

Toxic Impressions

BPA in thermal paper



A report by
Toxics Link

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 afore mentioned areas apart from creating awareness among several stakeholder groups.

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Toxics Link
for a toxics-free world

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Contents

Abbreviations	iv
Background	v
Introduction	1
1.1 About BPA	1
1.2 Health Impacts of BPA	2
1.3 Thermal paper and mechanism of printing	2
1.4 Advantages of thermal paper printing	3
1.5 Market size of thermal paper	4
Literature Review: BPA in thermal paper	5
2.1 Impacting human health and environment	5
2.2 Regulation of BPA in thermal papers	7
Rationale of the Study	9
3.1 Objectives	9
3.2 Sampling and Methodology	9
3.2.1 Sampling	10
3.2.2 Methodology for quantitative analysis of Bisphenol-A (Gas Chromatography method)	10
3.3 Scope	10
3.4 Standard preparation	10
Results and Discussion	11
Conclusion and Recommendations	13
5.1 Regulation of BPA in thermal papers	13
5.2 Suitable disposal of thermal papers	13
5.3 Awareness Generation	13
5.4 Alternatives	14
5.5 Research Agenda	14
Bibliography	15

Abbreviations

ADHD	Attention-deficit/hyperactivity disorder
BPA	Bisphenol-A
BIS	Bureau of Indian Standards
µg/day	Microgram per day
µg/g	Microgram per gram
µg/L	Microgram per litre
BPF	Bisphenol-F
BPS	Bisphenol-S
bw/day	Body weight per day
ECGs	Electrocardiograms
EC	European Commission
FDA	Food and Drug Administration
LC-MS	Liquid chromatography-mass spectrometry

Background

Bisphenol - A (BPA) is a known Endocrine Disrupting Chemical (EDC) that interferes with the production, secretion, transport, action, function and elimination of natural hormones of the human being. BPA can mimic our body's own hormones in a way that could be hazardous for one's own health. Children are most susceptible to the health impacts caused due to BPA exposure. Globally, countries have initiated actions to phase out BPA from children's products.

Since BPA is a known toxic chemical, Toxics Link has initiated work on EDCs and has been working for its phase out in children products. In 2014, Toxics link conducted a study on baby feeding bottles and found high content of BPA and campaigned to phase out BPA from baby feeding bottles. Finally, the Bureau of Indian Standards (BIS) phased out BPA use in feeding bottles as per IS 14625:2015.

In continuation to this campaign, Toxics Link carried out another research study on BPA presence in baby sippy cups and teether. The use of BPA in sippy cups is not regulated in India. Toxics Link study led the Bureau of Indian Standards to include sippy cups and other drinking accessories like teats, cup, spout and straw intended for feeding infant milk substitutes in the ambit of this regulation.

However, the studies also found that BPA presence in other products can be harmful to human health and environment. BPA is used in the thermal paper receipt and is very loosely bound with it. So, Toxics Link has carried this study on BPA in thermal (receipt) paper to get an understanding on the quantum of use of BPA in thermal paper and possible impacts on the human health and environmental hazards caused due to its exposure. This report also suggests the need of regulation of BPA in thermal paper in India and shifts to the alternatives to prevent the BPA exposure in the environment.

Introduction

1.1 About BPA

Bisphenol-A (BPA) is used as a monomer in the production process of polycarbonate plastics for day-to-day consumer products (e.g. baby feeding bottles, sippy cups, etc) and epoxy resin linings for food and beverage containers and for polyacrylate dental materials.

BPA is a well-known endocrine disrupting chemical. The issues concerning BPA is of global concern hence, as preventive measure countries have initiated actions to phase out BPA from various products considering its negative impact on human health.

Toxics Link conducted several research studies on children products including baby feeding bottles (2014), baby sippy cups (2016) and teething (2016). Varied levels of BPA were detected in these products. Surprisingly, the studies also revealed that BPA was detected in some products which were labeled as BPA free, 0 % BPA and safe for children. These studies helped catalyse government actions to notify the regulation to phase out BPA from children products including baby feeding bottles and sippy cups.

