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Factors affecting the concentration of bisphenol A in leachates from solid waste disposal sites and its fate in treatment processes

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Abstract The concentrations of bisphenol A (BPA) contained in landfill leachates from solid waste disposal sites were measured. The concentrations of BPA contained in leachates from industrial waste sites were in the range below the detection limit to 2800 μg/l, while those from municipal sites were in the range 26–8400 μg/l. The leachates from ash-rich sites contained relatively lower concentrations of BPA compared with organic-rich leachates. It is suggested that BPA concentration increases with time after the completion of reclamation in the case of ash-rich sites, whereas the concentration of BPA decreases with time in the case of organic-rich sites. A 7-year survey on a site in Japan showed neither a decrease nor an increase in the concentration of BPA during on-going reclamation. A leachate from a site in the Philippines contained high concentrations of BPA. A slight positive correlation was found between BPA concentrations and total organic carbon (TOC). A major portion of the BPA in leachates was found in dissolved and organic unassociated fractions, which cannot be precipitated by coagulation. More than 99.9% of the BPA contained in raw leachates was removed by a conventional series of treatment processes consisting of biological treatment, coagulation, sedimentation, sand filtration, and activated carbon adsorption.

Key words Bisphenol A · Leachate · Solid waste · Landfill sites · Hazardous substances

Introduction

Solid waste disposal sites are the destination of many types of chemical substance which are produced, consumed, and disposed of. Bisphenol A (BPA; CAS 85-05-7) is a potential endocrine disruptor, and is frequently found in landfill leachates from waste disposal sites. An earlier study by the National Institute for Environmental Studies, Japan, detected BPA in five out of eight samples of leachates, and the median concentration was 0.35 μg/l.[1] Higher concentrations were later reported by the same group.[2,3] BPA was also detected by our group with high frequency from leachate samples.[4] These results indicate that concentrations of BPA contained in landfill leachates are widely distributed. However, the factors affecting the concentration of BPA in landfill leachates are still unclear.

BPA has wide applications in industry, and is used in fungicides, and in chemical intermediate compounds for polycarbonate, epoxy, phenoxy, and polysulfone resins and plastic – rubber additives. BPA, whose Log Kow is 3.32–3.82, is moderately soluble in water.[5] Judging from the partitioning coefficient of BPA, it migrates easily compared with hydrophobic compounds such as dioxins. BPA is considered to be biodegradable by acclimatized microorganisms, and does not persist in the environment. However, it potentially disturbs the ecosystem of the area receiving leachates because the reported maximum concentration of BPA in leachates from disposal sites is higher than the algal EC50 of 1 μg/l.

This paper focuses on the concentrations of BPA contained in leachates, and in treated leachates from different solid waste disposal sites. Factors affecting BPA concentrations in landfill leachates were investigated. The fate of BPA in the treatment processes for leachates is also considered.

A review of the literature on BPA concentrations in landfill leachates

Most environmental monitoring results show that the concentrations of BPA in rivers are lower than 1 μg/l. A total of 116 samples of river water and 39 sewage effluents in Germany were measured, and they contained concentrations of BPA which were lower than 1 μg/l.[6] The reported range of contamination is below the predicted no-effect

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Table 1. BPA concentrations in landfill leachates reported in the literature

Source	Results with regard to BPA concentrations in solid waste landfill leachates
Shindo et al. 1998[8]	Leachates from industrial waste sites contained BPA at ND – 67 μg/l with a median concentration of 2.5 μg/l
Yasuhara et al. 1999[2]	Samples were taken from 11 landfill sites. Maximum 3000 μg/l and typically 10–100 μg/l, were reported at controlled landfill sites. Higher than 300 μg/l BPA was detected in a leachate from a 12-year-old site after completion of the reclamation of solid waste. The results for open dumpsites were below the detection limit without exception
Sakamoto et al. 2000[9]	Samples were taken from 21 landfill sites. BPA of 0.6–31 μg/l was detected at ash-rich municipal landfill sites, and older sites gave higher concentrations. Very high BPA concentrations, with a maximum of 5000 μg/l, were observed at sites of co-disposal of incineration ash and other bulky materials. In the case of industrial waste dumpsites, higher concentration was observed at sites filled with plastic wastes
Asakura et al. 2001[10]	Relatively low concentrations were reported for ash-rich landfill sites compared with the sites where combustible and incombustible domestic wastes are disposed of. Higher concentrations were observed for newer sites
Behnisch et al. 2001[11]	A municipal landfill site was investigated, and the BPA concentration was 0.13 μg/l
Yamamoto et al. 2001[3]	Samples were taken at 10 landfill sites in 1996. Maximum 17 200 μg/l and median 270 μg/l were reported at controlled landfill sites. A comparison with Yasuhara et al. 1999[2] has been made because some of the sites overlapped

