SCIENTIA CUM INDUSTRIA (SCI. CUM IND.), V. 2, N. 1, PP. 10 — 14, 2014

Occurrence of Bisphenol A in soil and leachate of a municipal landfill: effect of the sample acidification

Nathalia Cristine Viecelli*, Ricardo Perazzoli Baldasso**, Irajá do Nascimento Filho***, Kira Lusa Manfredini****

Abstract

The main objective of present study was the quantitative analysis of bisphenol A (BPA) in soil and leachate of a municipal sanitary landfill. The influence of the solvent polarity and pH over the quantitative analysis of BPA in the leachate was also investigated. The soil samples were collected from closed cells and extracted by Soxhlet extraction with ethanol. The liquid samples, from row leachate from the same sanitary landfill were extracted by Solid Phase Extraction (SPE) with C-18 cartridges and ethanol. The organic extracts from liquid and solid samples were analyzed by Gas Chromatography with Flame Ionization Detector (GC/FID). For the soil and liquid samples the average concentrations of BPA were 21.30 ($\pm$0.61) μg kg^{-1} and 26.83 ($\pm$2.69) μg L^{-1}, respectively. These results were far above the ones cited in the literature and are of special concern because BPA may disrupt the human endocrine system. The acidification allows the increase of 5% of the extraction efficiency. In this way, the acidification step is recommended for the quantification of BPA in samples where the concentration of this analyte is below 0.1%. In these cases the acidification step may avoid important loss of the analyte and improve the detection limit in the instrumental analysis.

Keywords
bisphenol A, soil, leachate, sanitary landfill, gas chromatography

I. INTRODUCTION

Bisphenol A (BPA), 4,4´-(1-methylethylidene) bisphenol (CAS no. 80-05-7), is widely used as a monomer in the production of polycarbonate and some epoxy resins that are commonly employed as adhesives and cover materials [1]. Figure 1 shows the chemical structure of BPA.

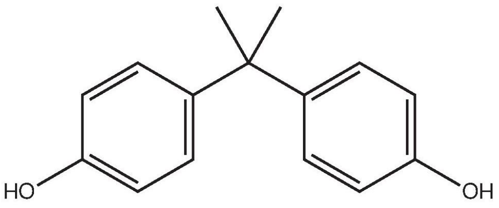

Fig. 1: Chemical structure of BPA

BPA improves some physical properties of polymeric materials, such as resistance, hardness, and thermal stability. BPA is an antioxidant highly resistant to chemical degradation and its environmental persistence may be due to the low vapor pressure and relatively low octanol–water partitioning coefficient [2], [3].

In the environment, most of the BPA (78 to 99.3%) is fixed in the soil [4]. In sanitary landfills, the BPA leached from the wastes is mixed with the leachate formed by the microbiological degradation of the organic content of refuse. Due to the action of rainfall, the leachate goes down through the landfill, and can contaminate the soil, surface and groundwater [4]. Under anaerobic conditions, BPA can be considered non-biodegradable [5] and may interact with humans and wildlife causing adverse effects. Some examples of these adverse effects are the formation of additional female organs, enlarged accessory sex glands, morphological and functional gonadal dysfunction and interference in the functioning of the endocrine system [6]–[11]. The endocrine disrupting action of BPA is recognized by important environmental agencies such as USEPA (United States Environmental Protection Agency), UKEA (United Kingdom Environmental Agency) and JEA (Japan Environmental Agency) [12]. BPA is also readily absorbed by skin [13] and this rote must contribute substantially for the human exposition to the free BPA monomer. BPA was also detected in the urine of pregnant women working as cashiers and women that consume canned vegetables, at least once a day [14]. There are many studies reporting the evaluation of artificial endocrine disruptors in wastewaters [3], [15]–[18], and the extraction of BPA and plasticizers such as di-n-butylphathalate and di(2-ethylhexyl) phthalate from wastewaters using the acidification to enhance the extraction efficiency [1], [19], [20].

Depending on certain soil conditions, like humidity and pH, the polymeric materials can release a relatively high

*Aluna do programa de doutorado em Engenharia do Ambiente da Universidade Técnica de Lisboa, Instituto Superior Técnico, pelo Ciências sem Fronteiras (CAPES).
**Mestrando do Programa de Pós-graduação em Engenharia e Ciências Ambientais da UCS.
***Instituto de Saneamento Ambiental da Universidade de Caxias do Sul, doutora em Eng de Recursos Hídricos e Saneamento Ambiental pela Universidade Federal do Rio Grande do Sul.
****Instituto de Saneamento Ambiental da Universidade de Caxias do Sul, mestranda do Programa de Pós-graduação em Engenharia e Ciências Ambientais da UCS.

