Gas chromatographic–mass spectrometric validated method for the determination of Bisphenol A in public-supply water: An investigation in Campo Grande, MS, Brazil

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ABSTRACT: A new validated method is described for determining bisphenol A (BPA) in surface and public-supply water samples. Recovery rates of 91% to 113%, with coefficients of variation below 8.9%, were obtained within the limit of detection (2.4 ng L\textsuperscript{−1}). Concentrations of 13 to 113 ng L\textsuperscript{−1} were found in tap water. An analysis of BPA stability in solid-phase extraction cartridges revealed that the analyte can be stored in such containers for at least 90 days. An evaluation of BPA leached from polyvinyl chloride (PVC) piping showed that BPA can contaminate water distribution systems.

Keywords: Bisphenol A; drinking water; PVC; SPE; GC/MS

Introduction

The primary objects of investigation of endocrine toxicology are xenobiotic compounds (exogen chemicals such as synthetic products and environmental pollutants, among others) that interfere with the production, release, transport, metabolism, binding, or elimination of natural hormones responsible for maintaining homeostasis and
for regulation of developmental processes. Xenobiotics include estrogen-mimicking compounds, antiandrogens, and molecules that interact with components of the endocrine system in the thyroid, pituitary gland, and hypothalamus, among other organs [1-4].

Endocrine disruptors are a class of compounds—including synthetic and natural hormones, natural substances, and a large number of synthetic chemicals—that interfere with endocrine functions. In the environment, concentrations in the order of milligrams or nanograms per liter are sufficient to adversely affect human and animal health [5], with outcomes including, but not limited to, increased incidence of breast cancer [6], declining sperm counts, decreased fertility [7,8], and birth defects secondary to fetal exposure [9-11].

One widely debated endocrine disruptor is bisphenol A (BPA), or 2,2-bis(4-hydroxyphenyl)propane, a monomer formed by two phenolic rings. BPA estrogenic activity was unexpectedly detected [12]. Its minimum effective concentration range is reported as 2280-4580 ng L⁻¹ [13].

In the plastics industry, BPA is an intermediate compound employed in the production of epoxy resins and polycarbonates, which are widely used, for instance, in food can coating and food and beverage packaging. Polymers employed in dental treatment may also contain BPA [14,15]. Akin to other synthetic estrogens, this compound has been evaluated in various matrices, in an effort to elucidate its behavior in different environments [16].

Studies conducted in the United States [17], Germany [16, 18, 19], Japan [20], and the Netherlands [21] have revealed BPA concentrations of less than 8 ng mL⁻¹ in river waters, with the exception of a river in Germany (21 ng mL⁻¹) where the compound was possibly released from a wastewater treatment station located in the vicinity of the sample collection plots [21].

In river waters, BPA can be degraded under aerobic [22, 23], but not anaerobic conditions [24]. Ten out of 11 bacterial species isolated from three rivers have been shown to biodegrade BPA, albeit with differences in removal rates (18-91%). Of these species, only Pseudomonas putida and an unidentified species of the same genus were capable of degrading the compound at high rates (around 90%) [22].

Despite bacterial degradation of BPA in river waters, its calculated half-life of 3-6 days may be sufficiently long to affect aquatic organisms [24].

A wide range of analytical methods have been developed to quantify BPA in aqueous samples (surface water [25-29], drinking water [30-32], mineral water [33, 34], seawater [27-36], residual waters [37] and sewage effluents [38, 39]). Published
analytical methods are often based on solid phase extraction (SPE) and derivatization and detection by gas chromatography coupled with mass spectrometry (GC-MS), as well as liquid chromatography coupled with mass spectrometry (LC-MS) or with fluorescence (LC-FL).

In Brazil, published studies on BPA remain scarce and the reports available focus on surface waters, drinking water, and sewage effluents. Values from 25 to 64200 ng L\(^{-1}\) for surface water and from 160 to 7300 ng L\(^{-1}\) for drinking water have been found in samples from Campinas and Araraquara (in São Paulo State), respectively [29, 38, 40, 41]. In other countries, concentrations of 5 to 26100 and 5 to 540 ng L\(^{-1}\) have been reported for surface water [21, 25, 26, 37, 42–47] and drinking water samples [31, 44–49], respectively — thus at times exceeding the minimum effective concentration range (2280-4580 ng L\(^{-1}\)) [13].

