—a case study. The Journal of Basic and Applied Zoology (2018) 79:52. https://doi.org/10.1186/s41936-018-0063-1

Nonylphenol generally gets released from NPEs (Nonylphenol ethoxylates) after its breakdown in the environment. The chemical has half-lives of 6-66 days in sediments, 14-30 days in water and >7 hours in the atmosphere which depends upon various parameters (aerobic conditions, anaerobic conditions, temperature, pH etc.).[3,4]

Though the chemical is being extensively used, however, the studies have confirmed that it has toxic chemical properties and has been categorized as **endocrine disrupting chemical** (EDC). After the toxic impacts of Nonylphenol came into the lime light, serious concerns were raised on the use of Nonylphenol in **1976** when the UK government signed a voluntary agreement[5] with industry to not to use the chemical in domestic detergents. Gradually, many countries have started restricting the use of chemical in various products. The UNEP has identified this chemical as the chemical of global concern and the research studies have confirmed that Nonylphenol is highly toxic to aquatic life and health of the developing fetus and young children.[6] The chemical is found to be persistent and moderately bio accumulative.[7]

United Nations Environment Programme (UNEP, 2003) has identified NP as a chemical of global concern in its region-based Assessment of Persistent Toxic Substances.

1.2 Production of Nonylphenol

Nonylphenol was first produced in 1940 and since then it has gained huge popularity in the production of NPE to be subsequently used as a surfactant. The chemical has been used in range of products including lubricant additives, formaldehyde resins, epoxy resins, and polymeric stabilizers apart from the large scale use in detergent.

The US, The EU, China and Japan are the major producer of Nonylphenol in the world. In 2012, it was reported that production of Nonylphenol in China is approximately 50000 tonnes per annum (Mao, et al., 2012). During that year the global annual production was about 200000 tones.

Some of the major producers of Nonylphenol are AkzoNobel N.V. (Netherlands), Clariant AG (Switzerland), The DOW Chemical Company (U.S.), Hunstman (U.S.), Stepan Company (U.S.), India Glycols (India), SABIC (Saudi Arabia), PJSC Nizhnekamskneftekhim (Russia), Solvay (Belgium), and PCC Exol SA (Poland) .

3 Regionally Based Assessment of Persistent Toxic Substances, Regional Report 2003, UNEP : pdf available on http://www.cep.unep.org/publications-and-resources/databases/document-database/unep/global-pts-unep.pdf/at_download/file

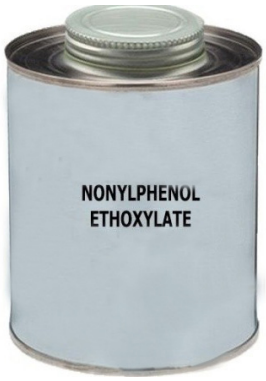
4 Zhen Mao, Xiao-FeiZheng, Yan-Qiu Zhang, Xiu-Xiang Tao, Yan Li, Wei Wang. Occurrence and Biodegradation of Nonylphenol in the Environment.Int J Mol Sci. 2012; 13(1): 491–505.

5 http://apps.sepa.org.uk/spripa/Pages/SubstanceInformation.aspx?pid=154

6 https://saferchemicals.org/get-the-facts/toxic-chemicals/npes-nonylphenol-ethoxylates/

7 Nonylphenol and nonylphenol ethoxylates action plan. U.S. Environmental Protection Agency (EPA). August 2010.

1.2.1 Status in India



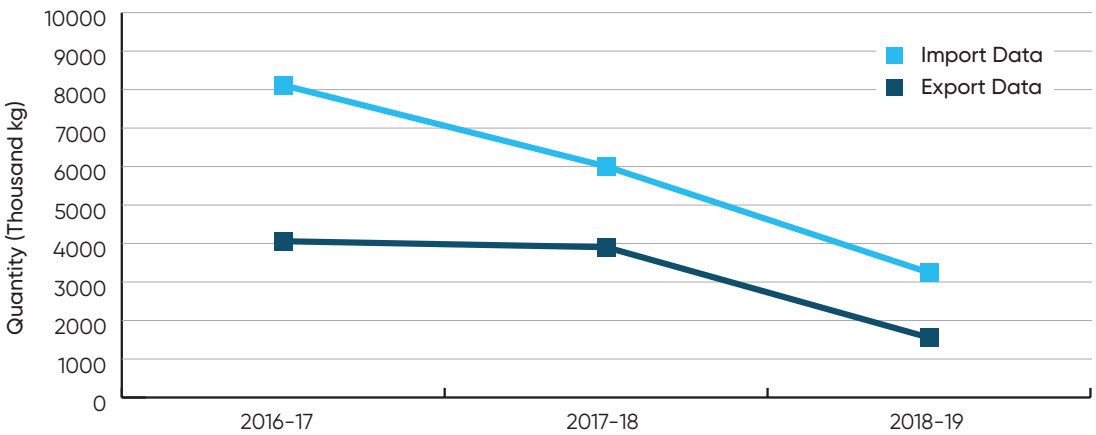
India, of late, has become one of the major users of Nonylphenol and its compounds. Though there is no available information on the total production of Nonylphenol in India, however, a report[8] states that the consumption of Nonylphenol ethoxylates has increased manyfold. The report also states that India consumes about 40,000 to 60,000 tons of Nonylphenol ethoxylate and there is a large scale use of chemical in the textile sector.

As per the DGFT data of Ministry of Commerce, India is importing and exporting Nonylphenol under the **HS Code 29071300 Octylphenol, Nonylphenol and their isomers, salts**. The country imports Nonylphenol from Taiwan (1935 thousand kgs- 2018-2019) and Korea (1186 thousand kgs- 2018-2019). Further, there is also significant export of the chemical from India to other countries such as China (2,028 thousand kgs- 2017-2018 and 560 thousand kgs- 2018-2019) and Singapore (1,828 thousand kgs- 2017-2018 and 915 thousand kgs- 2018-2019). **(Table 3)**

Table 2 Import/Export Data of Octylphenol, Nonylphenol and their isomers, salts in India

Import/Export	Quantity (Thousand kgs)		
	2016-2017	2017-2018	2018-2019
Import Data	8114	6005	3246
Export Data	4060	3905	1556

Figure 2 Import Export of Nonylphenol



The data depicts a decreasing trend in export and import of the compound.

8 https://www.downtoearth.org.in/news/authorities-clueless-carcinogen-np-in-a-large-number-of-products-in-india-4021

Table 3 Export (Nonylphenol, Octylphenol and its isomers) from India to major countries

Country	Quantity (Thousands kg)		
	2016-2017	2017-2018	2018-2019
China	2277	2028	560
Singapore	1431	1828	915

Table 4 Import (Nonylphenol, Octylphenol and its isomers) to India from major countries

Country	Quantity (Thousands kg)		
	2016-2017	2017-2018	2018-2019
Taiwan	6145	4596	1935
Korea	546	837	1186

1.3 Nonylphenol Ethoxylates and Its Use

Nonylphenol is the base chemical for the production of Nonylphenol Ethoxylate and has been widely used in a range of products. Mostly, NPE is used in the production of detergent, therefore, large scale use of the chemical goes in the textile sector as a cleaning agent. However, apart from textile, the chemical is also being used in other products. Further, the chemical has the property of antioxidant. So, it is being used to protect polymers and rubbers.

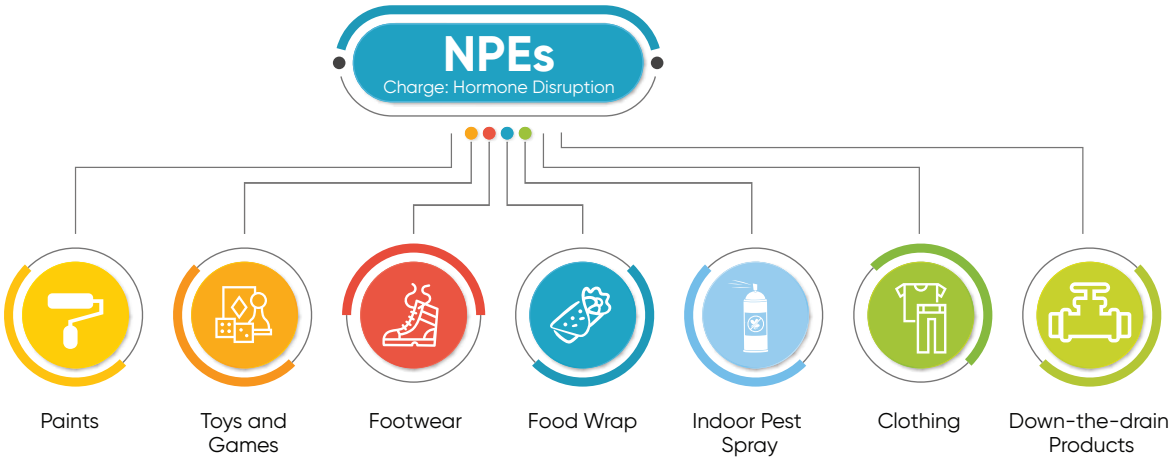
Nonylphenol is being used in following products:

- **Plastic** – Nonylphenol (NP) is used as an antioxidant and plasticizer in some plastic products (as a heat stabilizer in PVC plastic).[9,10] There is, thus, a possibility of migration from the plastic to its content.
- **Textile** – in this industry, it is used in detergents as a scouring, coating or waterproofing agents, in printing pastes and adhesives, and in dyeing.[11]
- **Pesticide** – It is used in pesticide products as "inert" ingredients (ingredients other than the named, active, pesticidal ingredient). They are used to increase the amount of a spray solution that remains on leaf surfaces, to make the spray droplets stick better to the leaf, and in general make the pesticide product more potent. It is also used as dispersant and emulsifier in the pesticides.[12]
- **Leather –** Used as surfactant.[13]
- **Paint –** Nonylphenol is also being used to harden the products by epoxy paint manufacturers.

