Bisphenol A emission factors from industrial sources and elimination rates in a sewage treatment plant

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Abstract Bisphenol A (BPA) is widely used for the production of epoxy resins and polycarbonate plastics and is considered an endocrine disruptor. Special *in vitro* test systems and animal experiments showed a weak estrogenic activity. Aquatic wildlife especially could be endangered by waste water discharges. To manage possible risks arising from BPA emissions the major fluxes need to be investigated and the sources of the contamination of municipal treatment plants need to be determined. In this study, five major industrial point sources, two different household areas and the influent and effluent of the corresponding treatment plant (WWTP) were monitored simultaneously at a plant serving 120,000 population equivalents. A paper producing plant was the major BPA contributor to the influent load of the wastewater treatment plant. All the other emissions from point sources, including the two household areas, were considerably lower. The minimum elimination rate in the WTTP could be determined at 78% with an average of 89% of the total BPA-load. For a possible pollution-forecast, or for a comparison between different point sources, emission factors based on COD-emissions were calculated for industrial and household point sources at BPA/COD-ratios between 1.4×10^{-6}–125×10^{-6} and 1.3×10^{-6}–6.3×10^{-6}, respectively.
Keywords Bisphenol A; emission factor; endocrine disrupters; risk management

Introduction

Bisphenol A (BPA) is widely used for the production of epoxy resins and polycarbonate plastics and is a chemical substance with a very high production rate. Polycarbonate (PC) plastics are convenient for the preparation and storage of all types of foods and beverages. Other products made with PC plastics, such as bike helmets and compact discs, are extremely durable and shatter resistant. Epoxy resins, such as those used in metal cans, have achieved wide acceptance for use. BPA is also used for the manufacture of thermal paper as well as to line water supply pipes and as dental material. Environmental releases are possible during manufacturing and the use of BPA. As BPA is widely utilized, both in households and industry, it can be expected to be present in raw sewage, wastewater effluents and concentrated in sewage sludge.

There is growing concern about the presence of compounds with estrogenic properties in our environment. These compounds may interfere with the reproduction of humans, livestock and wild animals, therefore much research is done on the occurrence, effects and possible risks of these compounds. Bisphenol A is one of these compounds under investigation (Harrison *et al.*, 1997; Soto and Sonnenschein, 1996; Ratnasabapathy *et al.*, 1997; Nagel *et al.*, 1997; Gaido *et al.*, 1997; Roy *et al.*, 1997; Colerangle and Roy, 1997).

A large number of anthropogenic chemicals are known for their estrogenic activity in recombinant yeast screen and mitogenic effects on estrogen-responsive human breast cancer cells. Bisphenol A showed weak estrogenic activity. The relative potency ranges from approximately 1×10^{-6} to 5×10^{-7} times less than 17 β-estradiol (Harris *et al.*, 1997). Based on *in vitro* receptor-interaction studies, the activity was estimated to be 2×10^{-3} fold lower than that of estradiol (BUA, 1997).

Besides all these factors, the predicted no effect concentration (PNEC) for surface water

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elaborated in the COMMPS-study for BPA is 32 μg/l (Frauenhofer Institut, 1999). BPA standards for surface water are promulgated by various countries of the European Union. In 1999, two Austrian studies investigated BPA concentrations in 17 wastewater treatment plant (WWTP) effluents and 34 surface water samples (Sattelberger and Scharf, 1999). The authors detected BPA in all effluent samples between 0.067–0.084 μg/l. Results for 34 surface water samples were mainly not detected (23 samples) with 11 samples ranging from 0.010–0.065 μg/l (limit of detection 0.010 μg/l) (Scharf and Sattelberger, 1999). From this perspective, research in the area of characterizing BPA in municipal and industrial wastewater and surface water is needed.

To manage possible risks arising from BPA emissions, the major fluxes need to be investigated and the sources of the contamination of municipal treatment plants need to be determined. In this study, five major industrial point sources, two different household areas and the influent and effluent of the corresponding treatment plant was monitored simultaneously at a plant serving 120,000 population equivalents (p.e.).