To date, BPA has not been included in American or European lists of priority pollutants or among the pollutants listed in ordinances 357/2005 of Brazil’s National Council for the Environment (Conama) [50] or ordinance 2.914 of the Health Ministry [51]. Furthermore, no standard analytical method for the compound is available from Standard Methods for the Examination of Water and Wastewater [52].

The present study evaluated the presence of BPA in the water supply system of Campo Grande, the capital city of Mato Grosso do Sul State, in Brazil, using SPE, GC-MS, and derivatization with \(N,O\)-bis(trimethylsilyl)trifluoroacetamide (BSTFA). The method proposed was validated in this work and can be applied to evaluate samples of surface and public-supply water. BPA stability in SPE cartridges was evaluated. The BPA leached from polyvinyl chloride (PVC) water pipes was qualitatively assessed.

**Material and Methods**

**Study area**

With 786,797 residents occupying an area of 8,096 km\(^2\), 2010 data, Campo Grande has the highest population density (97.2 inhabitants km\(^{-2}\)) in Mato Grosso do Sul [53].

Located in the state’s central region (between latitudes 20°13’N and 20°26’34”S and longitudes 53°36’E and 54°38’47”W), the county lies predominantly within the Paraná river basin, with a small northwestern portion extending into the Paraguay river basin [54].

The county’s water system supplies approximately 98% of households. Water is extracted from surface sources and underground aquifers. Major surface sources include the Guariroba, Lajeado, and Desbarrancado river catchment areas, which jointly account
for 65% of the total supply. The remaining 35% is drawn from wells [54]. Table 1 shows the amounts supplied by each type of source.

<table>
<thead>
<tr>
<th>Type of source</th>
<th>Catchment area</th>
<th>Input to the system (%)</th>
<th>Total input (%)</th>
<th>Output (m$^3$ month$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>Guariroba</td>
<td>51.86</td>
<td></td>
<td>3285321</td>
</tr>
<tr>
<td></td>
<td>Lajeado</td>
<td>12.71</td>
<td>64.87</td>
<td>804729</td>
</tr>
<tr>
<td></td>
<td>Desbarrancado</td>
<td>0.30</td>
<td></td>
<td>18697</td>
</tr>
<tr>
<td>Ground</td>
<td>Wells</td>
<td>14.97</td>
<td></td>
<td>947999</td>
</tr>
<tr>
<td></td>
<td>Special wells</td>
<td>20.16</td>
<td>35.13</td>
<td>1276857</td>
</tr>
</tbody>
</table>

**Table 1. Water output of the public supply system in Campo Grande, MS, Brazil [54]**

**Sample collection**

Surface and supply water samples were collected in 4 L amber glass bottles previously cleaned and rinsed with water from the sample source to prevent contamination. All samples were collected during a single sampling period—namely, 13-20 January 2010, when local precipitation is high. Collection took place from 8 to 10 a.m.

The samples were transported, stored at room temperature, and pre-concentrated in SPE cartridges within 5 h of collection.

**Surface waters**

Samples were taken from the Lajeado and Guariroba rivers, both of which supply the city. Sampling plots were located in private land, approximately 100 m upstream of the points of entry into the water treatment plant (WTP). At the sampling point, the Guariroba river is about 6 m wide and 2.5 m deep, whereas the width and depth of creek-sized Lajeado is 1.5 m and 0.6 m, respectively. River measurements were made with a measuring tape and depth gauge.

**Public-supply water**

Supply water samples were collected from nine residential water meters (Figure 1) located in the county’s urban area. The samples were identified as to their source (wells or WTP).

**Glassware cleaning**

All glassware was soaked in 5% Extran solution (MA-02 neutral, Merck) for 24 h and rinsed in running water, followed by a final rinse with distilled water. After being dried in an oven at 40 °C, the material was rinsed in methanol (Dinâmica, HPLC grade) to remove possible traces of BPA and dried again in an oven at 40 °C. Volumetric ware was cleaned in the same manner, but dried at room temperature.
Standards, solutions, and materials

A BPA (Aldrich, 95%) stock solution (100 mg L\(^{-1}\)) and working solutions (1.0 and 10.0 mg L\(^{-1}\)) were prepared in ethanol ( Vetec, 95%). An anthracene-d10 ( Supelco, neat) solution (200 µg L\(^{-1}\)) was prepared in HPLC-grade dichloromethane (Mallinckrodt) and employed as the internal standard (IS).