BPA, bisphenol A; ND, not delectable

concentration (PNEC) value, which is calculated with a safety factor of 1000.[6] A further study in Germany reported the concentrations of BPA in rivers to show a maximum of 0.272 μg/l.[7] The reported concentration range is of the same order as that in the review paper by Staples et al.[5] In 1998, the Ministry of Construction, Japan, reported that 68% of river water samples contained more BPA than the detection limit of 0.01 μg/l, and the maximum concentration was 0.94 μg/l.

Limited information is available on BPA concentration in landfill leachates from solid waste dumpsites. Table 1 summarizes the results of several studies carried out in Japan; no literature was found reporting BPA concentrations in countries outside Japan. According to these results, some of the leachates contained more than 1000 μg/l BPA, which is more than 1000 times higher than BPA concentrations in rivers or in sewage effluents. On the other hand, BPA concentrations from some dumpsites were lower than 1 μg/l. These results indicate that the range of BPA concentrations is wide.

According to Sakamoto et al.,[9] leachates with high concentrations of BPA were associated with relatively old sites where incinerator ash and plastics are co-disposed. Polyvinyl chloride, which includes BPA as a stabilizer, was reported to be one possible source of BPA in landfill leachates, as well as epoxy resin or polycarbonate.[12] The higher elution of BPA from polycarbonate plastic was observed in a high-pH environment,[13] which is consistent with the tendency for high-BPA leachates to be found at sites where both incinerator ash and plastics are disposed of. However, the co-disposal of ash and plastic wastes alone does not adequately explain high BPA concentrations.

The differences in the type of disposal site and the waste composition may affect in BPA concentration. The relatively high biodegradability of BPA may increase the differences in BPA concentrations in leachates. However, there are no reasonable and detailed explanations for the difference in BPA concentration in landfill leachates from solid waste disposal sites.

Materials and methods

Sampling locations

Landfill sites are categorized into three types according to regulations introduced by the Japanese government. The first category is the open dumpsite, which receives solid waste that is supposed to cause no pollution of leachates. Metals, plastics, glass, construction waste, and so on can be disposed of in this type of site, and neither waterproof liners nor treatment of leachates is required. The second category is the controlled site, which receives waste that possibly pollutes leachates. Sludge, domestic waste, incineration residual ash produced either from industrial or domestic waste, and so on are disposed of here. The third is the specially controlled site, which receives toxic waste.

Table 2 gives an outline of the landfill sites where samples were taken in this study. Five of the nine sites were controlled sites. The other four sites were open dumpsites. Sites A, D, and H were managed by local government, and filled mainly with incinerator ash and incombustible domestic waste. Among these, site A received plastic waste, which was collected as a sorting category of incombustible waste, while sites D and H received mainly incineration residuals from domestic waste and a small amount of plastics without incineration. The other sites were managed by private companies and received industrial wastes. If it was possible to divide the sites into several cells with different characteristics, a more detailed sampling was carried out. Site A was divided into A0, A-mix, A1, A2, A3, and A-ash according to