The chemical is generally used as surfactant in these products and there is a high chance of leaching of this chemical into various products.

9 Loyo-Rosales JE, Rosales-Rivera GC, Lynch AM, Rice CP, Torrents A. Migration of nonylphenol from plastic containers to water and a milk surrogate. J Agric Food Chem. 2004 Apr 7;52(7):2016-20.
10 Nonylphenol and nonylphenol ethoxylates action plan. U.S. Environmental Protection Agency (EPA). August 2010.
11 https://oecotextiles.wordpress.com/tag/nonylphenol-ethoxylates/
12 http://www.intertek.com/chemicals/testing-and-analysis/np-npe/
13 https://www.leathersustainability.com/chemical-audits-testing-leather/chemical-testing/apeo-npeo-testing/

Figure 3 Nonylphenol uses[14]

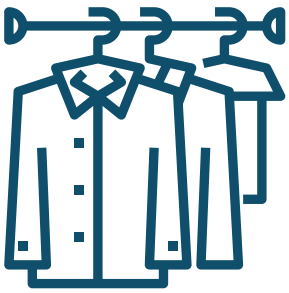


1.3.1 Nonylphenol and Textile

NPE, due to its amphiphillic properties, is substantially used as a surfactant in the textile industry. Therefore, Nonylphenol, through NPE, is being reportedly found in garments produced all over the globe. A study conducted by Greenpeace in 2012[15] found high concentration of NPEs in garments purchased from high end brands from 29 countries including India. Out of 141 garments purchased from across the world, 89 items had NPEs ranging from **1 ppm to 45,000 ppm**. Three out of nine garments purchased from India had Nonylphenol. Its presence in carpets can be of concern specifically for small children who crawl on the floor on carpets.

89 of **141** garments from **29** countries found NPE ranged from **1-45,000** ppm

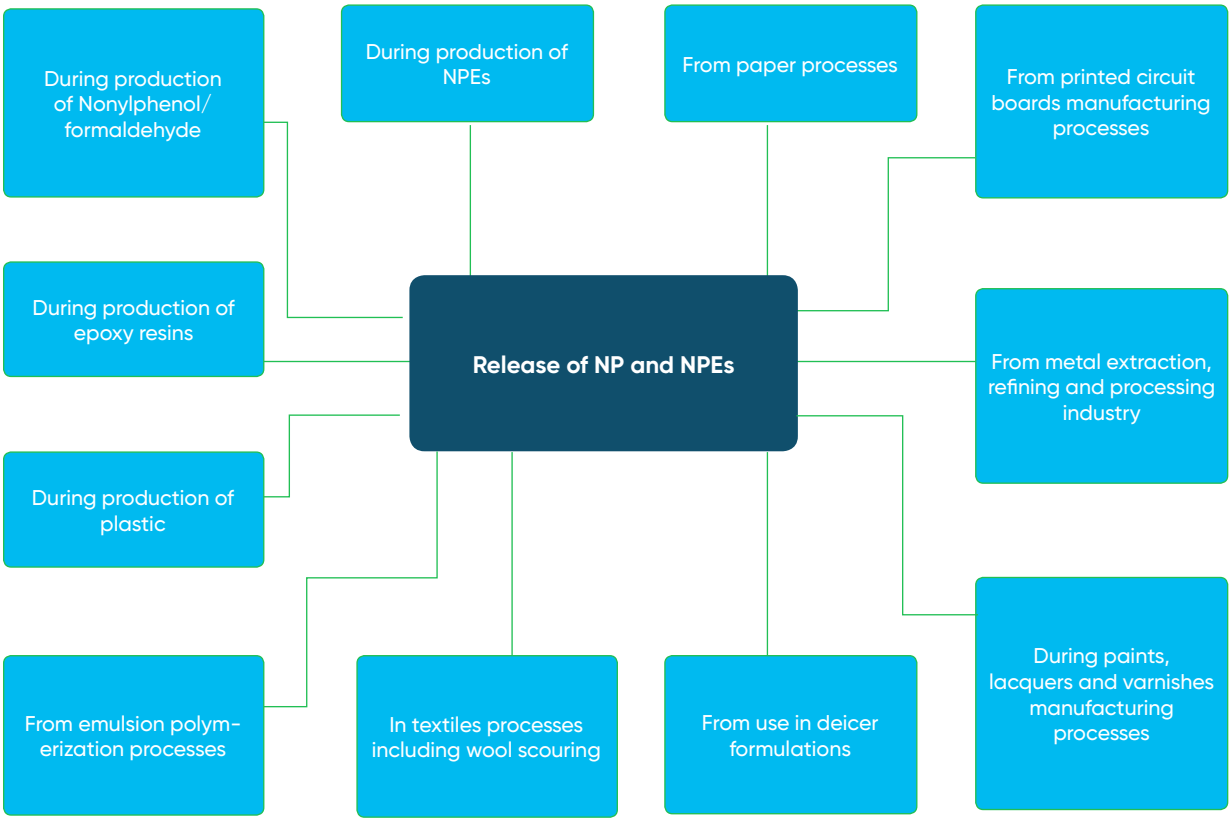
A similar study conducted by UK environment agency[16] assessed 100 cotton clothing (underwear) samples purchased from over 10 different non- EU countries such as India, China, Egypt, Turkey etc. The study detected NP in 28 of the tested samples in the concentration ranging from **3.3 ppm to 1759 ppm.**



In a study conducted by McIntyre in the year 1996, NP and its ethoxylates were found in a number of consumer products such as deodorant, fragrance, hair removal products, hair conditioner, and shampoo. In a sample of shampoo, NP was found in >10-30% by weight.

14 https://saferchemicals.org/get-the-facts/toxic-chemicals/npes-nonylphenol-ethoxylates/
15 Toxic Threads: The big fashion stitch up, Greenpeace, 2012
16 Nonylphenol ethoxylates (NPE) in imported textiles, Environment Agency, 2013