However, BPA is also used in other daily use variants apart from regular consumer products like teething, baby food cans, sippy cups. BPA is one of the constituent chemical used in thermal paper, which can contaminate environment and is likely to affect human health negatively.

Therefore, this study is carried out with a view to develop an understanding on BPA use in thermal papers used in India and requirement of a regulation to prevent BPA exposure in the environment.

1.2 Health Impacts of BPA

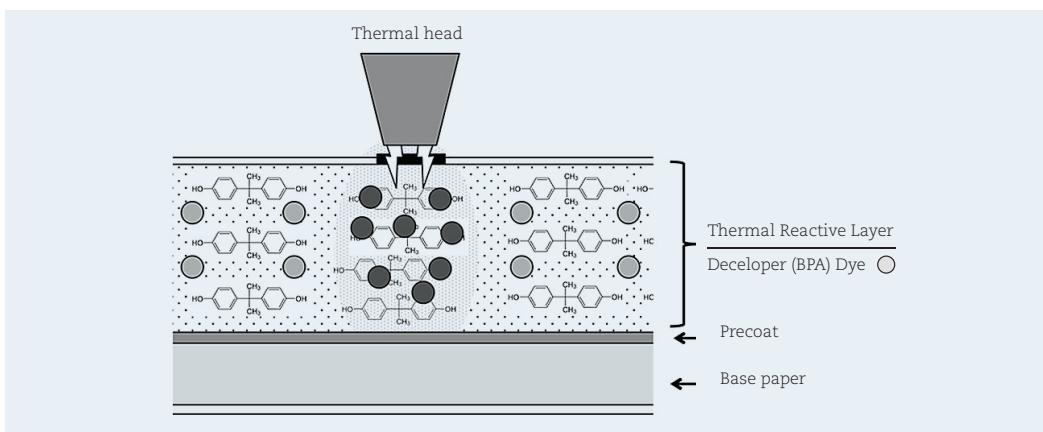
BPA is known for causing disruption in the endocrine system and there are studies which supports the claim that BPA can cause serious health hazards. [Toxics Link 2016]

- A study conducted on 244 mothers found that exposure to BPA before birth could affect the behavior of girls' at the age of 3, whose mother's urine contained high levels of BPA during pregnancy scored worse on tests of anxiety and hyperactivity
- Epidemiological studies found correlations between BPA exposure and heart diseases, liver toxicity and metabolic syndrome (diabetes, obesity)
- American Society for Reproductive Medicine (ASRM) found that women with the highest levels of BPA in the blood are more likely to face miscarriage than women with the lowest levels of BPA
- Researchers have reported that exposure to low doses of BPA lead to disruptive effects in androgen or estrogen responsive tissues, within the immune system, thyroid, and the developing nervous system
- Some studies in animals have confirmed that BPA can cause change in prostate growth and development, mammary gland organization, sexually dimorphic behavior, onset of oestrus cyclicity, early puberty, body weight and genital malformations

1.3 Thermal paper and mechanism of printing

Thermal papers are widely used by retailers to print the sale receipts in various sectors like grocery stores, gas stations and bank ATMs to ensure fast and accurate services. The thermal paper is also used by ticketing agencies, lottery systems and other businesses, which require

FIGURE 1: Schematic diagram of thermal receipt paper identifying the thermal reactive layer that contains BPA as a developer and a leuco dye, as well as stabilizers and binders