Table 2. Characteristics of landfill sites surveyed

Site	Type of site	Composition of waste	Note	Treatment process
A0	Controlled	Municipal (incineration ash, incombustible waste (main), industrial waste, others)	More than 10 years after completion of reclamation	Biological contactor, coagulation, filtration, activated carbon adsorption
Amix, A1–A3		The same as A0	Reclamation going on	
A-ash		Incineration ash	Reclamation going on	
B	Controlled	Industrial solid waste (sludge, etc.)	Reclamation going on	Biological contactor, coagulation, chemical oxidation, filtration, activated carbon adsorption
C	Controlled	Industrial solid waste (sludge, construction waste, etc.)	Reclamation going on	Biological contactor, coagulation, filtration, activated carbon adsorption
D1 D2	Controlled	Municipal solid waste (incineration ash (main), incombustible waste, others)	Reclamation completed Reclamation going on	Biological contactor, coagulation, filtration, activated carbon adsorption
E	Open dump	Industrial solid waste	Reclamation completed	No treatment
F	Open dump	Industrial solid waste	Reclamation completed	No treatment
G	Open dump	Industrial solid waste	Reclamation completed	No treatment
H	Controlled	Municipal solid waste (incineration ash, incombustible waste, others)	Reclamation going on	Reverse osmosis
I	Open dump	Industrial solid waste	Reclamation completed	No treatment
J	Controlled	Municipal solid waste (location; the Philippines)	Reclamation going on	Oxidation ponds

the different ages and compositions of the waste. Site D was divided into two cells of different ages.

Controlled sites are required to be equipped with leachate treatment processes by law. As shown in Table 2, a series with biological treatment/coagulation/filtration/activated carbon adsorption is a typical such process in Japan. In addition, site B had a chemical oxidation process. Site H used a reverse osmosis process instead of the conventional processes. The leachates were sampled between 1995 and 2002. Raw leachates from the ten sites presented in Table 2 were taken for chemical analysis. In addition, treated leachates were collected at the final stage of the leachate treatment facilities in the case of controlled sites in order to check the effectiveness of the leachate treatment. At site A, samples were also taken at several stages of the treatment processes.

Chemical analysis

Determining BPA concentration

A 100-ml sample for chemical analysis was applied to a solid-phase extraction disk (C18, 3M), and BPA was extracted from the sample. After the extraction, the disk was rinsed with 10% methanol, followed by elution with dichloromethane. The dichloromethane solution was concentrated to a final volume of 1 ml, and then subjected to analysis by gas chromatograph – mass spectrometry. Some of the samples were analyzed by a liquid – liquid extraction method to compare the results with those obtained by the solid-phase extraction method.

Partitioning analysis

In the survey conducted in 2002, three fractions of BPA, which comprised total BPA, dissolved BPA, and organic unassociated BPA, were measured. The liquid – liquid extraction technique was used in this survey instead of the solid-phase extraction method. A derivatization procedure by Bis[trimethylsilyl]trifluoroacetamide (BSTFA) was carried out to increase sensitivity. No significant differences were observed between the values with and without derivatization in analyses of the same sample except for lower-concentration samples. Dissolved BPA was defined as the BPA in the filtrate sample using GF/C glass-fiber filters with a nominal retention diameter of 1.2 μm. A coagulation test was conducted to measure the association of BPA with humic materials contained at high concentrations in the leachates. The coagulant used in this study was iron (III) chloride, at a dosage of 0.1%. During the coagulation, the pH was controlled at 5, in which condition 70%–90% of the total organic carbon (TOC) contained in leachate sample A coagulated. The supernatant after the coagulation test was subjected to analysis for organic-unassociated BPA.

General parameters

TOC (measured as mg C/l) was measured with a TOC analyzer (Shimadzu TOC-5000, Kyoto, Japan), and chloride ions were measured with an ion chromatograph (Yokogawa, IC-7000, Tokyo, Japan).

Results and discussion

Effect of the characteristics of waste disposal sites on the concentration of BPA

All the leachate samples surveyed in this study were divided into four groups according to leachate type. The first group contained the old sites, i.e., A0 and D1, the second group contained the high-TOC sites, i.e., A2, A3, and J, the third group contained the ash-rich sites, i.e., A-ash, D2, and H, and the fourth group contained the industrial sites.