Data de envio: 17/04/2014
Data de aceite: 26/05/2014

http://dx.doi.org/10.18226/23185279.v2iss1p10

quantity of organic compounds with toxicological potential, such as BPA. Synthetic endocrine disruptors, like BPA, may cause adverse health effects in aquatic organisms, even at concentrations as low as 0.1– 0.5 ng L^{-1} [21].

Despite the wide utilization and environmental relevance of BPA there is a lack of publications dealing with the study of this compound in soil and leachate of sanitary landfill. This is an important issue because large amounts of plastic materials are buried in sanitary landfills. In addition, the biological treatment usually applied for the leachate treatment, maybe insufficient for the complete removal of BPA. Also, the investigation about the influence of the extraction conditions (such as pH and solvent polarity) over the amount of the detected contaminant is still lacking in the literature.

II. METHODOLOGY

The methods of sample's collection and analysis were adapted from previous studies published by our research group [22], [23].

A. *Soil samples*

Five soil samples (500 g each) were collected from a closed cell of the São Giácomo sanitary landfill (Caxias do Sul, RS, Brazil). The samples were collected from a depth of 2 m below the landfill cover in glass flasks (500 mL) with the cap covered by aluminum foil. The flasks were previously washed with n-hexane and distilled water and dried at 300^{o}C. The same purification procedures were adopted with all the glass material that had direct contact with the samples. The soil particle size was homogenized in a steel sieve with 2 mm mesh. The soil was stored at 4^{o}C, protected from light until extraction (no more than 24 h after collection).

The soil samples were characterized by pH (potentiometric method in humid base), moiety (gravimetry), total nitrogen (Kjeldahl and titrimetric methods), total carbon (Walkley-Black method) and phosphorous (humid digestion and colorimetry).

After particle size homogenization, six soil aliquots with an average mass of 10.32 g (±0.24) were extracted by Soxhlet in 125 mL of ethanol by 4 h. After this, the organic extracts were dried overnight in a fume hood until constant mass and re-diluted with ethanol (1.0 mL) and analyzed by GC/FID. Throughout the extraction process, no plastic or rubber materials were allowed to come into contact with the samples.

B. *Model samples*

In order to access the effects of pH and solvent polarity over the amount of the extracted BPA, hydrochloric acid was added to two aliquots of 100 mL of two standard solutions of BPA (purity 99%, Fmaia, São Paulo, Brazil) at 1000 mg L^{-1}, until pH $\cong$ 2.0. Other two aliquots of 100 mL were extracted without the acidification step, generating the extracts shown in Table I.

TABLE I: Solvents and pH conditions and extracts nominations of the standard solutions extraction

pH	Solvent	Extract nomination
Acidic	Ethanol	A-E^{a}
Acidic	n-hexane	A-H^{b}
Normal	Ethanol	N-E^{c}
Normal	n-hexane	N-H^{d}

A-E^{a}= acidified sample extracted with ethanol
A-H^{b}= acidified sample extracted with n-hexane
N-E^{c}= non acidified sample extracted with ethanol
N-H^{d}= non acidified sample extracted with n-hexane

C. *Leachate samples*

The raw samples of landfill leachate were collected in glass bottles (1 L capacity) with caps protected by aluminum foil to prevent contamination. The sampling period was from 8:00 am to 6:00 pm, every 2 h. The total volume was of 6 L. All the samples were mixed and 1 L sample was collected from the mixture (composite sample). The samples were maintained at 4^{o}C and protected from light until the extraction procedures were performed at most 24 h after the collection. Figure 2 illustrates the sampling procedures.