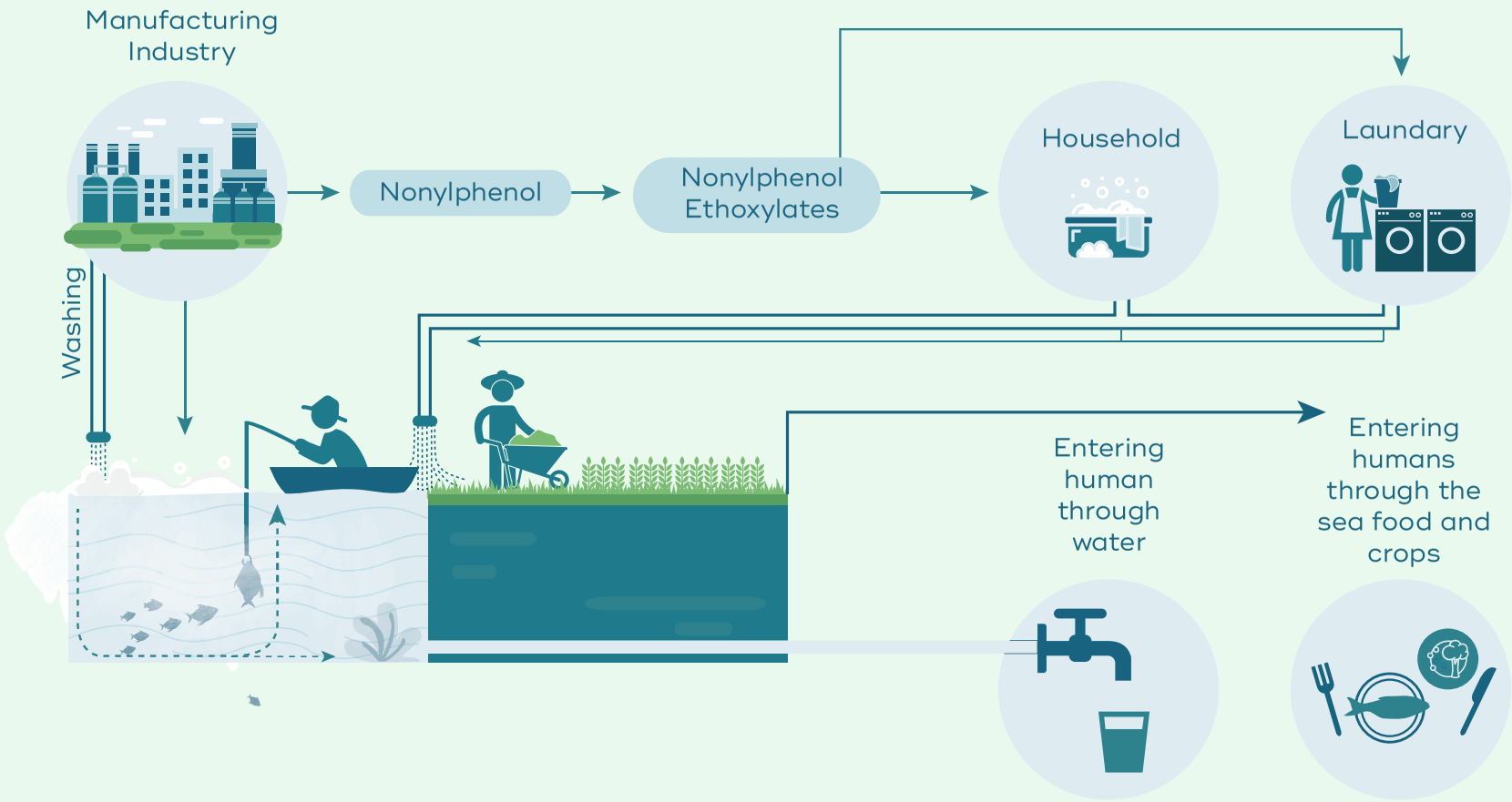
1.4 Nonylphenol and Environment



1.4.1 Fate of Nonylphenol in the Environment

NPE, upon entering the environment, breaks down into toxic compound Nonylphenol. Nonylphenol is thus being reported in a number of environmental matrices such as water and soil due to its extensive use in many industries. The occurrence of this compound in the environment can be clearly correlated with industrial discharges and other anthropogenic activities. Since, most of the applications of NP are in common consumer products such as detergents, they are usually disposed "down the drain" and thus enter the water bodies. Due to its physical–chemical characteristics, such as low solubility and high hydrophobicity, Nonylphenol accumulates in environmental compartments that are characterized by high organic content, typically sewage sludge and river sediments, where it persists. NP typically persists in the aquatic environment and is moderately bioaccumulative. However, it does not readily bio-degrade in the natural environment.

Figure 4 **Fate of Nonylphenol in the Environment**



1.5 Prevalence of Nonylphenol

1.5.1 Surface water

It has been established that Nonylphenol has multiple applications in various industrial sectors and since most of the industries discharge their untreated waste water into the water bodies, the chemical is now being commonly found in surface waters. NP has been detected widely in surface waters across the globe. In 2018, the presence of 4-Nonylphenol (4-NP) in the surface waters of Guandu river in the state of Rio de Janeiro, Brazil, was studied by **De Araujo, Frederico, et al. (2018) in Rural Federal University of Rio De Jenario**. The author observed that in 12 out of 19 samples, 4-NP was detected in the range of 1.73 and 2.32 µg/L and the study has raised alarm on the presence of high concentration of Nonylphenol in the river. The study has also suggested for periodic monitoring of Nonylphenol's concentration in river water samples.[17]

A similar study was conducted by **Subha Raju, et al. in 2018 in University of Madras**, India to assess the presence of Nonylphenol in marine environment in Chennai. Results depicted that all the studied samples were found to be contaminated with Nonylphenol. The study has observed the presence of Nonylphenol which ranges from 1.22 to 7.24 µg/l in water samples and 3.31 to 30.96 µg/kg in sediment samples which is well above the US EPA prescribed environmental safety limit of 1.7 µg/l.[18]

17 De Araujo, Frederico& F. Bauerfeldt, Glauco& Cid, Yara. (2018). Determination of 4-Nonylphenol in Surface Waters of the Guandu River Basin by High Performance Liquid Chromatography with Ultraviolet Detection. Journal of the Brazilian Chemical Society.29. 10.21577/0103-5053.20180079.

18 SubhaRaju, MadhumathiSivamurugan, KarunaGunasagaran, ThirunavukkarasuSubramani and MunuswamyNatesan Preliminary studies on the occurrence of nonylphenol in the marine environments, Chennai—a case study. The Journal of Basic and Applied Zoology (2018) 79:52. https://doi.org/10.1186/s41936-018-0063-1

Another study conducted by Selvaraj et al. in 2014 in Bharathidasan University, Tamil Nadu, India observed the presence of NP in three rivers viz. Kaveri, Vellar and Tamiraparini in India. Nonylphenol was found in the concentration from ND to 2200 ng/L[19] which is the quite high as compared to the prescribed phenolic compound standard (1.0 µg/l) for drinking water in India.

1.5.2 Water to Soil to crop

A large quantity of wastewater and sewage sludge is being reportedly used for agricultural purposes. This paves the way for a number of harmful chemicals into the soil and thus the crops. Nonylphenol is one such chemical. Having bioaccumulative properties, it has been making its way into our soil, sediments and a number of crops. As reported by **Vogel et al.** in their study on the migration ability of NP in soil, 730 days after application, up to 99% of the Nonylphenol remained in the topsoil profile, which could harm the crop yield and food safety through crop uptake and eventually pose a threat to human health by means of its enrichment and transmission within the food chain[20].

In a study conducted by **Jiang et al. (2019)**[21], NP was reported in a concentration of 18.03-23.89 mg/kg in a tomato plant. The study concluded decreased growth rate of the tomato plant and its seedlings due to NP exposure.

1.6 Fate of Nonylphenol during waste water treatment

> NP containing compounds in sludge are degraded into the more estrogenic Nonylphenol

Nonylphenol finds its way to the environment due to various industrial or household discharges. However, when the waste water passes through a treatment plant, most of the NP containing compounds, such as Nonylphenol (poly) ethoxylates, gets degraded aerobically into the shorter Nonylphenol ethoxylates or Nonylphenol. In the wastewater treatment plant, it is estimated that half of the NP gets absorbed on particles which then stay in the wastewater treatment plant as sludge or gets released into the aquatic phase and then settle on the sediment. According to the EU Risk Assessment Report, it was assumed that all NP containing compounds in sludge are degraded into the more estrogenic Nonylphenol. Nonylphenol is poorly soluble and unlikely to evaporate from the water. It remains suspended in the aquatic phase and further settles down to the sediments and also gets absorbed by aquatic animals.[22]

1.7 Nonylphenol in food products

Nonylphenol is now finding its way not only in the environment but also in many consumer and food products. As discussed above, it is being used in a wide array of industries including food packaging through which it might be migrating to the food products. Twenty five food-contact materials such as polystyrene and polyvinylchloride contained NP at concentrations of 64-287

19 Krishna Kumar Selvaraj, GovindarajShanmugam, SrimuraliSampath, D.G. Joakim Larsson, BabuRajendranRamaswamy. GC–MS determination of bisphenol A and alkylphenolethoxylates in river water from India and their ecotoxicological risk assessment. Ecotoxicology and Environmental Safety 99 (2014) 13–20

20 Accumulation and toxicological effects of nonylphenol in tomato (Solanum lycopersicum L) plants (2019): Lei Jiang, Yi Yang, Yong Zhang, Ying Liu, Bo Pan, Bingjie Wang & Yong Lin

21 Accumulation and toxicological effects of nonylphenol in tomato (Solanum lycopersicum L) plants (2019): Lei Jiang, Yi Yang, Yong Zhang, Ying Liu, Bo Pan, Bingjie Wang & Yong Lin

22 https://www.who.int/ipcs/methods/Nonylphenol.pdf

µg/g according to a study conducted by **Fernandes et al**[23]. In a Japanese study (Kawamura 2000), high levels of NP were found in plasticized PVC clings film[24]. The study detected NP in the concentration of 10 to 2600 µg/g in PVC wrapping film. It was also detected in different food contact products & infant/nursing- ware (made of Polystyrenes, Polycarbonate and Polypropylene) in the concentration- 17 to 499 µg/g.

Such presence questions the possible migration of the chemical from the packaging material to the food. A study conducted in 2011 in Sweden[25] found NP in fruits, cereal products, vegetables, and potatoes. The study also tested blood samples of nursing women to understand the transfer of the chemical from food to blood and found NP in detectable levels in 43% of the women. In a study conducted in Toronto found NP in fresh pork loin in the concentration of 0.53 mg/kg (in cooked sample) and 34 mg/kg (in raw sample).[26]

Table 5 **Presence of Nonylphenol in Environment and food products**

Year	Author	Matrix/Location	Title	Findings
WATER				
2014	Krishna Kumar Selvaraj, Govindaraj Shanmugam, Srimurali Sampath, D.G. Joakim Larsson, Babu Rajendran Ramaswamy	Kaveri, Vellar and Tamiraparini rivers, India	GC–MS determination of bisphenol A and alkylphenol ethoxylates in river water from India and their ecotoxicological risk assessment.	NP was found in the concentration from ND to 2200 ng/L.