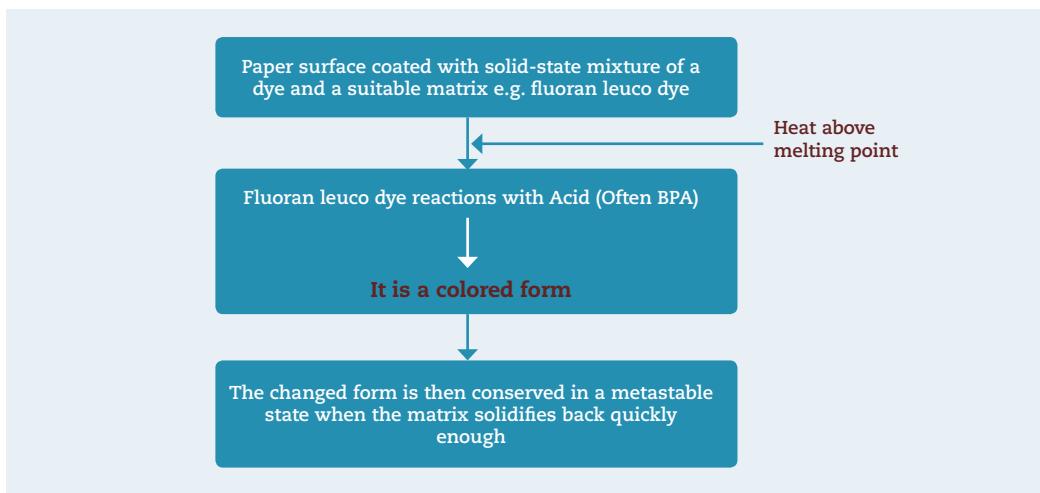


accurate and high-volume printouts. Specialized fields like healthcare sectors use high quality images produced by thermal printing for important and highly technical printouts for which accuracy is necessary, like electrocardiograms (ECGs), ultrasound printouts and prescription labels.

Figure 1 depicts a schematic diagram of thermal receipt paper identifying the thermal reactive layer that contains BPA as a developer and a leuco dye, as well as stabilizers and binders.¹

The detailed mechanism of the composition of thermal paper and color development after thermal reaction is presented in Figure 2.

FIGURE 2: Mechanism of printing



1.4 Advantages of thermal paper printing

Thermal paper printers are much faster than other types of printers resulting in less waiting time at the checkout line. The images created are of superior quality and clearer in comparison to other types of printing thus making them an integral component to be used everywhere. They are used in all places ranging from hospitals, where accuracy of a printout is critical to a local store, where itemized receipts through thermal printing help consumers to keep a better eye on their spending. The printers are also capable of printing high quality barcode scans directly on a receipt, making complex transactions like returns and exchanges much easier for customers, retailers' preventing shoplifting and falsified receipts that can

1 Hormann AM, Vom Saal FS, Nagel SC, Stahlhut RW, Moyer CL, et al. (2014) Holding Thermal Receipt Paper and Eating Food after Using Hand Sanitizer Results in High Serum Bioactive and Urine Total Levels of Bisphenol A (BPA). PLoS ONE 9(10): e110509. doi:10.1371/journal.pone.0110509

have a direct effect on its prices. Generally, thermal paper is coated with BPA which makes it extremely stable and heat-resistant. BPA is used in making coatings that gives thermal paper its unique properties which allows inkless printing.²

1.5 Market size of thermal paper

The global thermal paper market size was estimated at 1,154.8 kilo tons in 2015 and is expected to witness a substantial growth over the forecast period due to its extensive use in tags, labels, tickets and receipts. Its rising demand at point of sale (POS) terminals as an alternative to cash registers in the hospitality, warehouse, retail, and laboratory sectors is expected to be a favorable factor for its growth. POS was the largest application accounting for 81.9% of global volume share in 2015. The rising number of retail outlets and supermarkets in China, India and Saudi Arabia are due to increasing urban population and supportive government policies to promote investments which are expected to remain a key driver for the industry in the near future.³

India is growing market for the thermal paper industries with the changing the economic dynamics of the country. In India the thermal papers are manufactured here at the same time large quantity of these papers is being imported. South Korea is one of the biggest importers of thermal papers to India.