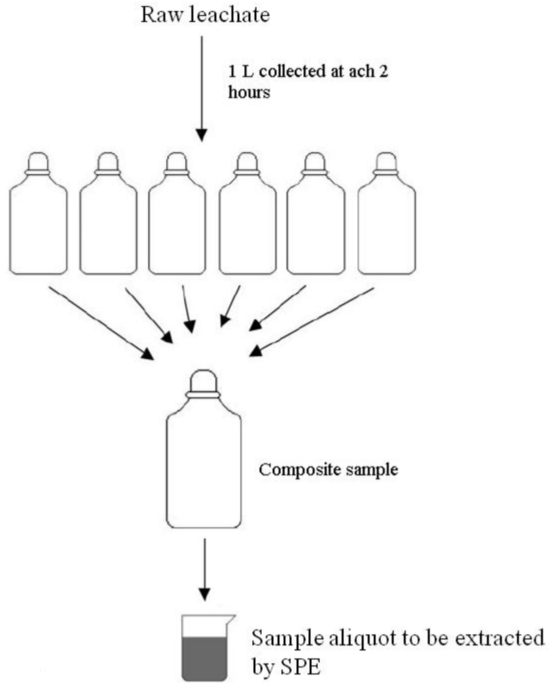

Fig. 2: Sample collection

The liquid samples were extracted by Solid Phase Extraction (SPE), using the better pH and solvent polarity conditions (as described in the II-B section). The SPE cartridges (SupelcleanTM LC-18 6 mL, Sigma-Aldrich) were previously conditioned by the sequential elution of methanol (5 mL) and methylene chlorine (5 mL). After each elution the cartridges were vacuum dried for 10 min. Finally, the cartridges were eluted with deionized water and vacuum dried for 20 min. A volume of 100 mL of the composite samples were extracted by passing through the cartridges previously conditioned. After the extraction, the organic extracts were dried with anhydrous sodium sulfate and the solvent volume was reduced to 1 mL by a gentle flux or pure nitrogen.

D. Recovery grade and detection limit

The recovery grade was measured by spiking a soil sample with a standard solution (20 μg L^{-1}). The detection limit was evaluated by the analysis of successive dilutions of a standard solution at 100 μg L^{-1}.

E. Reagents and solvents

All the reagents and solvents were of p.a. grade and, when necessary, distilled twice in a glass apparatus.

F. Instrumental analysis

A PerkinElmer Gas Chromatograph model Autosystem XL, with Flame Ionization Detector was used for identification of BPA by comparison between the retention times of the BPA sample peak and the standard compound. The quantification was done by the internal normalization method. An Elite-5 fused silica capillary column (30 m x 0.25 mm i.d. crossbond 5% diphenyl – 95% dimethyl polysiloxane, 0.25 μm film thickness) was used for the GC separation using the following oven temperature program: 150^{o}C (5 min hold) heating to 250^{o}C at 3^{o}C/min and heating to 300^{o}C at 10^{o}C/min (5 min hold). The injector temperature was 250^{o}C. The injection volume was 1.0 μL (n=3) in the split mode (1:50).

III. RESULTS AND DISCUSSIONS

For soil and liquid samples, the detection limit was 0.5 μg L^{-1} and the detector response was linear between 0.5 and 50 μg L^{-1} (R^2 = 0.913; equation: y = 0.424x – 0.078). The recovery grades were 75.95% (±5.13) and 98.73% (±4.51) for the soil and liquid samples, respectively. According Staples et al. [24] BPA present log Kow values of 2.20–3.82 and a log KOC for sediments and soils of 3.20. This may justify the lower recovery of BPA from the soil samples.

A. Soil samples

The average BPA concentration in the samples was 21.30 (±0.61) μg kg^{-1}. Yamamoto et al. [1] had reported average BPA concentrations of 0.27 μg L^{-1} in hazardous waste landfill samples. Thus, a landfill that receives only municipal solid wastes, like the one studied in our work can be considered much more hazardous with regard to the underground water contamination by BPA, than a typical hazardous waste landfill.

Samples of soil located outside the São Giacomo landfill (where the residues were not buried) show an average BPA concentration of 3.16 (±0.14) μg kg^{-1}, i.e. far below that found in the closed cells. This reinforces the hypothesis that the high concentration of BPA can be explained by the high content of polymeric material buried in the São Giácomo landfill. The non-observance of residue segregation (into organic and inorganic categories) could be the source of the high BPA concentration.

The physical-chemical and microbiological characteristics of the landfill soil can enhance the release of BPA from plastic residues. The soil sample's physicalchemical characteristics (Table II) show that the landfill cell is in an unstable methanogenic phase. In this phase the fermentation and hydrolysis of the residues generates, mainly, intermediary organic volatile acids. The leachate generated by this fermentation reduces the soil pH.

TABLE II: Physical-Chemical characterization of the soil samples

Parameter	Result	Method
pH	5.24	Potenciometric
Humidity (%)	38.7	Gravimetric
Nitrogen (%)	0.3	Kjeldahl – Titrimetric
Phosphorus (%)	<2.8	Humid digestion - Colorimetric
Organic carbon (%)	16	Walkley-Black

Thus, at this pH value (Table II), the BPA can be poorly ionized and must be adsorbed in the organic matter. This hypothesis is reinforced by the high organic matter content of the soil samples (Table II).