Methods and materials

Bisphenol A

Physico–chemical data indicate low volatility from aqueous solution with a Henry constant of 1×10^{-5} Pa $\times$ m^3/mol. Calculation of the partitioning behavior revealed the hydrosphere to be the most important target compartment (Mackay I 72.2% in water, 27.8% in soil and sediment; BUA, 1997).

The chemical structure of bisphenol A [2,2-Bis-(4-hydroxyphenyl)propan] is given in Figure 1.

Sites and waste water treatment plant (WWTP)

The treatment plant serves a town in Lower Austria with a population of about 40,000 inhabitants, including rural areas of surrounding villages. The study was carried out in 1996–1997. The WWTP was designed for 120,000 p.e. Approximately 60% of the COD load is discharged from industrial sources such as a paper company (about 40% of the total COD in the influent), a washing and cleaning company, wood and metal fabrication, a chemical and food producing company. The treatment plant is constructed for a daily load of approximately 36,000 m^3 of wastewater, removes nitrogen in a nitrification and denitrification step and has a corresponding sludge production of about 2,287 tons dry weight per year. Phosphorus is limited because of the unbalanced wastewater quality of the paper industry consisting of high COD concentrations combined with low phosphorus.

The paper company produces mainly printing paper and released the wastewater constantly during the day and night. The washing and cleaning company is under contract to hospitals to wash bed sheets and metal producing companies for cleaning rags. This wastewater was pre-treated in a microfiltration system before it entered the sewer. The chemical company was a finishing company where chemicals were mixed according to special recipes. Wastewater is produced by recycling and the cleaning of empty boxes. Owing to this the fluctuation of the wastewater quality is high. The wood and metal manufacturing company produces a variety of products including furniture. Another major contributor of wastewater is a chicken slaughterhouse.

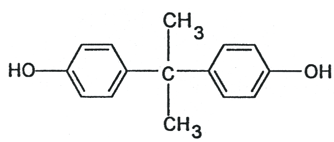

Figure 1 Chemical structure of bisphenol A

At the five sample sites, industrial samples were collected directly at the inflow into the public sewer. Samples at the two household areas, at the local hospital and the influent and effluent of the wastewater treatment plant were also taken. The influent sample site was situated behind the mixed grit chamber.

Sampling

Flow-proportional composite samples were taken four times over a period of five days within a time range of five months. Samples were taken by means of different automatic samplers simultaneously at all the different sampling sites. The flow was measured with the help of bubbler probes or was assessed by the pumping intervals of pump stations. Beside BPA, the samples were characterized by COD, BOD, nitrogen and phosphorus and by applying standardized methods.

Experimental

Samples were analyzed for BPA at the Department of Analytical Chemistry/Federal Environmental Agency of Vienna. Amber glass bottles were used for sewage sample storage.

The samples were homogenized with an Ultra Turrax (5 minutes, 13,500 rps), but not filtrated to determine the total content of BPA. Approximately 4 g K_2CO_3 was added to each 250 ml sample to adjust them to a pH of 10. Derivatization was performed by 2×5 ml fresh distilled acetanhydride in an ultrasonic bath with a temperature of 40°C. The clean up consisted of filtration with glass fiber filters (70 mm diameter; GF6) and C-18 solid phase cartridges. 1 ml isooctane was added as a keeper and the samples were evaporated in a gentle nitrogen stream. Anthracene d10 was added as an internal standard and the samples were analyzed with GC-MS HP 5972 [column (HP 5-MS; 30 m, 0.25 mm ID, 0.25 μm film thickness, 5% phenylsubst. Methylpolysiloxane) in the SIM mode (peak fragments 213 m/z; 119 m/z; 228 m/z; 270 m/z)]. Highly contaminated samples were also analyzed in the scan mode. Limit of detection was 0.5 μg/l and the limit of detection was 1.0 μg/l.

Results and discussion

In Table 1, the minimum, maximum and mean concentrations of BPA are presented and the calculation base (number of samples above determination limit/total number of samples) is given. The calculation of a mean with values below determination limit is difficult, therefore the mean concentration given in Table 1 was calculated using half of the concentration of the determination limit for data between the detection and determination limit. Data below the detection limit were not considered for this calculation.