² <http://www.thermalpaperfacts.org/facts-about-thermal-paper>

³ <http://www.grandviewresearch.com/industry-analysis/thermal-paper-market>

Literature Review:

BPA in thermal papers

2.1 Impact on human health and environment

BPA is commonly used due to its efficiency, availability and affordability. However, BPA a known endocrine disruptor is a cause of concern for the researchers' worldwide and number of research studies have been initiated linking BPA from thermal papers and its impact on human health and environment.

- A study conducted by Shelley Ehrlich et al in Harvard University of Public Health in 2015 found that found increase in BPA concentration in their urine after handling of receipts for 2 hrs continuously without gloves but no any increase of BPA was observed while using the gloves.⁴
- A study done by Annette M. Hormann et. al., the University of Missouri. 2014 concluded that the elevated levels of BPA were observed in the serum while holding the thermal paper. In their experiment, they have tried to establish linkages with BPA exposure effects and hand sanitizer. The study found that when a person holds thermal paper receipt immediately after using a hand sanitizer, there is high chance of release of BPA as a free chemical and absorb in to the body through the skin. The study also found that it was a combination of dermal and oral BPA absorption that led to a rapid and dramatic average maximum increase (Cmax) in unconjugated (bioactive) BPA of 7 ng/ml in serum and 20 mg total BPA/g creatinine in urine within 90 min.⁵



Research studies found “BPA free” labeled consumer products sold in market also showed presence of BPA,

- In 2013, researchers from Kannur University, Kerala, India analyzed thermal papers used at the local automated teller machine counters of India for detecting presence of BPA and the capability of paper to produce estrogen to those

⁴ Shelley Ehrlich, Antonia M. Calafat, Olivier Humbert, Thomas Smith, and Russ Hauser, Handling of thermal receipts as a source of exposure to Bisphenol A, JAMA. 2014 February 26; 311(8): 859–860. doi:10.1001/jama.2013.283735

⁵ Hormann AM, vom Saal FS, Nagel SC, Stahlhut RW, Moyer CL, et al. (2014) Holding Thermal Receipt Paper and Eating Food after Using Hand Sanitizer Results in High Serum Bioactive and Urine Total Levels of Bisphenol A (BPA). PLoS ONE 9(10): e110509. doi:10.1371/journal.pone.0110509

who have been exposed to BPA. The results of the study indicate that these papers can produce estrogen hormone like hormone-like effect on experimental systems. Further, the research study also has

stated that as tons of such receipts are being dumped into the environment, this can lead to the high amount of hormone disruptors are being deposited in the environment. Since BPA in thermal paper exists as free, un reacted molecule , there is the potential for mobility and therefore human exposure during handling of the receipt paper. Further the study also proposes the remedial measures to remove the estrogenic properties of the thermal paper with the purified laccase from ascomycete fungi.⁶

- Tinne Geens et al., 2012, did an estimation of the levels of Bisphenol A thermal paper receipts collected from Belgium and its exposure to human beings. In his study he found that out of the total 44 thermal paper samples, BPA was determined in 73 % of the total samples which had Concentrations between 0.9% and 2.1% (between 9 and 21 mg BPA/g paper), while remaining 27% of the samples had concentrations below 0.01% (0.1 mg BPA/g paper). Further he studied on BPA from thermal paper and its impact on the people who are exposed occupationally to thermal paper and try to establish linkages that whether frequent contact with the thermal paper is associated with an increase in urinary BPA excretion.⁷ In this analysis, urine samples were collected from 90 cashiers who use the handle the BPA receipts and 44 control samples. BPA was detected in all the samples. The median urinary total BPA concentration was found to be 3.54 µg/L (2.89 µg/g creatinine) for controls and 8.92 µg/L (6.76 µg/g creatinine) for cashiers. Hence the study concluded that significant increase in urinary total BPA concentration was observed for cashiers handling thermal paper receipts daily.
- In another experiment carried out in France by Zalko D. et al., 2010, with viable skin models demonstrated extensive uptake and biotransformation of BPA following the absorption in the skin. In his research paper, he has demonstrated that the trans dermal exposure is contributed significantly to BPA exposure in human, when direct contact with BPA (free monomer) occurs. Incidentally, thermal papers are important source of free BPA.⁸