23 4-Nonylphenol (NP) in Food Contact Materials:Review, Analytical Methodology and Occurrence, Alwyn R Fernandes, Martin Rose, Claire Charlton, 2008

24 https://hal.archives-ouvertes.fr/hal-00577422/document

25 4-Nonylphenol and bisphenol A in Swedish food and exposure in Swedishnursing women, Irina Gyllenhammar, Anders Glynn, Per Ola Darnerud, SannaLignell, Rob van Delft, Marie Aune, 2011

26 https://www.canada.ca/en/health-canada/services/environmental-workplace-health/reports-publications/environmental-contaminants/canadian-environmental-protection-act-1999-priority-substances-list-assessment-report-nonylphenol-ethoxylates.html

Year	Author	Matrix/Location	Title	Findings
2018	De Araujo, Frederico, Glauco F. Bauerfeldta and Yara P. Cid	Guandu River Basin, Brazil	Determination of 4-Nonylphenol in Surface Waters of the Guandu River Basin by High Performance Liquid Chromatography with Ultraviolet Detection	NP was found in 12 out of 19 water samples in the range of 1.73 and 2.32 µg/L
2018	Subha Raju, Madhumathi Sivamurugan, Karuna Gunasagaran, Thirunavukkarasu Subramani and Munuswamy Natesan	Water and Sediments, India	Preliminary studies on the occurrence of nonylphenol in the marine environments, Chennai—a case study.	Nonylphenol was found in the range of 1.22 to 7.24 µg/l in water samples and 3.31 to 30.96 µg/kg in sediment samples.
CROP				
2019	Lei Jiang, Yi Yang, Yong Zhang, Ying Liu, Bo Pan, Bingjie Wang & Yong Lin	Tomato crop, China	Accumulation and toxicological effects of nonylphenol in tomato (Solanum lycopersicum L)	NP was reported in a concentration of 18.03-23.89 mg/kg in a tomato plant. The study concluded decreased growth rate of the tomato plant and its seedlings due to NP exposure.
FOOD PRODUCTS				
2000	Kawamura, Y	Food Contact material (PVC Cling, Polystyrenes, Polycarbonate and Polypropylene)	Nonylphenol in food contact plastics and toys.	NP was detected in PVC at 10 to 2600 µg/g and in different food contact products & infant/nursing- ware (made of Polystyrenes, Polycarbonate and Polypropylene) in the concentration- 17 to 499 µg/g.
2008	Alwyn R Fernandes, Martin Rose, Claire Charlton	Food contact material- PVC and polystyrene	4-Nonylphenol (NP) in Food Contact Materials: Review, Analytical methodology and Occurrence	NP was detected in twenty five food-contact materials at concentration 64-287 µg/g. The study pointed out to the possibility of migration of the chemical to food products.
2011	Irina Gyllenhammar, Anders Glynn, Per Ola Darnerud, SannaLignell, Rob van Delft, Marie Aune	Food material- fruits, cereal products, vegetables, and potatoes. Blood of nursing women	4-Nonylphenol and bisphenol A in Swedish food and exposure in Swedish nursing women	NP was detected in the food samples above the limit of quantification. NP was found in detectable levels in blood samples of 43% of the women

1.8 Nonylphenol and Toxicity

1.8.1 Effects of Nonylphenol on Aquatic organisms

Nonylphenol is being found extensively in water bodies across the world. Thus, it became imperative to understand the impacts that it causes to the aquatic organisms. Many studies have been conducted to understand the linkage between the presence of NP and detrimental impacts on the aquatic life and have found the chemical in various organisms. A study conducted by L. Luo, et al. in 2017 in China found NP in the concentration of **0.82 ng/ml in fish**.[27] A similar study conducted by Dodder et al., in 2014 in California detected NP in the concentration of 96-3000 ng/g in Mussels.

- Feminization of aquatic organisms,
- Decreasing male fertility and
- Decreasing survival rate of fish

To further understand the presence of 4-NP in water samples and its toxicity and tissue accumulation, a study was conducted by **Gautam et al. in 2014** in India. NP was detected in the concentration of 12.40 mg/L and in 16.29 mg/L in water samples drawn from river Ganga and river Varuna at three different sites that witness high anthropogenic activities or are located near a city wastewater treatment efflux point. Bioaccumulation study depicted the presence of the chemical in different tissues and organs of the fish confirming its ability to migrate from water to biota. The study found that tissues accumulated NP in a concentration (64 and 160 mg/L). It further stated that brain accumulated the highest concentration of 4-NP while muscle showed the lowest uptake. Gill, liver, kidney, ovary and plasma showed intermediate ranges of accumulation[28].

Another study conducted by **Sun et al. in 2017**, concluded an inhibited growth effect on zebrafish at an exposure of 200 µg/L of NP. A study by EU also linked exposure of NP to cause slight changes in the estrous cycle length, timing of vaginal opening, ovarian weight, and sperm/spermatid count in laboratory animals (EU, 2002).

Effect of Nonylphenol on Fish Populations

Further, research studies have depicted the effects on the aquatic organisms of this widely present endocrine disruptor. Most of the tests indicate that estrogenic effects may start to occur at around 10-20 µg/L.[29] Since, this chemical has the ability to mimic estrogen a laboratory found NP displacing estrogen from its receptor site in rainbow trout.[30] The chemical is also capable of

27 L. Luo, Y. Yang, Q. Wang, H. Li, Z. Luo, Z. Qu, et al. (2017) Determination of 4-n-octylphenol, 4-n-Nonylphenol and bisphenol A in fish samples from lake and rivers within Hunan Province, China

28 Toxicity and tissue accumulation of 4-nonylphenol in the catfish Heteropneustes fossilis with a note on prevalence of 4-NP in water samples (2014): Geeta J Gautam, Radha Chaube, and Keerikattil P Joy

29 https://www.who.int/ipcs/methods/Nonylphenol.pdf

30 https://www.who.int/ipcs/methods/Nonylphenol.pdf

causing feminization of aquatic organisms, decreasing male fertility, and decreasing survival rate of young fish[31]. It is also found to be responsible for damaging kidneys, decreasing body weight, and inducing stressed behavior in fish population[32].

1.8.2 Impacts of Nonylphenol on Human Health

> Nonylphenol observed in amniotic fluid of pregnant women

There are a number of empirical studies depicting human health impacts of Nonylphenol. NP is a persistent, toxic, bio-accumulative chemical which acts as a hormone disruptor and can be responsible for a number of human health effects. Nonylphenol upon entering the human body gets rapidly and extensively absorbed in the gastrointestinal tract from where it is widely distributed throughout the body but with the highest concentration in fat.[33] Humans are getting exposed to NP through water, soil, food crops, paints, cosmetics etc., the largest contributor to the exposure is intake of fish (70-80%[34] of the daily dose). This exposure may result into a burning sensation, cough, labored breathing, sore throat, unconsciousness, skin irritation and burns. Upon ingestion, it may cause abdominal pain, diarrhea, nausea and sore throat[35]. The **US EPA in its Action Plan** for NP and NPE points out that NP's acute (oral and dermal) toxicity is low and though it is highly irritating and corrosive to the skin and eye, it does not have significant skin sensitizing potential. NOAELs (No Observed Adverse Effect Levels) and LOAELs (Lowest Observed Adverse Effect Levels) for systemic toxicity (based on body weight or body weight gain) in repeat dose rat oral toxicity studies range from 13 to 100 mg/kg-bw/day and from 43 to 400 mg/kg-bw/day, respectively.

Another study[36] conducted by **Jubendradass et al. in 2011** in India analyzed the long term effects of NP on rats. The animal was exposed to NP at the doses of 15, 150 and 1500 µg/ kg body weight per day for 45 days. The researchers' found an increase in the generation of Hydrogen peroxide (H_2O_2) and lipid peroxidation were increased, and a decrease in the activities of antioxidant enzymes. The study concluded that NP downregulates insulin signaling in liver, which could be due to ROS (reactive oxygen species) production and oxidative damage.

Concerns have been raised on NP's potential to cross the placental barrier and cause detrimental growth impacts on the developing fetus. In 2017, **Shekhar et al., in 2017 in SRM University, Tamil Nadu, India** conducted a study[37] to understand the in utero fetal exposure levels of NP as well as analyzed the transfer of the chemical from maternal blood to the fetus. Fifty three pregnant women were tested for NP, the results showed the presence of NP in concentration of 9.38ng/mL in maternal blood and in 8.44ng/mL in amniotic fluid. Its presence in the amniotic fluid points out to the potential risk that the chemical poses to the developing fetus.

31 Nonylphenol in the environment: A critical review on occurrence, fate, toxicity and treatment in wastewaters
32 https://ehp.niehs.nih.gov/doi/10.1289/ehp.8058
33 Evaluation of nonylphenol toxicity in etroplus maculatus (bloch, 1795):response on gill antioxidant defense system (2016) : K.P. Asifa, K.C. Chitra
34 https://www.who.int/ipcs/methods/Nonylphenol.pdf
35 https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1032
36 Long-term exposure to nonylphenol affects insulin signaling in the liver of adult male rats (2011): R Jubendradass, SC D'Cruz, PP Mathur
37 S. Shekhar, S. Sood, S. Showkat, C. Lite, A. Chandrasekhar, M.Vairamani, et al. (2017), Detection of phenolic endocrine disrupting chemicals (EDCs) from maternal blood plasma and amniotic fluid in Indian population

Since NP has the capacity to mimic estrogen, human body is prone to hormonal impacts of NP. To further understand its presence in the human breast milk, a couple of studies were conducted confirming the presence of the chemical in the breast milk raising questions on its toxic impacts. **Chen at al.[38] in 2010 in National Health Research Institute, Taiwan** found NP in the breast milk and associated its presence with the consumption of fish oil tablets. The study talks about the possibility of the possible source of Nonylphenol being the consumption of fish which in turn might be bio-accumulating NP through waste water discharge in the water body. In a study conducted by **Ademolloa et al. in 2008 in Higher Institute of Health, Italy,** NP was found in human breast milk in the concentration of 32 ng/mL[39]. To further establish the linkage between concentrations of NP to fish intake, a TDI assessment was undertaken in this study which concluded a maximum NP daily intake of 3.94 mg/kg/day, which is close to the TDI of 5 µg/kg body weight (bw) proposed by the Danish Institute of Safety and Toxicology. The presence of NP in breast milk is a significant concern as breast milk is a major source of nourishment for newly born baby, who are in early stages of development. Such high levels of EDCs in breast milk can be associated with negative effects on neurological development, growth, and memory function.