BPA derivatization was performed with BSTFA containing 10% trimethylchlorosilane (Fluka, 99%).

Ethyl acetate (J.T. Baker) and methanol ( Dinâmica), both HPLC grade, were used for SPE. In the pre-concentration step, 200 mg/3 mL Strata-X cartridges (Phenomenex, USA) were employed in a 12-position vacuum extraction box (Supelco) coupled to a vacuum pump (Tecnal).

Witness sample

Witness sample testing was performed to find a BPA-free water sample for use in the recovery assays. Tap water samples collected from Campo Grande and the adjoining county of Nova Alvorada do Sul were tested, as were samples of distilled, bidistilled, ultrapure (Milli-Q), and well water. Traces of BPA were found in all samples except that from Nova Alvorada do Sul (pH 7.9)—which was therefore selected as the witness sample. Traces of BPA detected in distilled water were probably released from plastic and metal parts of the distillation equipment.
Sample preparation

Pre-concentration and purification

The SPE cartridges were conditioned by serial rinsing (at a constant 3 mL min⁻¹ flow) with 50 mL of ethyl acetate, 5.0 mL of methanol (followed by a 5 min rest), and 15.0 mL of BPA-free water. Subsequently, 1.0 L of sample previously filtered through qualitative filter paper (to trap particulates) was transferred to a SPE column at an approximate flow rate of 3 mL min⁻¹. After sample pre-concentration, the cartridges were washed with 9:1 (v:v) water : methanol solution and vacuum-dried for 90 min [36].

Elution was performed with 5.0 mL of methanol at a flow rate of 2 mL min⁻¹ and the eluate was allowed to dry under a nitrogen flow. The resulting extract was redissolved in methanol and transferred to a 2 mL vial [36].

Derivatization with BSTFA

The extract was dried again under a gentle stream of nitrogen, and derivatization was performed by adding 100.0 µL of anthracene-d10 solution (internal standard) and 10.0 µL of BSTFA. The flask was shaken for 30 s and kept in an oven at 40 °C for 10 min. The derivatized sample was then dried under a gentle stream of nitrogen, completed to 1.0 mL with dichloromethane, and analyzed by GC-MS. Figure 2 depicts the derivatization reaction of BPA with BSTFA [55].

![Figure 2. BPA derivatization with BSTFA.](image)

Stability of BPA in SPE cartridges

Samples spiked with BPA (50 ng L⁻¹) were pre-concentrated in SPE cartridges.
After vacuum drying for 90 min, the cartridges were wrapped in aluminum foil and stored under refrigeration at −10 °C for subsequent elution and analysis.

Analyses were performed in triplicate 1, 2, 3, 5, 7, 15, 30, 45, 60, and 90 days after analyte pre-concentration. The analysis was performed immediately after pre-concentration furnished the first point of the curve depicting BPA in-cartridge stability.

**BPA leaching from PVC piping**

BPA leaching from PVC pipes was evaluated using BPA-free tap water from Nova Alvorada do Sul and a segment of residential-purpose PVC 6.3 pipe for cold water (750 kPa nominal pressure, 50 mm inner diameter, compliant with Brazilian technical norm NBR 5648)—the predominant type of piping employed in the water supply network of Campo Grande.

A roughly 1 m-long pipe segment was cut into 10 cm-long sections, which were kept in 40 L of BPA-free water (pH 7.9) at room temperature in a covered aluminum container. Aliquots of 1 L were withdrawn in triplicate over the course of 60 days, at varying intervals. The volume was manually stirred for 30 s before each aliquot was taken. The samples were analyzed to monitor changes in the concentration of BPA leaching from the pipe material.

**Analyses**

The analyses were performed at the Department of Chemistry of the Universidade Federal de Mato Grosso do Sul in a GC 2010 high-resolution gas chromatograph coupled to a QP-2010 Plus mass spectrometer (Shimadzu) equipped with an AOC-20i autosampler. An Rtx-5MS chromatographic column (30 m × 0.25 mm × 0.25 μm, from Restek) was employed. The injection volume was 1 μL in splitless mode.