“Touching the thermal paper after using hand sanitizer is unsafe”

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- 6 Divya L M, Prasanth G K, Sadashivan C, 2014, Elimination of estrogenic activity of thermal paper using laccase from Trichoderma sp NFCCI-2745, Applied biochemistry and biotechnology, 2013; 169 (4) doi:10.1007/s12010-012-0016-y
- 7 Tinne Geens, Leo Goeyens, Kurunthachalam Kannan, Hugo Neels, Adrian Covaci. Levels of bisphenol-A in thermal paper receipts from Belgium and estimation of human exposure. Science of the Total Environment, 2012, 435 436; 30–33
- 8 Zalko, D., et al. Viable skin efficiently absorbs and metabolizes bisphenol A. Chemosphere (2010), doi:10.1016/j.chemosphere.2010.09.058 (article in press)

2.2 Regulation of BPA in thermal papers

Globally efforts are being made to phase out or restrict the use of BPA in thermal papers considering the precautionary principle.

TABLE 1 Regulation of BPA in thermal papers

Countries	Status of use of BPA in thermal paper
Japan	Banned BPA since 2001 ⁹
Belgium	Banned BPA in thermal papers in 2011 ¹⁰
Suffolk County Legislature, New York	Law to ban BPA use in thermal papers starting from 2013 ¹¹
Illinois & New York	Ban use of BPA containing receipt paper in 2012 legislative sessions ¹²
Connecticut (USA)	Prohibited BPA use in thermal papers from either 2013 or 2015 depending upon the availability of commercial alternatives before 30 June 2013 ¹³
France, Denmark, Sweden, Mariland, Washington, Vemount, Canada, Minnesota, Maschettetus	Banned BPA in thermal papers ¹⁴
European Union	BPA concentration in thermal paper to be reduced to less than or equal to 0.02% weight (200 ppm) before 2 January 2020 ¹⁵
South Korea	Developments in restricting BPA use in till receipts ¹⁶
Taiwan	Developments in restricting BPA use in receipts ¹⁷

9 https://www.epa.gov/sites/production/files/2015-09/documents/bpa_ch2.pdf

10 https://en.wikipedia.org/wiki/Bisphenol_A#Regulation

11 <https://www.pca.state.mn.us/sites/default/files/p-p2s10-13.pdf>

12 <http://www.tuv-sud.com/home-com/resource-centre/publications/e-ssentials-newsletter/consumer-products-e-ssentials/vol.-68/california-proposition-65-recent-updates>

13 Barraza, L. (2013). A new approach for regulating bisphenol A for the protection of the public's health. *The Journal of Law, Medicine & Ethics*, 41 (s1), 9-12

14 <http://daily.bhaskar.com/news/nat-top-atm-paper-slip-receipt-can-cause-cancer-contains-harmful-chemicals-4656089-nor.html>

15 <https://echa.europa.eu/documents/10162/370b5de7-9507-f1b4-edc6-80ef2e5cd781>

16 <https://chemicalwatch.com/47659/south-korea-ngos-call-for-bpa-ban-in-till-receipts>

17 <http://www.chinapost.com.tw/taiwan/national/national-news/2011/01/06/286548/Carcinogen-found.htm>

ALTERNATE SOLUTIONS

There can be non-phenol alternatives for BPA use in thermal papers. Some of them are listed below:

- Pergafast (evaluated as EPA alternatives assessment)
- Urea urethane (evaluated as EPA alternatives assessment)
- Ascorbic acid

However, there are still gaps in the evaluation of their health and environmental impacts.

