Bisphenol A contamination of wastepaper, cellulose and recycled paper products

M. Gehring, D. Vogel, L. Tennhardt, D. Weltin & B. Bilitewski
Department of Waste Management, Dresden University of Technology, Germany.

Abstract

Hormonal disturbances caused by environmental pollutants have become one of the most important issues regarding environmental and human health. Bisphenol A (BPA), octylphenol and nonylphenol are three prominent xenobiotic endocrine active compounds (EACs) mimicking natural female sex hormones (estrogens). Since both BPA and alkylphenol polyethoxylate surfactants are used in paper production the contamination of recycled paper products with these compounds can be expected. Therefore, the contamination of wastepaper, toilet paper and cellulose samples with selected EACs has been investigated. With one exception, all xenoestrogens studied were determined in all toilet paper samples at very high concentrations of 2 – 430 mg/kg dry mass (dm). The concentration of BPA in toilet paper amounted to 3.2 mg/kg dm, 45.5 mg/kg dm and 46.1 mg/kg dm. In seven fractions of separately collected municipal wastepaper the concentrations of BPA amounted to 0.093 to 5.1 mg/kg dm. In three types of cellulose the EAC concentrations were below or hardly above the respective limit of quantitation. Toilet paper, thus, was shown being an important source of xenoestrogen emissions to wastewater. Thermal paper again is assessed being a major source for the contamination of recycled paper products with BPA. Because of the distinct contamination with xenoestrogens, both paper waste and recycled paper products should not be mixed with biological waste *e.g.* for co-composting or co-fermentation in order to derive organic fertilisers.
Keywords: endocrine active compounds, environmental estrogens, wastepaper, toilet paper, cellulose, bisphenol A, nonylphenol, ethoxylates, endocrine disruption

1 Introduction

Municipal wastewater is polluted with a variety of organic substances of both natural and xenobiotic origin [1]. An increasing number of these compounds are identified to interacting with the hormonal (endocrine) systems of humans and wildlife [2]. These substances are called endocrine active compounds (EACs). Many EACs interfere with the endocrine system through direct binding to and de-/activation of steroid hormone receptors [2]. Substances mimicking natural female sex hormones, i.e. 17β-estradiol, via this biochemical mode of action are called estrogenic endocrine disrupting compounds (estrogenic EDCs) [3]. If EACs are not satisfactory removed during sewage treatment they are emitted with sewage treatment plant (STP) effluents to the receiving water bodies [1]. The agricultural use of sludge contaminated with EACs may lead to the pollution of soils, surface waters and groundwater with EACs [1,4]. So, especially aquatic organisms can be exposed to and impacted by EACs directly or indirectly emitted to surface waters after sewage treatment.

One of the most prominent xenobiotic estrogens, frequently called xenoestrogens, is bisphenol A (BPA, 2,2-bis-(4-hydroxyphenyl)propane) [2]. BPA is mainly processed to polycarbonate plastics, epoxy resins and the flame retardant tetrabromobisphenol A [5]. In its monomeric form it is used as an antioxidant in plasticisers [5] and in the colour developing layer of thermal papers [5,6].

4-*tert*-octylphenol (OP) and branched 4-nonylphenol (NP) are two other important estrogenic EDCs. Both are transformation products of the respective polyethoxylate surfactants (OPnEOs, NPnEOs) which are used for instance in cleaning agents, as wetting agents and as emulsifiers, *e.g.* in the deinking of recovered paper in order to clean the fibres from colours, glues etc. [6]. Since water solubility of APnEOs decreases with the length of the ethoxylate sidechain, short-chained APnEOs can be expected to adsorbing considerably to paper fibres during deinking.

BPA, OP, NP, and alkylphenol polyethoxylates (APnEOs) are frequently detected in wastewater and sewage sludge [1,7,8]. Under anaerobic conditions, APnEOs are terminally degraded to the respective alkylphenols (APs) [9,10]. The APs themselves are degraded solely under aerobic conditions [9,10]. Therefore, the anaerobic treatment of sewage sludge contaminated with APnEO results in formation and accumulation of APs [9,10].