The injector and detector temperatures were 270 and 280 °C, respectively. The column temperature program began with a 2 min period at 120 °C, followed by heating to 210 °C (at 15 °C min⁻¹) and finally to 270 °C (at 10 °C min⁻¹). The final temperature was maintained for 4.7 min. The carrier gas (helium 5.0, White Martins, analytical grade) was flowed at 1.2 mL min⁻¹. Total analysis time was 19 min.

Ion monitoring in scan mode covered the interval from m/z 60 to 500. The ions detected in SIM mode were at m/z 357 and 372. The spectra were obtained using the electron impact technique, with an impact energy of 70 eV. Chromatograms, mass spectra, and analyte quantification were obtained using GCMS Solutions software (Shimadzu).

**Method validation**

Validation was based on the following recommended criteria: selectivity, working
range, linearity, sensitivity, accuracy, precision, limit of detection (LD), and limit of quantification (LQ) [56, 57].

Results and Discussion

Method validation

Selectivity

The method’s selectivity was evaluated by comparing a sample spiked with 30 ng L\(^{-1}\) BPA with the witness sample and the blank. No chromatographic peaks were found with retention times equal to or close to that of BPA. No analyte was detected in the witness sample. These results demonstrated that samples collected from Nova Alvorada do Sul were suitable for the recovery assays run during the validation step, allowing BPA to be unequivocally detected and quantified.

Limit of detection (LD) and limit of quantification (LQ)

Calculation of the LD and LQ of the equipment was based on baseline signal-to-noise ratio, using solutions of known concentrations [56, 57]. These limits were 3.5 and 10.0 µg L\(^{-1}\), respectively.

The method’s LD and LQ were calculated as proposed by Their and Zeumer [58], yielding values of 2.4 ng L\(^{-1}\) and 10 ng L\(^{-1}\), respectively, with \(m\) and \(n = 5\) and \(m + n – 2\) degrees of freedom.

These results are considered very good, revealing the method’s ability to detect and quantify BPA at concentrations similar to those reported in the literature [16, 21, 25, 26, 31, 37, 41–49].

Working range, linearity, and sensitivity

The method’s working range was 10 to 100 µg µL\(^{-1}\).

Linearity was evaluated by injecting BSTFA-derivatized BPA standards. The equation of the curve obtained using anthracene-d10 as the internal standard was \(y = 0.0170x – 0.0760\), with \(R = 0.9964\), revealing a strong correlation between the concentrations studied and the signal generated by the equipment.

Huber’s test [59] with a linear coefficient different from zero was employed for consistent rejection of outliers. As shown in Figure 3, none of the values of \((A – a)/C\) was off-limits, thus confirming the linearity of the analytical curve. Additionally, a value of \(R = 0.9964\) indicates excellent linearity.

Curve slope shows that the method is sufficiently sensitive to distinguish between concentration values in close proximity.
Recovery assays

Recovery assays were performed to investigate the method’s precision and accuracy. Table 2 shows the results obtained for spiked samples.

![Linearity curve](image)

**Figure 3.** Linearity curve.

<table>
<thead>
<tr>
<th>Level of fortification (ng L(^{-1}))(^a)</th>
<th>CV(%)(^b)</th>
<th>Rec (%)(^c)</th>
<th>(t) calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7,0</td>
<td>113</td>
<td>-7,8 \times 10^{-1}</td>
</tr>
<tr>
<td>30</td>
<td>8,9</td>
<td>91</td>
<td>4,2 \times 10^{-2}</td>
</tr>
<tr>
<td>50</td>
<td>6,4</td>
<td>94</td>
<td>-3,1 \times 10^{-1}</td>
</tr>
</tbody>
</table>

\(a\) Concentration of BFA in the matrix; \(b\) Coefficient of variation; \(c\) Average recovery. 
\(t\)\(_{\text{tabulated}}\) (95%) 2,776; \(t\)\(_{\text{tabulated}}\) (99%) 4,604; \(n = 5\).

**Precision and accuracy**

Coefficients of variation (CV) from 6.4% to 8.9% demonstrated the method’s precision, considering the 20% maximum limit recommended in the literature [56, 57].