Technical alternatives to prevent BPA exposure through thermal papers include:

Matrix printing

Inkjet prints

Thermal transfer printing

Use of E-tickets and payments using mobile can also be adopted to minimize the exposure

Rationale of the Study

Bisphenol-A is a well-known Endocrine Disrupting Chemical (EDC) that can affect health of human beings particularly children who are most vulnerable to its exposure. With the growing quantum use of thermal papers in day-to-day life and no system for collection of used slips, in most of the cases these thermal papers are dispersed into the surrounding environment, contaminating the ecosystem as well as the food chain. Although, many countries have initiated actions to phase out or restrict BPA from thermal papers however, there is no information and discussion being initiated on the possible impact of the chemical from thermal papers in India. Therefore, this study is first of its kind in Indian context largely focusing on analysis of presence of BPA used in thermal papers in India. Further, the study is aimed to catalyze discussion on the management of BPA in thermal papers at the upstream and downstream level.

3.1 Objectives

The present study has the following objectives:



- ✓ To detect the presence of Bisphenol-A (BPA) in thermal papers used in different stores in Indian market
- ✓ To highlight the need of BPA regulation for thermal papers in India

3.2 Sampling and Methodology

Chemicals required during experimental analysis of BPA in thermal papers

1. BPA from Sigma-Aldrich
2. HPLC grade water
3. Ethyl Acetate (HPLC grade)
4. Methanol (HPLC grade)
5. Acetonitrile (HPLC grade)

3.2.1 Sampling

In this study, total twelve (12) samples of thermal papers were collected randomly from different markets in New Delhi. The samples collected included both known and local brands of different manufacturers and suppliers. Out of twelve, two samples were printed with bank name (provided to the respective bank with their swipe machine). All the samples were collected in duplicate and sent to Department of Biotechnology, Banaras Hindu University, Varanasi for quantitative analysis of BPA.

3.2.2 Methodology for quantitative analysis of Bisphenol-A (Gas Chromatography method)

Twelve samples of thermal paper receipt were used in this study. 100 mg of each thermal paper receipt were cut into small pieces and extracted for 60 minutes in 1 mL of pure water at room temperature. After the extraction process, BPA quantity that passed into water was analyzed through High Performance Liquid Chromatography (HPLC). HPLC analysis was carried out on a Agilent 1200 Series HPLC system equipped with a C18 column (100 x 2.1 mm, particle size 2.7 μ m) using a mobile phase composed of water/acetonitrile (60:40, v/v) at a flow rate of 1 mL/min and column temperature at 30 °C. Fluorescence excitation and emission wavelength for BPA detection was 225 nm and 310 nm respectively. The chromatograms were processed using software.

3.3 Scope

This test method covers determination of Bisphenol-A (BPA) using gas chromatography and detecting using mass selective detection.

3.4 Standard preparation

BPA standard solution was prepared by dissolving 1 mg of AR-grade BPA in 1 ml of Acetonitrile.