> Fish oil tablets could be one of the possible sources of Nonylphenol

> Nonylphenol observed in breast milk raise the concern of new born baby health

Nonylphenol has made its way not only in the breast milk, blood and urine but also in various tissues of the human body. A study conducted by **Muller et al. in 1997 in Swiss Federal Institute of Technology, Switzerland** confirmed this presence. The authors tested adipose samples taken from 25 human cadavers (4 collected in 1983-84 and 21 in 1994). These cadavers thought to be non-occupationally exposed were tested for NP and NP1EO and NP2EO. The study found NP in the concentrations of 19.8 to 84.4 ng/g[40]. Such high concentrations in the adipose tissues points out to the potential health hazard the chemical may pose to humans. Although this study particularly focused on the non-occupationally exposed bodies, perhaps the occupationally exposed humans will be at a greater risk.

1.9 Nonylphenol can be carcinogenic

The research studies have confirmed the human health impacts of Nonylphenol, concerns were raised about its potential to cause carcinogenic effects on the human body. Since, the chemical has also been classified as an endocrine disrupting chemical (EDC) and is found to be having a number of reproductive and hormonal effects on the exposed humans. It has been detected in human breast milk, blood, and urine and is associated with reproductive and developmental effects

38 G.-W. Chen, W.-H.Ding, H.-Y.Ku, H.-R.Chao, H.-Y.Chen, M.-C. Huang, et al. (2010) Alkylphenols in human milk and their relations to dietary habits in Central Taiwan

39 N. Ademolloa, F. Ferraraa, M.Delise, F.Fabietti, E. Funaria (2008). Nonylphenol and octylphenol in human breast milk

40 https://www.canada.ca/en/health-canada/services/environmental-workplace-health/reports-publications/environmental-contaminants/canadian-environmental-protection-act-1999-priority-substances-list-assessment-report-nonylphenol-ethoxylates.html

in rodents.[41] It has been found to be highly toxic to fish, aquatic invertebrates, and aquatic plants[42]. It increases the risk of developing inflammatory bowel disease by promoting or prolonging adverse progression of inflammation in the gastrointestinal tract[43].

Studies have thus established the linkage of NP with cancer. In-vitro studies have shown that it can enhance the progression of cancer by functioning as an estrogenlike factor[44]. A study conducted by **Yang et al.**, in 2017 examined the effect of NP on Colorectal cancer cells (cells responsible for causing colon cancer) and concluded that the presence of NP induces the cells and increases the chances of colon cancer. [45] World Health Organization in its risk assessment of Nonylphenol concluded that as per the in-vitro estrogenic data, the chemical has estrogenic activity, of 3-6 orders of magnitude less potent than estradiol[46]. A study treated mice with NP and found that they developed mammary cancer and also experienced higher rates of metastasis at younger ages. [47] In a similar study, male rainbow trouts exposed to NP produced a protein Vitellogenin which is normally produced in females as a response to estrogen hormone. The chemical was also found to be replacing estrogen in female rainbow trouts. [48]

Various studies are linking NP with breast cancer. A study conducted by **Vivacqua et al. in 2003** explained that NP can enhance the proliferation of breast cancer cells, due to its agonistic activity on ERα (estrogen receptor α) in estrogen-dependent and estrogen-independent breast cancer cells. It has also been argued that its estrogenic effect coupled with its widespread human exposure could potentially influence hormone-dependent breast cancer disease. [49] In a similar study, cell proliferation was stimulated by NP at concentrations between 22 and 2203 mg/L in human breast cancer cells. [50]

Nonylphenol can cause reproductive and hormonal impacts on human health. Studies have linked the chemical to cancer and have found its impact on cancer cells in human body.

41 https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-nonylphenol-and-nonylphenol-ethoxylates
42 Bisphenol A, nonylphenols, benzophenones, and benzotriazoles in soils, groundwater, surface water, sediments, and food: a review AlessandoCareghini& Andrea FilippoMastorgio& Sabrina Saponaro& Elena Sezenna, 2014
43 https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1032
44 Yang X1, Huang H1, Wang M1, Zheng X1, Xu J2, Xie M1 (2017): Effect of nonylphenol on the regulation of cell growth in colorectal cancer cells..
45 Yang X1, Huang H1, Wang M1, Zheng X1, Xu J2, Xie M1 (2017): Effect of nonylphenol on the regulation of cell growth in colorectal cancer cells..
46 https://www.who.int/ipcs/methods/Nonylphenol.pdf
47 https://www.bcpp.org/resource/alkylphenols/
48 https:// https://www.who.int/ipcs/methods/Nonylphenol.pdf
49 The food contaminants bisphenol A and 4-nonylphenol act as agonists for estrogen receptor α in MCF7 breast cancer cells (2003): Adele Vivacqua, Anna Grazia Recchia, Giovanna Fasanella, Sabrina Gabriele. Amalia Carpino, Vittoria Rago, Maria Luisa Di Gioia, Antonella Leggio, Daniela Bonofiglio, Angelo Liguori, Marcello Maggiolin
50 https://www.who.int/ipcs/methods/Nonylphenol.pdf

Some more human and animal-based research studies are presented below.

Table 6: Toxicity impacts of Nonylphenol on Aquatic organisms and Humans

Year	Author	Matrix/ Location	Title	Findings
AQUATIC ORGANISMS				
2005	Acevedo R, Parnell PG, Villanueva H, Chapman LM, Gimenez T, Gray SL, Baldwin WS	Mice	The contribution of hepatic steroid metabolism to serum estradiol and estriol concentrations in nonylphenol treated MMTVneu mice and its potential effects on breast cancer incidence and latency.	Mice exposed to NP (at 45mg/kg/day) developed mammary cancer and also experienced higher rates of metastasis at younger ages
2014	Geeta J Gautam, Radha Chaube, and Keerikattil P Joy	Water and Catfish	Toxicity and tissue accumulation of 4-nonylphenol in the catfish Heteropneustes fossilis with a note on prevalence of 4-NP in water samples	NP was detected in the concentration of 12.40 mg/L and in 16.29 mg/L in water samples drawn from river Ganga and river Varuna. Tissues accumulated NP in a concentration (64 and 160 mg/L). It further stated that brain accumulated the highest concentration of 4-NP while muscle showed the lowest uptake. Gill, liver, kidney, ovary and plasma showed intermediate ranges of accumulation.
2017	Dong Sun, Qi Chen, Ning He, Pan-pan Diao, Lixing Jia & Shunshan Duan	Zebrafish, China	Effect of environmentally-relevant concentrations of nonylphenol on sexual differentiation in zebrafish: a multi-generational study	The study found estrogenic effects of NP on Zebrafisha t a concentration of 200 µg/L. This concentration of NP resulted in inhibited growth of zebrafish.
2017	L. Luo, Y. Yang, Q. Wang, H. Li, Z. Luo, Z. Qu, et al.	Fish, China	Determination of 4-n-octylphenol, 4-n-Nonylphenol and bisphenol A in fish samples from lake and rivers within Hunan Province, China	NP was detected in the concentration of 0.82 ng/ml in the fish samples.
HUMAN HEALTH				
1997	Muller S.	Adipose tissue	Risk evaluation of bioactive compounds in humans. I. Synthetic musk fragrances. II. Alkylphenols. A dissertation submitted to the Swiss Federal Institute of Technology Zurich for the degree of Doctor of Natural Sciences	NP was detected in the concentrations of 19.8 to 84.4 ng/g. Such high concentrations in the adipose tissues points out to the potential health hazard the chemical may pose to humans.