Recovery rates from 70% to 120% showed the method to be accurate, according to published parameters for the analysis of pesticide residues [56, 57].

The significance of mean recovery rates for each spiking level was assessed using Student’s \(t\) test [60], adopting Rec = 100% as the null hypothesis (\(H_0\)) and Rec \(\neq\) 100% as the alternative hypothesis (\(H_1\)).

All calculated \(t\) values were found to fall within the acceptance region of \(H_0\). At 95% and 99% confidence levels, no differences were detected between measured recovery values and those accepted as true—a finding that validates the method’s
accuracy for the purposes of the present investigation.

**Stability of BPA in SPE cartridges**

Data concerning the conservation of samples in the SPE cartridges are shown in Figure 4, revealing that pre-concentrated BPA can remain unaltered in the cartridges under refrigeration for at least 90 days as shown by recovery rates exceeding 81% and CVs below 3.8%. Although variable, analyte recovery lay within recommended levels (above 80%), confirming the method’s accuracy and precision even when the analyte is stored for 90 days. A further advantage of in-cartridge storage is the smaller storage space required, compared to the much larger volumes of water required in other methods. In addition, BPA is not promptly degraded or absorbed by cartridge walls.

![Figure 4. Stability curve for BPA in SPE cartridges kept under refrigeration (~10 °C).](image)

**BPA leached from PVC piping**

See Figure 5.

BPA concentration increased significantly over the first 5 days, showing that BPA leaches from PVC piping in Campo Grande’s water distribution network, with potential contamination risks. After 5 days, however, the concentration of leached BPA decreased, possibly owing to degradation, since the compound has a reported half-life of 3-6 days in surface waters [24].

These results explain why BPA-free water suitable for use as a witness sample in the recovery assays was found in neighboring Nova Alvorada do Sul but not in Campo Grande: in Nova Alvorada do Sul all public-supply water is extracted from artesian wells.
and distributed through metal tubing. Water treatment in this county is limited to chlorination.

Levels of BPA leached from PVC piping were similar to those found by Yamamoto and Yasuhara [61] (4.0-1730 µg L⁻¹) for PVC hoses soaked in BPA-free water at room temperature for variable periods (0-24 h).

![Figure 5. Curve for BPA leaching from PVC piping (water, room temperature).](image)

**Public-supply water samples**

The analytical results (Table 3) lay within the calibration curve bracket, with the exception of sample G3, whose final extract was subsequently diluted to 2.0 mL with dichloromethane and retested.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Geographic Coordinates</th>
<th>BFA (ng L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guariroba River (GR)</td>
<td>20°30'10.32&quot;S 54°14'56.19&quot;O</td>
<td>26 ± 1.5</td>
</tr>
<tr>
<td>Lageado River (LR)</td>
<td>20°32'21.75&quot;S 54°30'41.11&quot;O</td>
<td>13 ± 1.9</td>
</tr>
<tr>
<td>Lageado 1 (L1)</td>
<td>20°31'53.61&quot;S 54°35'36.87&quot;O</td>
<td>24 ± 0.56</td>
</tr>
<tr>
<td>Lageado 2 (L2)</td>
<td>20°29'55.34&quot;S 54°39'24.21&quot;O</td>
<td>21 ± 0.90</td>
</tr>
<tr>
<td>Lageado 3 (L3)</td>
<td>20°33'12.99&quot;S 54°38'49.95&quot;O</td>
<td>23 ± 0.93</td>
</tr>
<tr>
<td>Guariroba 1 (G1)</td>
<td>20°26'15.25&quot;S 54°36'36.58&quot;O</td>
<td>26 ± 2.3</td>
</tr>
<tr>
<td>Guariroba 2 (G2)</td>
<td>20°29'6.93&quot;S 54°36'12.74&quot;O</td>
<td>35 ± 3.2</td>
</tr>
<tr>
<td>Guariroba 3* (G3)</td>
<td>20°28'19.62&quot;S 54°37'5.78&quot;O</td>
<td>114 ± 3.0</td>
</tr>
<tr>
<td>Well 1 (W1)</td>
<td>20°28'5.47&quot;S 54°38'5.11&quot;O</td>
<td>ND</td>
</tr>
<tr>
<td>Well 2 (W2)</td>
<td>20°31'22.12&quot;S 54°40'11.70&quot;O</td>
<td>&lt;LQ</td>
</tr>
<tr>
<td>Well 3 (W3)</td>
<td>20°31'38.43&quot;S 54°36'28.50&quot;O</td>
<td>&lt;LQ</td>
</tr>
</tbody>
</table>

LD = 2.4 ng L⁻¹; LQ = 10 ng L⁻¹; n = 3. <LQ = lower than LQ but higher than LD. *Sample diluted to 2.0 mL with dichloromethane; ND = non detected (concentration below LD).