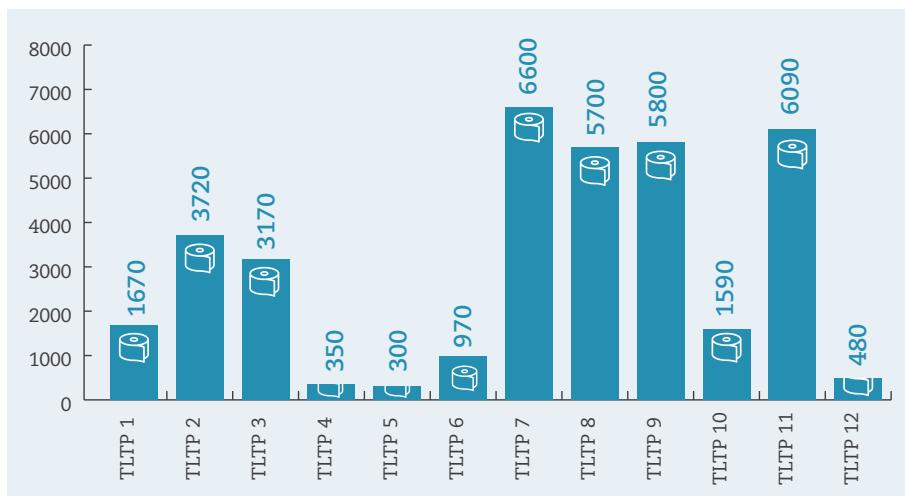
Results & Discussion

- Bisphenol-A was detected in all the collected samples with varied levels
- Concentration of BPA is found to be between 0.03% (300 ppm) and 0.66 % (6600 ppm) in thermal papers
- Maximum concentration of BPA in thermal paper was found to be 0.66 % (6600 ppm)
- There is no established correlation between the presence of high amount of BPA and its impact on the printing

TABLE 2 Concentration of BPA in thermal papers

Sampling ID	Description	% BPA Conc (mg/100mg paper)	PPM
TL TP -1	Small sized roll used for slip generated in ATM, Jungpura	0.167	1670
TL TP -2	Small sized roll used for slip generated in ATM, Bhogal	0.372	3720
TL TP - 3	Small sized roll used for slip generated in ATM, Lajpat Nagar	0.317	3170
TL TP - 4	Big size, used for generation of bill in stores, grocery shops etc, Bhogal	0.035	350
TL TP - 5	Big size, used for generation of bill in stores, grocery shops etc, Nehru Place	0.03	300
TL TP - 6	Big size, used for generation of bill in stores, grocery shops etc, Nehru Place	0.097	970
TL TP - 7	Big size, used for generation of bill in stores, grocery shops etc, Kotla	0.66	6600
TL TP - 8	Medium sized roll, Malviya Nagar	0.57	5700
TL TP - 9	Big size rolls - Amazon Online	0.58	5800
TL TP -10	For printing bills at the outlet, Jungpura Extension	0.159	1590
TL-TP-11	Big size rolls - Amazon Online	0.609	6090
TL-TP-12	Big size rolls, Bhogal	0.048	480

FIGURE 3 Concentration of Bisphenol A in thermal papers (ppm)



Conclusion

and Recommendations

BPA generally binds very loosely with the thermal papers. Nevertheless in India there is no downstream management system in place for the used thermal papers. Hence there is every possibility that BPA from the thermal paper will leach into the environment and contaminate the ecosystems. In this context, the study proposes the following recommendations.

Toxics Link would like to propose the following recommendations in the context of the present study.

5.1 Regulation of BPA in thermal papers

There are countries across the globe taking actions to either phase out or reduce the limits of BPA content in thermal paper. Therefore, as a precautionary approach, India should also regulate BPA in thermal papers to minimize the risk and impact on human health and environment.

5.2 Suitable disposal of thermal papers

The research study indicates high content of BPA in thermal papers in India. There is no proper disposal system in place for these thermal papers and they finally enter into the ecosystem. Further, there is a possibility that these BPA containing thermal papers may get recycled and contaminate the other products. Therefore, suitable guidelines should be developed considering the overall management of these papers.

5.3 Awareness Generation

Stakeholders awareness is another key factor to minimize the risks associated with BPA. The relevant agencies should step in to create awareness among the stakeholders to prevent the possible impact of BPA from thermal papers. Some of the suggested measures are

- Avoid taking receipts unless one really need them as very often these receipts end up in the trash and contaminating the environment
- Go for on-line receipts as far as possible
- Wash your hands after touching the thermal receipts
- It is advisable to use gloves to minimize the risks while handling BPA coated receipts. The govt can issue guidelines in this regard considering the public health

5.4 Alternatives

In India, BPA free thermal papers are used widely and so it is possible to shift to the alternatives for producing thermal papers considering their negative impact on human health and environment.

5.5 Research Agenda

There are only few research studies on possible impact of BPA in Indian context. Therefore, more research studies may be developed on its impact on human health and environment.

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