Figure 1 shows the BPA concentrations of the samples divided into the four groups. The average concentration is shown if the samples were taken several times from the same location. It was very difficult to characterize industrial sites in terms of BPA concentration, because the disposed materials are different, and the exact composition of the waste is difficult to clarify. An important characteristic of the industrial waste disposal sites is that not only controlled sites B and C, but also open dumpsites F, G, and I produced leachates with a high BPA concentration. According to regulations introduced by the Japanese government, it is not necessary for open dumpsites to be equipped with leachate treatment facilities or with waterproof liners. Open dumpsites can receive plastic waste, construction waste, and so on, although sludge and other materials that possibly pollute leachates cannot be disposed of in open dumpsites. It is necessary to clarify the reason for the high BPA concentrations of the leachates from some of the open dumpsites where waste that potentially pollutes leachate should not be disposed of.

The other three groups in Table 2 consist of landfill sites for municipal solid waste managed by local government. The category where the highest BPA concentrations were observed was the high-TOC sites. High concentrations of BPA, i.e., more than 1 mg/l, were observed not only at site A in Japan, but also at site J in the Philippines. The origins of the BPA are probably similar in both Japan and the Philippines. In an earlier stage of this study, the possibility that BPA is synthesized at the inlet of the gas chromatograph from the high concentration of humic substances contained in the sample was considered, and it was assumed that the BPA detected was not contained in the original sample. However, this possibility is unlikely, because a change in both extraction methods and purification methods did not change the BPA concentration detected. This result for high-TOC leachates clearly indicated that the co-disposal of garbage, sludge, incineration ash, and plastics may lead to a high concentration of both TOC and BPA in leachates.

At old sites of municipal solid waste landfill sites, the concentration of BPA decreases with the age of the site at high-TOC sites. This was found by comparing sites A2, A3, and A0. This finding is consistent with the results of a survey by Asakura et al.[10] On the other hand, a comparison between D1 and D2 indicates that the concentration of BPA increases with the age of the site at ash-rich sites. This finding is consistent with a survey by Sakamoto et al.[9] At high-TOC sites, biological activity may be related to the elution of BPA from plastics, because high levels of BPA were detected when TOC was high. On the other hand, at ash-rich sites, the decomposition of organic materials, including plastics, is slow. This may be related to the gradual increase in BPA concentration after closure of the sites. In addition, a decrease in the organic content in the wastes due to recent advances in incineration technology may be related to lower concentrations of BPA at newer ash-rich sites.

Figure 2 shows the correlation between BPA and TOC concentrations. All the results from the samples taken before leachate treatment were plotted. A slight positive correlation was found between high BPA concentration and high TOC concentration. A high organic content in the leachate is possibly one of the factors causing high BPA levels. The presence of macromolecular organic substances, such as humic substances, enhances the migration of hydrophobic compounds such as long-chain phthalic acid esters.[14] However, the presence of humic substances would not have a significant effect on the mobility of BPA in the

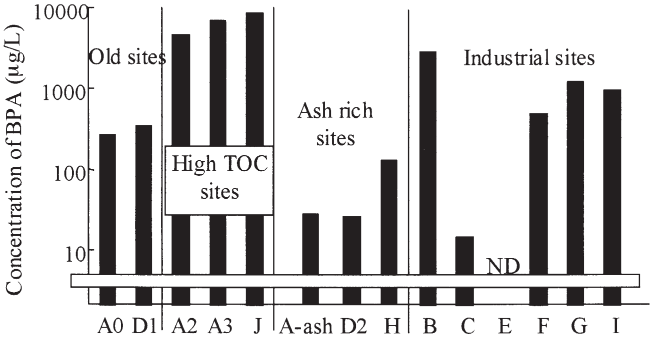

Fig. 1. BPA concentrations in the different categories of dumpsites. *BPA*, bisphenol A; *TOC*, total organic carbon; *ND*, not delectable