Year	Author	Matrix/ Location	Title	Findings
2003	Adele Vivacqua, Anna Grazia Recchia, Giovanna Fasanella, Sabrina Gabriele. Amalia Carpino, Vittoria Rago, Maria Luisa Di Gioia, Antonella Leggio, Daniela Bonofiglio, Angelo Liguori, Marcello Maggiolin	Human Breast cells	The food contaminants bisphenol A and 4-nonylphenol act as agonists for estrogen receptor α in MCF7 breast cancer cells	The study found that NP can enhance the proliferation of breast cancer cells, due to its agonistic activity in estrogen-dependent and estrogen-independent breast cancer cells. It has also been argued that its estrogenic effect coupled with its widespread human exposure could potentially influence hormone-dependent breast cancer disease.
2008	N. Ademol-loa, F. Fer-raraa, M.Delise, F.Fabietti, E. Funaria	Breast milk	Nonylphenol and octylphe-nol in human breast milk	NP was detected in concentration of 32ng/ml. The study concluded seafood as one of the most important sources of exposure to NP in Italy.
2010	Chen GW, Ding WH, Ku HY, Chao HR, Chen HY, Huang MC, Wang SL	Breast milk	Alkylphenols in human milk and their relations to dietary habits in Central Taiwan	The study detected NP in the breast milk and associated its presence with the consumption of fish oil tablets and processed food products.
2011	R Jubendradass, SC D'Cruz, PP Mathur	Rats	Long-term exposure to nonylphenol affects insulin signaling in the liver of adult male rats	The study concluded that NP downregulates insulin signaling in liver, which could be due to ROS (reactive oxygen spe-cies) production and oxidative damage.
2017	Shekhar S, Sood S, Showkat S, Lite C, Chandrasekhar A, Vairamani M, Barathi S, San-tosh W.	Maternal blood and amniotic fluid, India	Detection of phenolic en-docrine disrupting chemi-cals (EDCs) from maternal blood plasma and amniotic fluid in Indian population	Fifty three pregnant women were tested for NP, the results showed the presence of NP in concentration of 9.38ng/mL in maternal blood and in 8.44ng/mL in amniotic fluid. The study raised concerns on the potential risk that the chemical poses to the developing fetus.
2017	Yang X, Huang H, Wang M, Zheng X, Xu J, Xie M	Colorectal cancer cells	Effect of nonylphenol on the regulation of cell growth in colorectal cancer cells.	The study tested effects of NP on COLO205 colorectal cancer cells. It concluded that the presence of NP induces the cells and increases the chances of colon cancer.

1.10 Regulations and Standards

The research studies across the globe have confirmed health and the environmental impact of Nonylphenol. Hence the countries have adopted regulations and issued advisories to reduce the use of Nonylphenol as much as possible.

Table 7: Regulations in various countries

Country	Details on regulations	Guideline value
Canada	Canada has identified Nonylphenol as a toxic chemical and took a number of steps to address the issue. A Priority Substance Risk Assessment was conducted in 2001, after which Nonylphenol was listed on Schedule 1 [51] of the Canadian Environmental Protection Act 1999 (the Toxic Substances List).	Freshwater – 1.0 µg/L Marine – 0.7 µg/L (Interim Guideline)
European Union (EU)	The EU member states and industry have agreed to phase out Nonylphenol ethoxylates in all detergent applications by the year 2000.[52] The EU has passed a directive 2003/53/EC in July 2003, which restricts the marketing and use in Europe of products and product formulations that contain more than 0.1% of NPE or NP. This applies to many industries such as the textile and leather industries, pulp & paper industries, agriculture, cosmetic and for domestic purposes as well except in the case of closed application systems where no release into waste waters occurs. This directive came into force from July 2005[53]. Further in 2016[54], it restricted NPE concentration to 0.01 % in textile articles entering the market after 2021. NP and NPEs were included on the first list of chemicals for priority action towards achieving the OSPAR Convention target of ending discharges, emissions and losses of hazardous substances to the marine environment of the north-east Atlantic by 2020.	0.01% (textile products)
China	In the year 2017,[55] Nonylphenol and Nonylphenol polyoxyethylene ether have been included in the priority chemicals list in the country. Nonylphenol was included in the national standards for food-to-contact material in the year 2017 by National Health and Family Planning Commission (NHFPC).	The standard is devised as 10ppb (0.010mg/kg) for all food contact materials including plastics, rubber, and adhesives.
The United States Environmental Protection Agency (US EPA)	Published an Action Plan for Nonylphenol and Nonylphenol Ethoxylates in 2010. Significant New Use Rules (SNURs) were subsequently proposed for Nonylphenol (CAS RN 25154-52-3) and its isomers which prohibits new use without prior approval (US EPA, 2015).[56] It has also been included in Contaminant Candidate List 4 (CCL 4) of EPA in 2016 and it may lead to a future regulation under the Safe Drinking Water Act (SDWA).	EPA has established water quality criteria for NP of 6.6µg/L for acute exposures and 1.7 µg/L for chronic exposures.[57]

51 https://www.canada.ca/en/environment-climate-change/services/canadian-environmental-protection-act-registry/substances-list/toxic/schedule-1.html
52 https://www.who.int/ipcs/methods/Nonylphenol.pdf
53 https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2003:178:0024:0027:en:PDF
54 http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32016R0026&from=EN
55 http://www.cirs-reach.com/news-and-articles/China-MEP-Published-List-of-Priority-Chemicals.html
56 Technical Brief- Nonylphenol and NonylphenolEthoxylates, American Dairy Products Institute
57 Nonylphenol (NP) and NonylphenolEthoxylates (NPEs), Action Plan: USEPA, 2010

Country	Details on regulations	Guideline value
Denmark	The country in January, 2005[58] banned the use of Nonylphenol and Nonylphenol Ethoxylates in: • industrial cleaning with few exceptions • cleaning in private homes • manufacture of textiles and leather with few exceptions • emulsifier in agricultural teat dips • metal manufacturing with few exceptions • production of paper and paper pulp • cosmetic products and other personal care products except in spermicides • pesticides	-
India	There are no specific standards for Nonylphenol or Nonylphenol ethoxylates for water and wastewater in the country; however standards for Phenolic compounds are listed in the standards for drinking water. • Bureau of Indian Standards (IS 4707 (Part 2:2009) have prohibited the use of Nonylphenol in cosmetics.	Phenolic compounds (as C6 H5 OH) As per IS 10500: 2012[59]. 0.001 mg/l, Max and 0.002 mg/l General standards for discharge of environmental pollutants Part-A: Effluents – as per The Environment (Protection) Rules, 1986 mg/l, Max for Inland surface water 5.0 mg/l, Max for Pubic sewer and Marine coastal

1.11 Alternatives of Nonylphenol

The extensive usage of NP and NPE as surfactants, along with its toxic properties, has lead to the search for safer alternatives of the chemical to be used as surfactants. NPE belonging to a wider class of chemicals called APEs, cannot simply be replaced by another APE as they might have similar estrogenic properties as that of NPE. Thus, a due analysis of the wider array of chemicals that we are surrounded by is required to list out suitable alternatives to NPE.

The US EPA's Design for the Environment (DfE) Program[60] conducted such assessment and prepared a list of eight safe surfactants after analysis of over 300 chemicals which can be used as alternatives to NPEs.

58 https://www2.mst.dk/Udgiv/publications/2007/978-87-7052-566-4/html/kap09_eng.htm
59 Nonylphenol, Factsheet No. 57, March 2018, Toxics Link
60 DfE Alternatives Assessment for NonylphenolEthoxylates, May 2012

Eight safe surfactants which can be adopted as alternatives to NPEs are:

1. C9-11 Alcohols, ethoxylated (6EO)
2. C12-15 Alcohols, ethoxylated (9EO)
3. Ecosurf EH-9
4. D-Glucopyranose, oligomeric, decyloctyl glycosides
5. Benzenesulfonic acid, C10-13-alkyl derivs., sodium salts
6. Sodium lauryl sulfate
7. Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-dodecyloxy-, sodium salt
8. Sorbitanmonostearate

All the proposed alternatives were assessed based on the following criteria:

Table 8 **Criteria for Safer Surfactants**

Acute Aquatic Toxicity (L/E/IC50 Value)	Rate of Biodegradation
≤1 ppm	May be acceptable if biodegradation occurs within a 10-day window without degradates of concern*
>1 ppm and ≤10 ppm	Biodegradation occurs within a 10-day window without degradates of concern*
>10 ppm	Biodegradation occurs within 28 days without degradates of concern*

**Degradates of concern are compounds with high acute aquatic toxicity (L/E/IC50 = 10ppm) and a slow rate of biodegradation (greater than 28 days).*

CHAPTER 2

Research Methodology

2.1 Objectives of the study

The issue of NP toxicity is being addressed globally, as there is substantial progress in limiting the use of the compound in detergent as well as in various products. However in India there are hardly any interventions on the toxicity of Nonylphenol. In this context, this study was conducted with the following objectives:

1. To analyze the presence of Nonylphenol in detergents sold in Indian market
2. The understand the fate of Nonylphenol in river and lake water
3. To bring policy attention for suitable action on the issue of Nonylphenol

2.2 Sampling

A set of twelve detergent powder (including two duplicate) samples from a local market in New Delhi and twelve surface water samples (including one duplicate) were collected from rivers and lakes from the different parts of the country with the help of partner NGOs. In case of detergents, known and easily available brands were chosen and in case of water sampling, two different points were selected at most of the locations. The points were selected after preliminary site assessment and considering the anthropogenic activities or industrial discharge in and around them.

2.3 Protocol

- Water samples were diluted with Millipore water and filtered by using a PTFE syringe filters (AXIVA) after which it was injected into HPLC.
- The NP concentration of the raw liquid sample was calculated by multiplying the dilution factor with the concentration of NP (ppm) obtained after dilution.