In Germany, approximately 0.5 Mio t of toilet paper are emitted to wastewater per year [11]. Hence, toilet paper represents one of the most important mass fluxes of solid material into municipal STPs. The rate of recovered paper input to production of hygiene papers amounts to approximately 75 % [12]. Since both BPA and APnEOs are used in paper production the contamination of recycled paper products with these compounds can be hypothesised. TP then can be expected to being an important source for BPA and APnEOs/APs in wastewater and sewage sludge. In order to verify this hypothesis, the concentrations of BPA and four alkylphenolic compounds (APX) in toilet paper, wastepaper and cellulose samples have been investigated.

2 Materials and methods

2.1 Sample description

Three sorts of toilet paper (TP) made from 100 % recycled paper have been purchased from local supermarkets in Dresden, Germany, in autumn 2001. Three sorts of import cellulose (CL) were kindly supplied by Mr. Rainer Spörl, PTS Paper, Heidenau, Germany. Major properties of the TP and CL samples studied are summarised in table 1.

Table 1: Sample description, toilet paper and cellulose

toilet paper	TP1	TP2	TP3
dry matter content [%]	95.2	94.2	94.0
loss on ignition [%]	82.7	98.9	97.9
mass per area [g/m^2]	62.5	68.6	46.8
no. of layers	1, crepe	3	2
cellulose	CL1	CL2	CL3
dry matter content [%]	96.6	96.1	97.3
loss on ignition [%]	99.9	99.7	99.6
wood	spruce, pine	eucalyptus	spruce
disintegration	sulphate	sulphate	sulphite
bleaching [1]	ECF	ECF	TCF

[1] ECF: elemental chlorine free bleaching, TCF: total chlorine free bleaching

Wastepaper (WP) collected in the city of Dresden was separated from impurities, sorted out and separated into seven fractions: brown and grey corrugated board (WP1), advertising supplements (WP2), magazines (WP3), catalogues (WP4), newspapers (WP5), free advertising papers (WP6) and chromo board (WP7). Sampling, preparation, and storage of wastepaper samples are given in detail elsewhere [13].

Table 2: Sample description, wastepaper

sample	dry matter content [%]	loss on ignition [%]	description [1]
WP1	94.6	92.8	corrugated board
WP2	95.6	78.0	advertising supplements
WP3	95.9	68.7	magazines
WP4	96.2	70.7	catalogues
WP5	94.6	98.7	newspapers
WP6	94.7	88.9	free advertising papers
WP7	94.9	86.6	chromo board [2]

[1] sample from Dresden, Germany; [2] sample from from Neuss-Norf, Germany

2.2 Sample preparation and GC/MS measurements

Both sample preparation and method of determination of the target compounds by gas chromatography/mass spectrometry (GC/MS) basically followed [14] and are given in detail elsewhere [3,15]. The samples have been freeze-dried and extracted by Soxhlet extraction. TP samples were then prepared using the complete procedure described by [3,15]: After successive clean-up of the extracts by means of size exclusion chromatography (SEC) and a silica gel bed, derivatisation (silylisation) and determination of the target compounds by GC/MS followed, respectively. Then a simplified procedure excluding the SEC step was found to be optimal for the preparation of paper and cellulose samples.

Three 1 – 2 g aliquots of a paper sample were simultaneously extracted and prepared for determination of EACs. BPA, OP, NP, and, in part, 4-nonylphenol monoethoxylate (NP1EO) and 4-nonylphenol diethoxylate (NP2EO) have been determined in this study. BPA-d_{16} and 4-*n*-nonylphenol were used as surrogate standards (SSs). Since attention initially was turned only to BPA and NP, no specific SS for the quantitation of other target compounds was added. Therefore OP, NP1EO, and NP2EO were also quantified in relation to 4-*n*-nonylphenol.

Recovery of the SSs was calculated as proportion of the mean peak area in all sample aliquots in relation to the mean peak area in all calibration standards. With the exception of BPA-d_{16} in WP4 the mean recovery of the two SSs in all types of WP and CL samples amounted to 76.4 – 122.0 %, respectively [3,15]. For unknown reasons recovery of BPA-d_{16} in WP4 was only 13.7 %. In the TP samples the recovery of the SSs was in general $\leq$ 6 % [3,15], obviously caused by the SEC clean-up of the extracts. In addition, since concentrations of EACs were unexpected high, i.e. in the case of BPA, chromatographic peaks in part were not clearly quantifiable. Thus, interpretation of the TP data is subject to some restrictions.