With the exception of sample W1, BPA was detected in all samples.
The compound was also detected in water from both rivers that feed Campo Grande’s supply network—a worrying finding, since these waterbodies account for roughly 65% of the county’s water supply.

Worldwide, chemical industries and landfills are usually the main culprits for BPA contamination, but since no industrial plants are present in the study area, contamination can probably be attributed to improper installation and maintenance of landfills.

Given a lack of permits for sample collection immediately upstream and downstream of the WTP’s intake and discharge points, it was not possible to ascertain whether or not BPA is efficiently removed at the treatment plant.

However, BPA levels in samples of WTP water collected from household was even higher than in river waters, suggesting the existence of an additional source of BPA. Our data suggest that this potential source of contamination is PVC pipes, which account for 78% of the tubing used in the water distribution network of Campo Grande.

While in the USA, Canada, Japan, and many European countries the environmental impact of endocrine disruptors, especially BPA, has been the focus of debate, few studies have addressed methods for the detection and quantification of these potentially hazardous compounds—hence the timeliness of the present study.

To our knowledge, official regulations on maximum permitted BPA levels in water for human consumption are lacking worldwide. Broader monitoring would ideally provide more comprehensive data to support public policies designed to limit water contamination by BPA and other endocrine disruptors.

In toxicological terms, the results of the present study raise concerns, given the estrogenic activity exhibited by BPA even at concentrations below 1 ng L⁻¹. However, the mere finding of BPA in tap water does not necessarily imply a potential health risk, whose evaluation requires an assessment of estrogenic activity using biological assays, among them in vitro and/or in vivo immunoassays based on the generation of antibodies and/or receptors capable of binding specifically to estrogenic compounds [10-12].

Given the unfeasibility of replacing PVC with alternative materials in the water supply systems of entire counties, new processes would have to be applied to ensure removal of this endocrine disruptor. Activated carbon filters for drinking water, for instance, are highly efficient (>99%) for the removal of BPA at concentrations of less than 15 mg L⁻¹ [62].

Other methods include ozonation [63], advanced oxidation processes [64], nanofiltration membranes, and reverse osmosis [65].

However, because BPA is just one of many endocrine disruptors, the treatment of
water for human consumption should cover other compounds of the same class in a bid to prevent deleterious effects.

**Conclusion**

In this study, the quality of water from the public distribution network of Campo Grande was evaluated for BPA content. Samples were collected not only from households but also from the waterbodies that feed the county's WTP. The proposed method, also validated here, employed Strata-X polymer-phase SPE cartridges, derivatization with BSTFA, and GC-MS detection. The method exhibited excellent precision and accuracy, with recovery rates from 91% to 113%, CVs of less than 8.9%, and LD and LQ of 2.4 and 10 ng L\(^{-1}\), respectively. Fast, efficient, and simple to operate, the proposed method can be reliably applied to quantify BPA at low concentrations, in the order of nanograms per liter.

The possibility of storing the analyte in SPE cartridges for at least 90 days without analytical impairment is a highly relevant contribution for future studies of BPA based on SPE.

The range of BPA values found in surface water samples (13-26 ng L\(^{-1}\)) and samples collected from household water meters (ranging from nondetectable levels to 114 ng L\(^{-1}\)) and the finding that BPA actually leaches from PVC pipes strongly suggest that the piping material used in the water supply network is implicated in BPA contamination. Although BPA levels were inferior to the minimum effective concentration range for this compound (2280-4580 ng L\(^{-1}\)), BPA’s deleterious effects warrant its listing in ordinances 2.914 of the Ministry of Health and 357/2005 of CONAMA [50, 51]. Studies focused on alternative materials safer than PVC and investigations on new techniques for removing contaminants are expected to help mitigate the current risks.

**Acknowledgments**

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