Figure 5: Sampling locations on Map

The locations or water sampling are as follows:

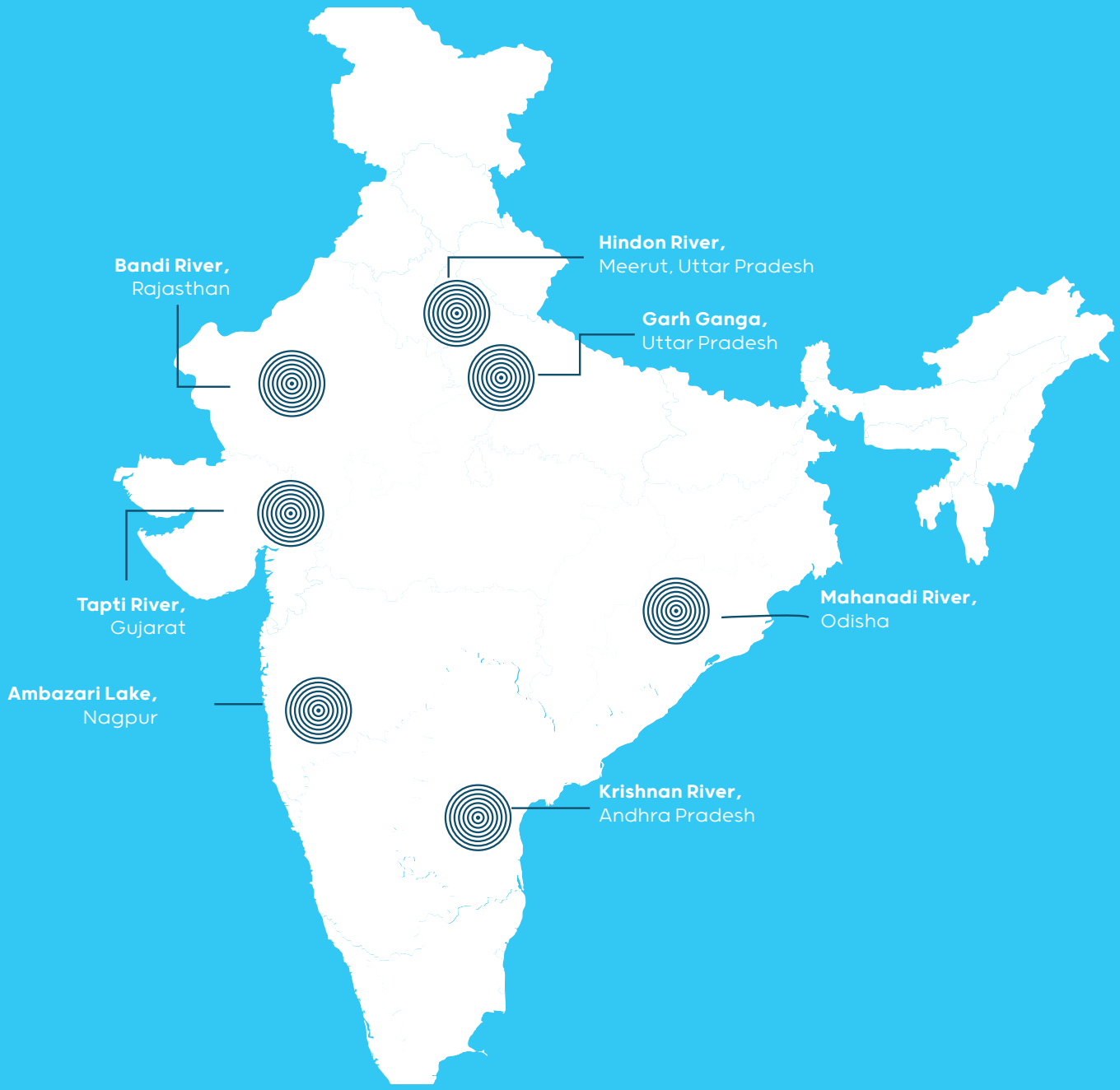


Figure 6: River water collection at Bandi River, Rajasthan.

- For detergent samples: A certain quantity of sample was dissolved in a certain quantity of Millipore water, sonicated for 10 minutes and then the filtered sample was analyzed by HPLC.
- The NP content in the powder sample was calculated in wt. % w.r.t. the mass of the powder sample dissolved in water.
- HPLC analysis was carried out in a liquid chromatography (Agilent: Infinity 1220 LC) equipped with an Oyster BDS Premium C18 column and variable wavelength detector.
- Acetonitrile/water (70:30) was used as mobile phase with a flow rate of 1 mL/min.
- The wavelength was set at 280 nm.

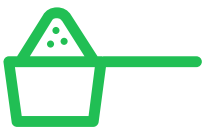
CHAPTER 3

Results and Discussion

The results of the analysis are divided in three parts i.e. detergents, river water and lake water and are presented below.

3.1 Presence of Nonylphenol in detergent samples

In the present study, twelve detergents samples (including two duplicate) were collected and analyzed. All of the analyzed samples detected Nonylphenol in the concentration which varied between 0.82 and 11.92 wt%. The highest concentration was observed in detergent 3, while the lowest was in detergent 9. The concentration of Nonylphenol in detergent samples were analyzed in weight percent (wt. %). Since, the detergent samples were solid and NP was not present in a homogeneous phase. This precisely means that if samples are taken from these solid samples from different areas then different values of NP may derive, hence the results of detergent samples are expressed in wt%.



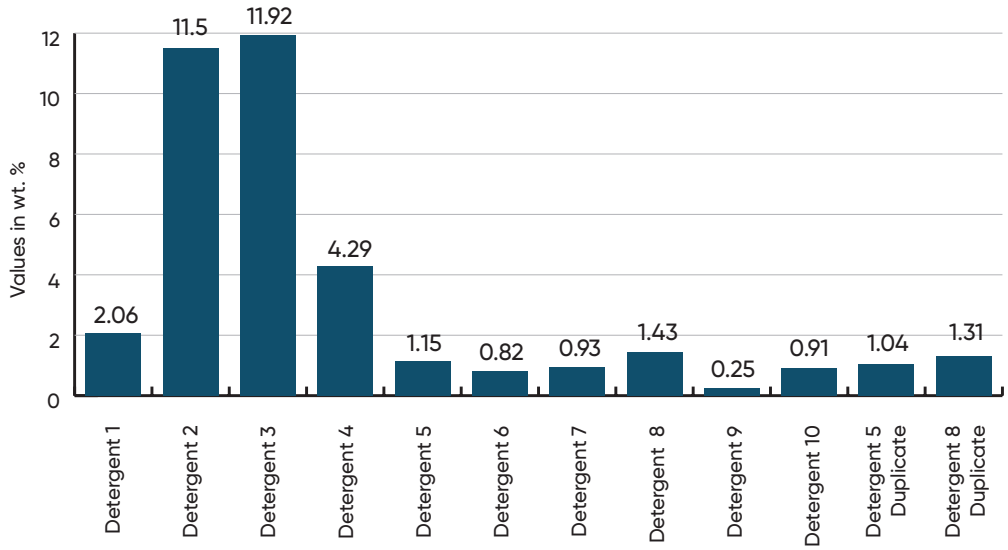
Very high amount of Nonylphenol found in analysed detergent samples

Table 9 Concentration of Nonylphenol in detergent samples

S. No.	Samples	Code	Nonylphenol (in wt. %)
1	Detergent 1	TL-N13	2.06
2	Detergent 2	TL-N14	11.5
3	Detergent 3	TL-N15	**11.92**
4	Detergent 4	TL-N16	4.29
5	Detergent 5	TL-N17	1.15
6	Detergent 6	TL-N18	0.82
7	Detergent 7	TL-N19	0.93

S. No.	Samples	Code	Nonylphenol (in wt. %)
8	Detergent 8	TL-N20	1.43
9	Detergent 9	TL-N21	**0.25**
10	Detergent 10	TL-N22	0.91
11	Detergent 5 Duplicate	TL-N23	1.04
12	Detergent 8 Duplicate	TL-N24	1.31

Figure 7 Nonylphenol concentration in detergent samples



3.2 Presence of Nonylphenol in river water samples

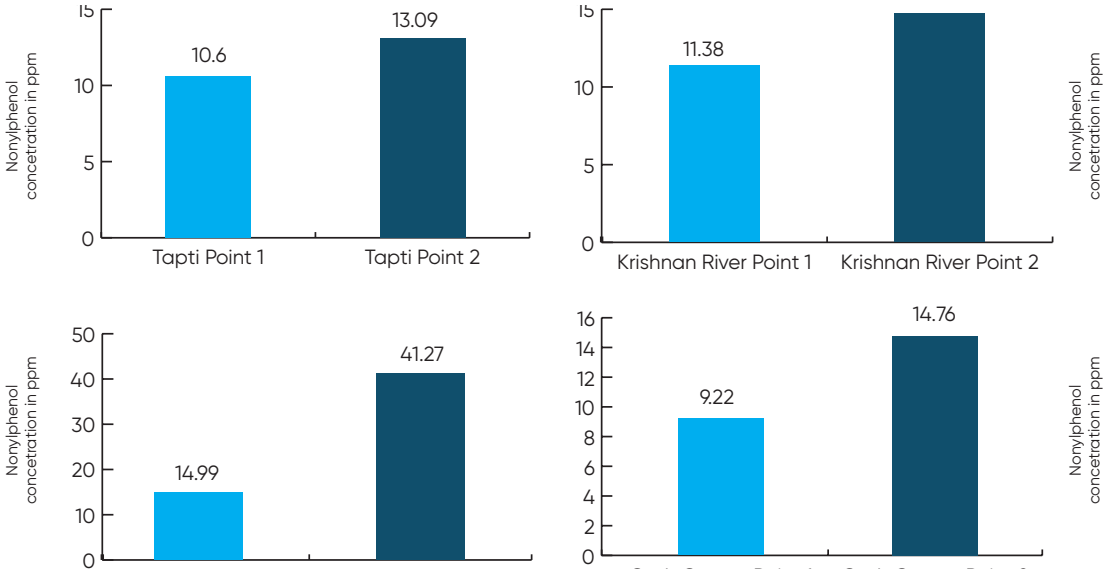
> All analysed water sampled found Nonylphenol and the difference in point 1 and point 2 is notable