3 Results and discussion

3.1 Toilet paper

With the exception of OP in TP3 all xenoestrogens studied were determined in all toilet paper samples at very high concentrations of 2 – 430 mg/kg dm (table 3, figure 1). The concentration of BPA in the TPs amounted to 3.2 mg/kg dm, 45.5 mg/kg dm and 46.1 mg/kg dm. The concentrations of OP, NP and BPA in TP1 and TP2 systematically exceeded those in TP3 by a factor of up to 15, respectively. Taking the concentrations of OP, NP, NP1EO, and BPA in TP1 and TP2 into account, the concentration of NP2EO in TP2 has to be estimated being exceptional high.

Table 3: Concentrations of xenoestrogens in paper samples (mg/kg dm)

	OP	NP	NP1EO	NP2EO	BPA
TP1	2.2	68.9	11.6	74.1	45.5
TP2	5.1	67.5	31.1	428	46.1
TP3	n.d.	14.3	10.0	57.3	3.2
C1	n.d.	n.d.	n.q.	n.d.	(n.q.)
C2	n.d.	n.d.	n.d.	n.d.	(n.q.)
C3	n.d.	0.04	0.06	0.16	(n.q.)
WP1	0.09	0.70	n.m.	n.m.	4.23
WP2	0.03	0.48	n.m.	n.m.	1.32
WP3	0.06	0.40	n.m.	n.m.	0.21
WP4	0.09	1.01	n.m.	n.m.	0.09
WP5	0.03	0.96	n.m.	n.m.	3.24
WP6	0.03	0.92	n.m.	n.m.	2.56
WP7	0.04	0.74	n.m.	n.m.	5.10

n.d.: not detectable (< limit of detection); n.m.: not measured; n.q.: not quantifiable (> n.d. but < limit of quantitation); (n.q.): triplicates partly n.d., n.q. or hardly > n.q., assessed as n.q.

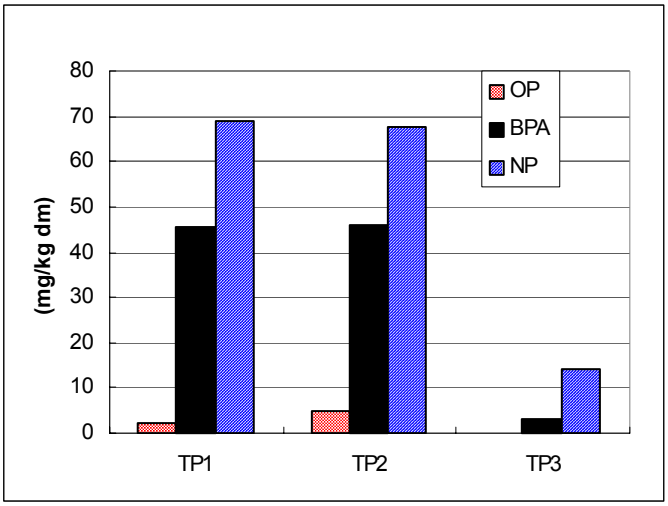

Figure 1: Concentrations of xenoestrogens in toilet paper

In the cases of TP1 and TP2, the BPA concentration exceeded the maximum concentration determined in wastepaper by one order of magnitude (table 3). Amongst others, accumulation of BPA during processing of WP to TP, a higher BPA content in the input material and a combination of these two possibilities could have caused this situation. Despite of the restrictions to data interpretation described above it can be stated that these BPA concentrations accord well with the data published by [17] who determined BPA concentrations of 0.6 –

24 mg/kg in 9 recycled paper products for kitchen use (MEAN = 6.21 mg/kg, paper made from 80 – 100 % recycled paper). Approximately 0.5 Mio. t of toilet paper per year are disposed with wastewater in Germany [11]. Assuming that the general mean BPA concentration in toilet paper amounts to 31.6 mg/kg DM as calculated for the three sorts of toilet paper studied, 16.6 t of BPA are annually emitted with TP to wastewater.

3.2 Wastepaper

The BPA concentrations in the WP samples amounted to 0.093 to 5.1 mg/kg dm (table 3, figure 2). The highest concentrations of BPA were determined in corrugated board and chromo board (WP1, WP7), whereas the lowest concentrations were detected in magazines and catalogues (WP3, WP4). The BPA concentrations in the seven classes of WP obviously correspond to the respective proportion of wastepaper reused for production [6].