Table 1 Minimum and maximum concentrations of bisphenol A in the wastewater of different sources (μg/l)

Sample sites	Minimum value (μg/l)	Maximum value (μg/l)	Mean (μg/l)	Number of samples
Metal/wood manufacture	2.6	35	17	(4/4)
Chemical industry	2.5	50	18	(4/4)
Hospital	nd	1.0	–	(1/2)
Paper production	28	72	41	(4/4)
Cloth washing company	1.0	8.9	5.2	(4/4)
Food industry	nd	3.8	2.1	(3/4)
Household area I and II	nd	5.8	2.3	(6/8)
Influent WWTP	10	37	21	(7/7)
Effluent WWTP	nd	2.5	1.5	(2/5)

nd, not detected

The paper company, the wood and metal company and the chemical company reached upper concentrations of BPA of more than 30 μg/l with wide fluctuations, although the concentrations represent weekly averages. Low concentration ranges were observed in the samples of the washing and cleaning company, the food industry, as well as in the hospital and the households samples.

The variability of the BPA emissions of the influent and effluent samples and the elimination is shown in Figure 2. The marked bars (*) indicate emission data below the limit of detection. The average elimination was calculated for case 1 (data below detection limit = 0) to be 96% and for case 2 (data below detection limit = detection limit 0.5 μg/l) 89%.

For the selection of the major contributor and the priority setting of local risk management the concentrations in the wastewater will not be satisfying, but emission loads need to be compared. Figure 3 clearly indicates on a logarithmic scale that the paper producing company is the main contributor to the BPA load in the influent. Due to the large hydraulic load of the paper company and the high concentrations in the samples the contribution to the load was enormous.

For a comparison between different companies or even between different sectors on a broader scale of the decision making process, other indicators are needed in addition.

As wastewater is a complex matrix and emitted from different sources and processes indicators insensitive to dilution are essential. In order to develop a tool for environmental management specific emissions of different industrial sources need to be reported on a comparable base. This base needs to be easily determined and should be widely used already. For that reason the chemical oxygen demand (COD) was chosen, as it has been used in civil engineering for a long time. The BPA/COD ratio is insensitive to dilution. This is important as BPA concentrations might be high due to water saving techniques. In these cases, COD concentrations will also rise in relation to these.

The BPA/COD ratio was calculated according to Eq. (1):

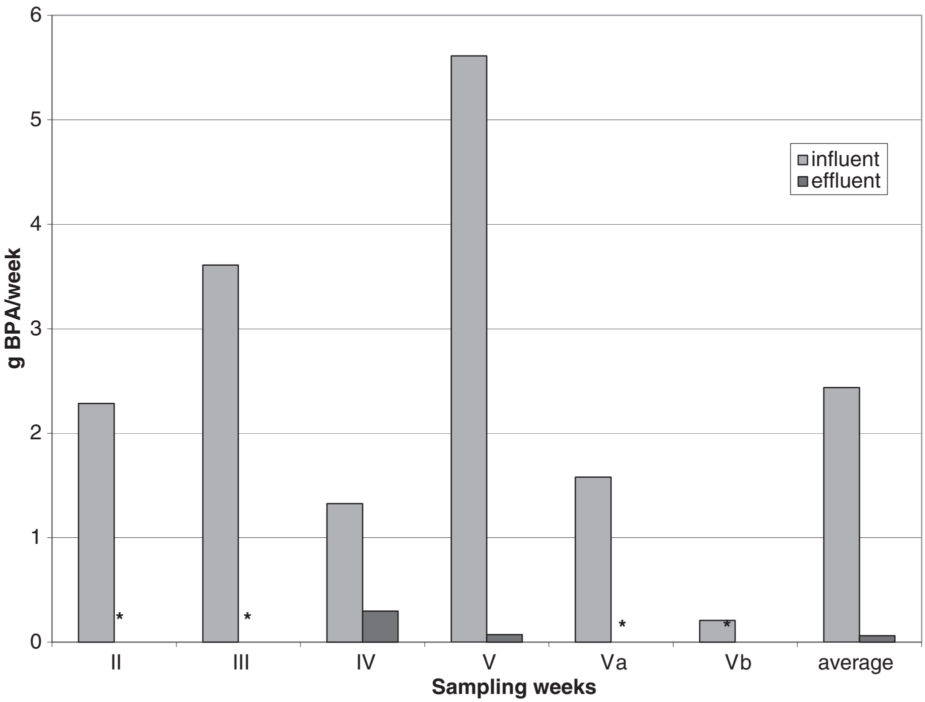

Figure 2 Weekly loads of bisphenol in the influent and effluent samples of the wastewater treatment plant