In this study, samples were collected from two different locations of the river (point one and point two) to get an understanding on the impact of anthropogenic activities on Nonylphenol concentration. Point one of the river was chosen as a point before and point two as the point after the anthropogenic activity (washing of clothes, industrial discharge etc.). The study has reaffirmed that there is a correlation between high concentration of Nonylphenol and anthropogenic activities, as in all the samples the concentration of Nonylphenol was higher at point two. In River Tapti, an increase in NP concentration of 2.5 ppm between the two different points was noted. River Krishnan and Ganga depicted similar types of results. But a very high difference was observed at Bandi River, i.e., 41.27 ppm of Nonylphenol at the second point which was accounting for an increase of 26.28 ppm (Table 2 and Fig. 4). Such high concentration at second point of Bandi River perhaps attributes to the industrial discharge from the textile industries located near the river. And it is to be noted that Nonylphenol is used extensively in textile industries.

Table 10 Concentration of Nonylphenol in point 1 and point 2 in different rivers

SN	Sample	Location	Code	Nonylphenol (ppm)
1	Tapti Point 1	Gujarat	TL-N2	10.60
2	Tapti Point 2	Gujarat	TL-N3	13.09
3	Krishnan River Point 1	Andhra Pradesh	TL-N4	11.38
4	Krishnan River Point 2	Andhra Pradesh	TL-N5	14.72
5	Bandi River Point 1	Rajasthan	TL-N6	14.99
6	Bandi River Point 2	Rajasthan	TL-N7	41.27
7	Garh Ganga Point 1	Uttar Pradesh	TL-N8	9.22
8	Garh Ganga Point 2	Uttar Pradesh	TL-N9	14.76

Figure 8 Concentration of Nonylphenol in point 1 and point 2 in the different rivers



3.3 Presence of Nonylphenol in other surface water samples

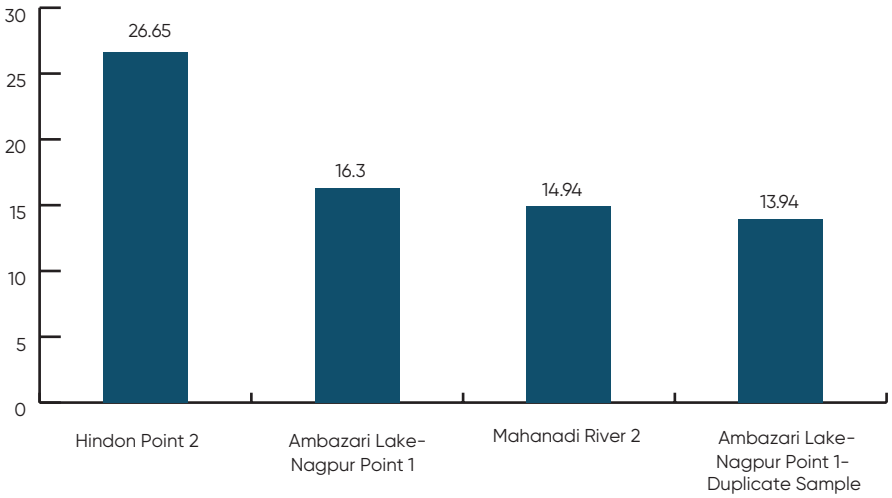
In this study, four other water samples were also analyzed for the concentration of Nonylphenol. Two out of four samples were collected from River Hindon, Meerut and River Mahanadi, Odisha (one each). Third sample was from Ambazari lake, Nagpur, Maharashtra, water from Ambazari lake was also analyzed in duplicate (sample four).

Nonylphenol was observed in all analyzed samples. The concentration of Nonylphenol varied between **13.94 ppm** and **26.65 ppm**. The highest concentration was observed in River Hindon while the lowest concentration was observed in the lake water sample.

Table 11 Concentration of Nonylphenol in other surface water samples

SN	Sample	Location	Code	Nonylphenol (ppm)
1	Hindon River in Ghaziabad	Meerut	TL-N1	26.65
2	Ambazari Lake-Nagpur	Maharashtra	TL-N10	16.30
3	Mahanadi River in Cuttack	Odisha	TL-N11	14.94
4	Ambazari Lake-Nagpur Duplicate Sample	Maharashtra	TL-N12	13.94

Figure 9 Concentration of Nonylphenol in other surface water samples



The results have established the fact that Nonylphenol is being extensively used In India. Some of the important observations coming out of this study are:

- Nonylphenol has been found in very high quantity in all the detergent samples tested
- The concentration of Nonylphenol in detergent ranges from 11.92 wt. % to 0.25 wt. % which is substantially high
- Concentration in the detergent samples is found to be very high in the products of international corporations whereas they have declared their products to be free of Nonylphenol in other countries.
- Nonylphenol is also detected in very high quantity in the river samples including water samples of the Ganga River.
- Highest concentration of Nonylphenol was detected in the river Bandi in Rajasthan which is a textile hub of India.

3.4 Conclusion

The research studies have confirmed human health impacts of Nonylphenol, and raised concerns about its potential to cause carcinogenic effects on the human body. The chemical has also been classified as an endocrine disrupting chemical (EDC) and is found to be having a number of reproductive and hormonal effects on the exposed humans.

The results have reflected the grim environmental scenario of the use of Nonylphenol in India. Nonylphenol has been accepted globally as a toxic chemical of high concern because of its health impacts as the chemical is found to be having a number of reproductive and hormonal effects on the exposed humans. Similarly concerns were raised about its potential to cause carcinogenic effects on the human body. In the present study, the chemical is found to be astonishingly high in detergents as well as in river water. NPE use is directly attributed to its high presence in detergents. However apart from detergent, there can be other possible sources of Nonylphenol contamination in the river water samples. Nevertheless, detection of Nonylphenol at downstream of the river as well as in lake water has raised serious concerns on the level of contamination in the rivers and lakes in India. Further there is every possibility that the drinking water may have also been contaminated with Nonylphenol which needs further investigation. Further highest concentration of Nonylphenol was detected in Bandi River in Pali district in Rajasthan; a textile hub in India is an indication of excessive use of Nonylphenol in textile industries.

There can be other possible sources of Nonylphenol contamination in river water samples

Another important aspect of the study is the adoption of double standard by the international corporations in phasing out of Nonylphenol in the detergent. Though many of the international corporations have claimed that Nonylphenol has been phased out in their products, however the study confirmed the presence of high quantity of Nonylphenol in products sold by their Indian subsidiaries. [61-62] Here, it is pertinent to mention that EU and some of the countries have taken decisive actions to phase out Nonylphenol since late 2000. This is clear example of how the voluntary approach has failed in absence of the regulations for the management of this chemical.

3.5 Road map to phase out Nonylphenol

Nonylphenol is a toxic chemical of high concern and concerted actions have been initiated globally to restrict the use of this chemical in products as far as possible to minimize its adverse impacts on the environment and human health. However, unfortunately in India, hardly any awareness or interventions have been made to restrict the use of this chemical except for a restriction on the use of Nonylphenol in cosmetics. Therefore, there is a dire need of developing a road map to phase out the chemical in the country. Some of the suggested recommendations are:

- To ban the use of Nonylphenol in detergents, one of the major sources of environmental contamination.
- Generation of data to assess the possible impacts of the chemical on human health and environment.
- To create an inventory of the usage of Nonylphenol in different sectors in the country.
- To carry out substantial research studies on the presence of Nonylphenol in water bodies and develop policy to denominate the chemical from the environment.
- To revise industrial effluent standards to prevent the entry of NP in the environment.
- To bring standards on Nonylphenol in drinking water and in food to protect human health and the environment.

61 https://us.pg.com/ingredients/
62 https://www.unilever.com/Images/es_people_tcm244-409740_en.pdf

- To promulgate suitable regulations in the country to phase out the chemical in other products as well.
- To initiate a legal action against the corporations for practicing double standard based on the polluter pay principle.
- There is also need to check the Nonylphenol presence in drinking water as well the possible revision of drinking water standard at par with the global standard in context of Nonylphenol.
- Adoption of technology to decontaminate Nonylphenol in water
- Assessment and adoption of available alternatives.

Finally the chemical management needs utmost attention in the current scenario and there may be cases where the chemical is being prohibited elsewhere but may be allowed in India. So, the country may look for devising a target for the sound chemical management at national and global levels.

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