The OP and NP concentrations in wastepaper amounted to 0.03 – 0.09 mg/kg dm and 0.40 – 1.01 mg/kg dm, respectively. No correlation occurred between the concentrations of the three EACs. The BPA oncentrations in WP were 1 – 2 orders of magnitude lower than the concentrations determined in two of the three sorts of toilet paper, respectively (see above, table 3).

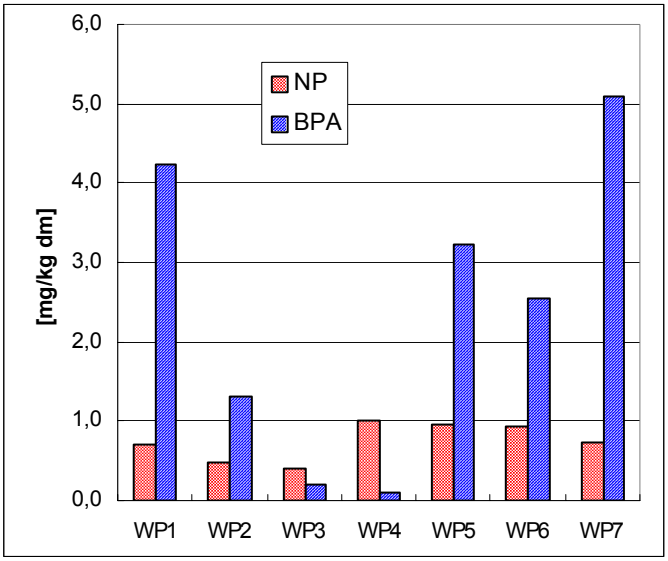

Figure 2: Concentrations of xenoestrogens in wastepaper

3.3 Cellulose

In order to prove the hypothesis that BPA does not derive from natural material, three different types of cellulose subsequently were investigated. Indeed, no or very little amounts of BPA were detectable in the CL samples. OP was not detectable in cellulose at all whilst NP, NP1EO, and NP2EO were determined in one of the three samples at 35.7 – 164.3 µg/kg dm (table 3). Hence, the BPA and APX concentrations in the CL samples were in general below or hardly above the respective limit of quantitation. These results are in accordance with data published by [17] who determined BPA concentrations in virgin paper below 0.1 mg/kg (N = 11). The low but detectable BPA concentrations in CL3 as well as the fact that this cellulose was the only one produced by means of total chlorine bleaching and magnesia bisulphite process indicate contamination during production. This contamination could be either inherent in this technology or specific for this certain case.

4 Conclusions

Toilet paper was shown to being an important source of xenoestrogen emissions to wastewater. Thermal paper again is estimated being a major source for the contamination of recycled paper with BPA. Thermal paper represents a very small portion of the entire paper production but due to its extremely high BPA content it certainly mainly causes BPA input into the paper cycle. Because of the distinct contamination with the xenoestrogens OP, NP, BPA, NP1EO, and NP2EO, paper waste as well as recycled paper products should not be mixed with biological waste in order to derive organic fertilisers, *e.g.* via co-composting or co-fermentation (see also [3,8,15]).

With regard to the considerable contamination of wastepaper with BPA, the moderate water solubility of BPA [5] and the limited extent of desorption during 24 h leaching experiments (data not shown, see [3]) we also conclude that continuous emissions of BPA with leachate from landfills receiving significant masses of wastepaper can occur under anaerobic conditions.

Future research should investigate i.e. the distribution (dissipation) pathways of the target compounds within in the paper cycle.

Acknowledgements

This work was supported by the Dresden University of Technology, Dresden, Germany, and the Forum for Waste Management and Contaminated Site Remediation, Pirna, Germany. We want to thank our laboratory assistants Ms. Marén Hertrich, Ms. Dagmar Gerbet, and Mr. Axel Bierwolf .

References

[1] Birkett, J.W. & Lester, J.N. (eds.). *Endocrine Disrupters in Wastewater and Sludge Treatment Processes*, London: IWA Publishing, Lewis Publishers/CRC Press, 2003.

[2] National Research Council, *Hormonally Active Agents in the Environment*, Washington: National Academic Press, 1999.