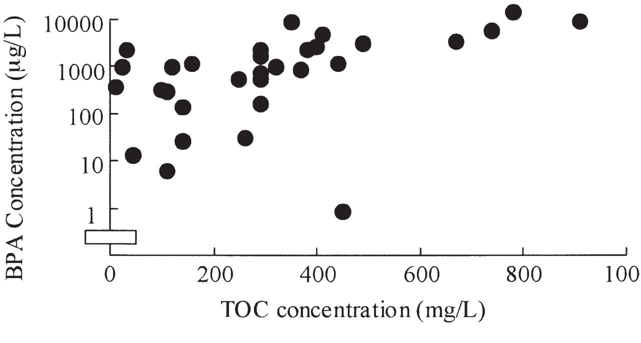

Fig. 2. Correlation between TOC and BPA contained in raw leachates

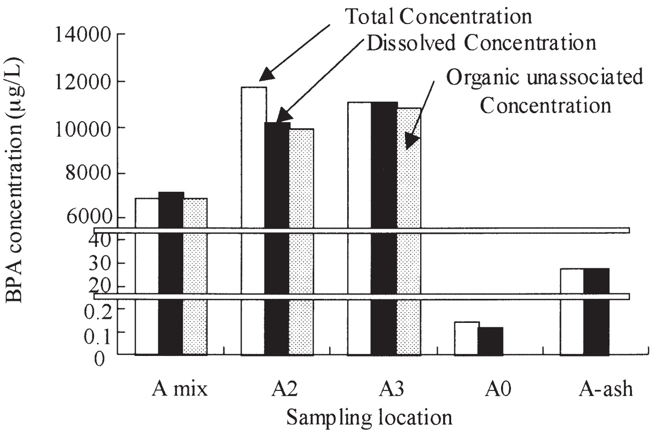

Fig. 3. Total, dissolved, and organic-unassociated concentrations of BPA in five different leachates

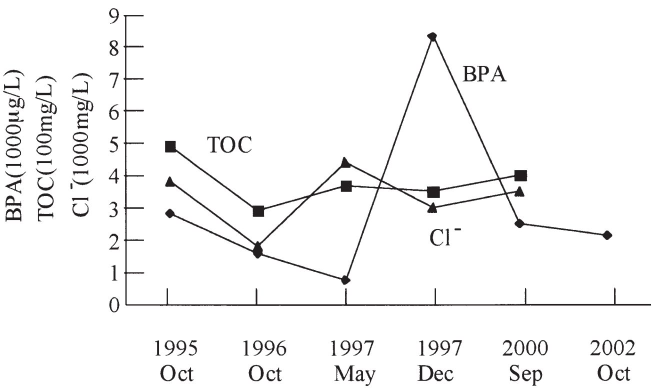

Fig. 4. Change in BPA concentration between 1995 and 2002 at site A

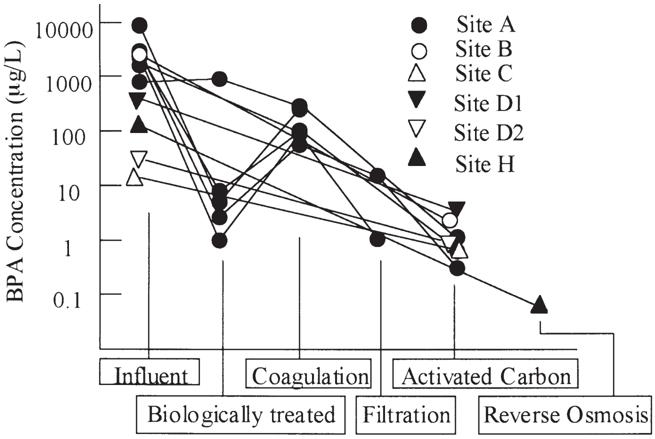

Fig. 5. Change in BPA concentration in leachate treatment stages

environment, judging from the K_{ow} value. Biological activity would play a more significant role in the BPA concentrations in the leachates from solid waste disposal sites.

Laboratory experiments show that the higher elution of BPA from polycarbonate plastic is associated with a high-pH environment.[13] The measured pH of the leachate was 8.0–8.3 for site A, 6.9–8.2 for industrial sites B, C, E, F, and G, and 11.0 for ash-rich site D2. A higher pH was not necessarily associated with a higher concentration of BPA.

Adsorption onto suspended solids of BPA

Figure 3 shows the results of partitioning BPA into three fractions. Particle-associated BPA, which was calculated as total concentration minus dissolved concentration, was negligible compared with total BPA. The result that most of the BPA remained after the coagulation treatment indicates that BPA in the leachates is not strongly bound to macromolecular organic substances. The result that BPA in leachates is neither adsorbed nor bound was confirmed with different samples of leachate with different natures. Particle-associated BPA was negligible not only in the highly colored samples of A-mix, A2, and A3, but also in the more stabilized leachates of A0 and A-ash. Coagulation experiments were not carried out for A0 and A-ash because coagulation was difficult owing to the low organic content of the sample. The weaker binding behavior of BPA is explained by the relative hydrophilic nature of BPA, whose K_{ow} is 3.3–3.8, while the K_{ow} of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin is around 6.8. The suspended solid (SS) concentrations of A0, A2, A3, and A-ash were 2, 19, 14, and 14 mg/l, respectively.