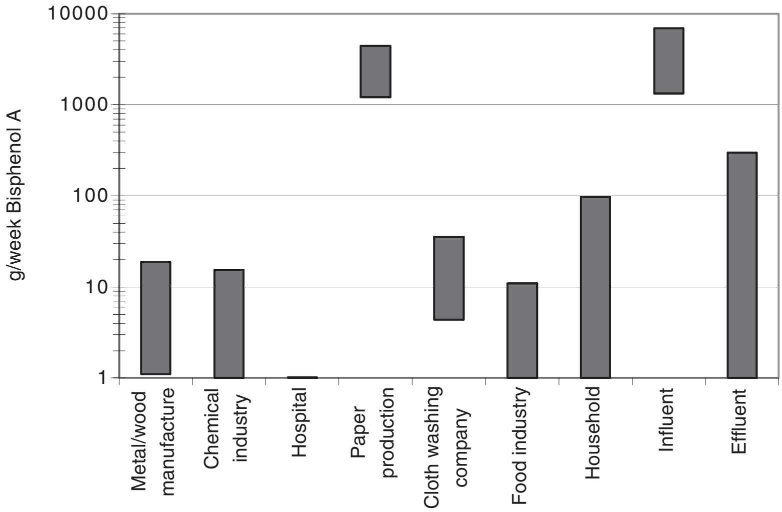

Figure 3 BPA emission loads from different sources

$$\frac{\text{BPA}}{\text{COD}} = \frac{\text{kg BPA emissions / day}}{\text{kg COD emissions / day}} \tag{1}$$

Table 2 presents BPA/COD ratios calculated for different sources on a weekly basis. To make Table 2 easier to read, values are multiplied using a factor of 10^6.

The data in Table 2 indicates that the emission ratios are more similar than the loads. This means that low BPA emissions are combined with low COD emissions and high BPA emissions are coupled with high COD emissions. As a very high portion of the total COD load, and also the BPA-load, was contributed from the paper production the ratio is comparatively high (34×10^{-6}–125×10^{-6}) as the concentrations of BPA in the influent of the WWTP were also high. The effluent showed emission ratios in the range of 21×10^{-6}–69×10^{-6} due to the low COD concentration. The ratios represent a worst-case scenario as the data below detection limits are not considered. Calculated with the detection limit of BPA the potential ratio in the effluent is 10×10^{-6}.

With the help of BPA/COD ratios, the assessment of the emission status of industrial companies and sectors, as well as the comparison of the emissions of different companies independent of their size and the prediction of the performance of selective elimination processes, will be possible.

Table 2 BPA emissions based on COD emissions from different sources (data $\times 10^{-6}$)

	BPA/COD ratio $\times 10^{-6}$		
Sampling sites	**min**	**max**	**BPA data below detection limit**
Metal/wood manufacture	2.1	21	
Chemical industry	1.7	42	
Hospital	2.3	2.3	2.0
Paper production	34	125	
Cloth washing company	2.5	19	0.5
Food industry	1.4	9.8	
Household	1.3	6.3	0.4
Influent WWTP	29	152	
Effluent WWTP	21	69	10

Conclusions

The assessment of the environmental performance of industrial plants needs additional indicators. Pollutant/COD ratios could be used for the development of environmental indicators. The database needs to be improved and different pollutants and sources should be added into a matrix. The matrix will provide a database for a comparison of emission figures compiled for the same environmental sectors and for the decision making process in the field of environmental policy. The emission factors and indicators will allow the estimation of the environmental performance of a single enterprise in comparison with the whole sector and, due to the fact these indicators are not biased by the size of a company and an economic sector, to compare the environmental performance of a given sector over time and between countries.

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