[3] Gehring, M., *Verhalten von Bisphenol A bei der kommunalen Abwasserentsorgung*, PhD thesis, Dresden University of Technology, Germany, in preparation. (in German)

[4] Vogel, D., Gehring, M., Tennhardt, L., Weltin, D. & Bilitewski, B., Mobility and Fate of Endocrine Disrupting Compounds (EDCs) in Soils after Application of Sewage Sludge to Agricultural Land, Proc. of the 4th Int. Conf. of the ORBIT Assoc. on Biological Processing of Organics, ed. P. Pullammanappallil, A. McComb, L.F. Diaz & W. Bidlingmaier, Weimar: ORBIT Assoc., vol. 2, pp. 241–250, 2003.

[5] European Chemicals Bureau, European Union Risk Assessment Report: 4,4'-isopropylidenediphenol (Bisphenol-A), http://ecb.jrc.it/existing-chemicals/, 2003, accessed 09/01/2004.

[6] Baumann, W. & Herberg-Liedtke B., *Papierchemikalien: Daten und Fakten zum Umweltschutz*, Berlin: Springer, 1993. (in German)

[7] Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, St.D., Barber, L.B. & Buxton H.T., Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance. *Environmental Science and Technology*, **36**, 1202–1211, 2002.

[8] Gehring, M., Tennhardt, L., Vogel, D., Weltin, D. & Bilitewski, B., Efficiency of sewage sludge treatment technologies to eliminating endocrine active compounds, this volume.

[9] Maguire, R.J., Review of the persistence of nonylphenol and nonylphenol ethoxylates in aquatic environments, *Water Quality Research Journal of Canada*, **34/1**, pp. 37–78, 1999.

[10] Bennie D.T., Review of the Environmental Occurrence of Alkylphenols and Alkylphenol Ethoxylates. *Water Quality Research Journal of Canada*, **34/1**, pp. 79–122, 1999.

[11] Bilitewski, B., Massenstromanalyse für Papier und Altpapier im Jahr 2000 in Deutschland. Präsentation der INTECUS GmbH, Dresden, auf der Sitzung des ZELLCHEMING-Fachausschusses RECO für Altpapierverwertung, 19.04.2002, Köln, Sitzungsunterlagen. (in German)

[12] VDP – Verband Deutscher Papierfabriken, Statistik. http://www.vdp-online.de/Statistik/statistik.html, accessed 14.03.2002.

[13] Schulkies, V., *Einfluss der getrennten Sammlung von grafischem und Verpackungspapier auf den Schadstoffgehalt im Altpapier am Beispiel von Pentachlorphenol und Polycyclischen Aromatischen Kohlenwasserstoffen*, PhD thesis, Dresden University of Technology, Germany, 2002. (in German)

[14] Fromme, H., Küchler, T., Otto, T., Pilz, K., Müller, J. &Wenzel, A., Occurrence of phtalates and bisphenol A and F in the environment, *Water Research*, **36**, pp. 1429–1438, 2002.
[15] Tennhardt, L., Potenzial technischer Abwasser- und Klärschlamm-behandlungsverfahren zur Elimination endokrin aktiver Substanzen, PhD thesis, Dresden University of Technology, in preparation. (in German)
[16] Fiege, H. & Voges, H.-W., Phenol Derivatives: Alkylphenols. *Parkinsonism Treatment to Photoelectricity. Ullmann's Encyclopedia of Industrial Chemistry, vol. A19*, ed. Elvers, B., Hawkins, St. & Schulz, G., pp. 313–342, 1991.
[17] Vingaard, A.M., Körner, W., Lund, K.H., Bolz, U. & Petersen, J.H., Identification and Quantification of Estrogenic Compounds in Recycled and Virgin Paper for Household Use as Determined by an In Vitro Yeast Estrogen Screen and Chemical Analysis. *Chemical Research in Toxicology*, **13**, pp. 1214–1222, 2000.

Please refer to as:

Gehring, M., Tennhardt, L., Vogel, D., Weltin, D., Bilitewski, B. (2004): Bisphenol A Contamination of Wastepaper, Cellulose and Recycled Paper Products. In: Brebbia, C. A., Kungulos, S., Popov, V., Itoh, H. (eds.): Waste Management and the Environment II. WIT Transactions on Ecology and the Environment, vol. **78**, Southampton, Boston: WIT Press, 294 – 300.