Concentration change in BPA between 1995 and 2002 at site A

Figure 4 shows the results of the changes in concentrations of BPA and their correlation with those of chloride ions and TOC. It is difficult to extract the correlation between concentrations of BPA and those of chloride ions and TOC. During the 7 years of the survey, no increase or decrease in the trend in BPA concentrations was observed. A steady BPA concentrations was achieved. Site A is a large-scale landfill site where solid waste was continuously dumped during the 7-year survey. The fluctuations of BPA concentrations was probably due to rainfall and to changes in the water level of the leachate inside the site.

If the leachate contamination caused by BPA had been caused in the past, a time-dependent decrease in the concentration of BPA would have been observed. If the origins of BPA were the pesticide additives sprayed at the landfill site, a concentration changes due to changes in the pesticides would have been observed. The 7-year survey at site A shows neither a decrease nor an increase in the concentration of BPA. This suggests that BPA originates from the waste carried into the site.

The fate of BPA in leachate treatment processes

BPA is a moderately biodegradable substance. Figure 5 shows the fate of BPA in leachate treatment processes.

Surveys were carried out six times at site A, and samples from every treatment stage were taken, while only final effluent samples were taken from other sites. The reason why sudden low concentrations were observed at the biological stage at site A is not clear. There may have been problems at the sampling point. Another possibility is further biodegradation or adsorption during the storage of the samples, because a considerable quantity of biological sludge particles remained in the samples. More than 90%–99% of BPA was removed in the biological treatment stages combined with coagulation. Most of the BPA was probably removed in the biological process, because the coagulation process cannot remove dissolved BPA, as discussed in the partitioning analysis. A further reduction in BPA concentration was observed at the sand filtration stage and at the final activated carbon adsorption stage. A total 3-log (99.9%) removal was achieved in the leachate treatment process at site A, which consisted of a rotating biological contactor, coagulation by iron oxide, sand filtration, and activated carbon adsorption.

At site B, a 3-log reduction in BPA concentration was also observed. At sites C, D1, and D2, however, there was less reduction than at sites A and B, which was probably due to low influent concentrations. The efficient removal of BPA by leachate treatment processes is consistent with previous reports.[10,11,15] At site H, where reverse osmosis treatment was employed, a 3-log reduction was achieved only by the reverse osmosis treatment. More than 90% removal of the BPA contained in raw leachates was observed using conventional leachate treatment processes, and effluent concentrations were less than 10 μg/l. This concentration level is consistent with the report by Sakamoto et al.[9] in which 19.8 μg/l is the maximum concentration for treated leachates from municipal solid waste disposal sites.

Conclusions

Concentrations of bisphenol A (BPA) contained in landfill leachates from solid waste disposal sites were measured. The concentrations of BPA contained in leachates from industrial waste sites were in the range ND to 2800 μg/l, while those from municipal sites were in the range 26–8400 μg/l. The leachates from ash-rich sites contained relatively lower concentrations of BPA compared with organic-rich leachates. It is suggested that the BPA concentration increases with time after the completion of reclamation in the case of ash-rich sites, whereas the concentration of BPA decreases with time in the case of organic-rich sites. A 7-year survey on a site in Japan showed neither a decrease nor an increase in the concentration of BPA during ongoing reclamation. A leachate from a site in the Philippines contained high concentrations of BPA. A slight positive correlation was found between BPA concentrations and TOC. A major portion of the BPA in leachates was found in dissolved and organic-unassociated fractions, which cannot be precipitated by coagulation. More than 99.9% of the BPA contained in raw leachates was removed by a conventional series of treatment processes consisting of biological treatment, coagulation, sedimentation, sand filtration, and activated carbon adsorption.

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