Therefore, the low pH and high organic content conditions conjugated with the presence of plastic material in the wastes, created a favorable environment for the BPA release into the sanitary landfill soil.

B. Model samples

Figure 3 shows the concentrations of BPA in the model samples extracted with and without acidification and ethanol and n-hexane.

No BPA peaks were detected in the non acidified model samples extracted with nhexane (N-H). In this way, the bar is absent in Figure 3. The model samples extracted with ethanol showed the highest recovery grade (A-E and N-E). The increase in the recovery grade promoted by the samples acidification was of 5.5% in the ethanol extracts. This result suggests that, if the ethanol concentration in the samples is higher than 0.1%, the acidification procedure can be discarded from the sample handling procedures. It is well known that the excessive sample handling can introduce important quantitative errors by the analyte's loss. On the other hand, if the BPA concentration in the samples is below 0.1%, the acidification process can improve the analyte's extraction.

The affinity between BPA and the ethanol phase can be explained by its chemical structure (Figure 1), the analyte's physical-chemical properties and the water and ethanol dipole moments.

The relative water solubility of BPA may be due to the two hydroxyl groups attached to the benzene rings. These hydroxyl groups can perform hydrogen bonds with the water molecules.

The sample acidification may break these hydrogen bonds because the acid may promote the strongest dipole interactions with water, due to the higher dipole moment of HCl (in relation to the BPA). In this way, the BPA molecules (free from the water hydrogen bonds) can migrate from the water phase to the stationary phase.

During the elution process, the ethanol hydroxyl groups may perform hydrogen bonds with the adsorbed BPA and release this compound from the stationary phase. The n-hexane is a

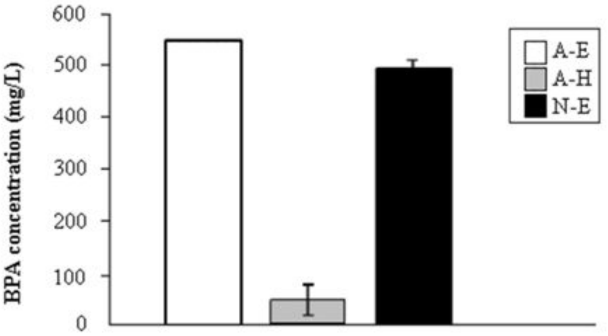

Fig. 3: Influence of pH and solvent polarity over the of BPA extraction from the model samples. The errors bars represent ± standards deviations. A-E = acidified sample extracted with ethanol; A-H = acidified sample extracted with n-hexane; N-E = non acidified sample extracted with ethanol.

non polar molecule without hydroxyl groups and desorbs less efficiently the BPA from the stationary phase.

The average concentration of BPA in the raw leachate samples extracted with ethanol and without the acidification step was 26.83 (±2.69) μg L^{-1}.

IV. CONCLUSIONS

The BPA concentrations in the in the soil and liquid samples of the São Giácomo landfill are far above that found in leachate of hazardous wastes. This is a worrying result since this contaminant can migrate to the surface and underground waters, near the sanitary landfills. BPA is a pollutant suspected of estrogen activity. The largest amount of BPA detected in the leachate samples suggests the migration of this contaminant from the soil to the aqueous phase. This may pose an important risk for surface and underground waters.

It is very reasonable to assume that the sources of most of the BPA found in this sanitary landfill are non-segregated domestic wastes. Therefore, it is extremely important to re-link environmental education programs focusing on the segregation of domestic wastes in inorganic, organic and recyclable categories. Likewise, the environmental laws have to be reviewed and expanded to include the plasticizers concentrations in the environment as a parameter for the soil quality and the treatment of sources of potential water pollution.

The sample's acidification allows the formation of stable interactions (like hydrogen bonds) among the hydrochloric acid and water molecules. The BPA elution was favored when the cartridge was washed with a polar solvent (ethanol). In this procedure, the hydrogen bonds among the BPA and HCl molecules were favored.

The acidification allows the increase of 5% of the extraction efficiency. In this way, the acidification step is recommended for the quantification of BPA in samples where the concentration of this analyte is below 0.1%. In these cases the acidification step may avoid important loss of the analyte and improve the detection limit in the instrumental analysis.

Our next step will be to evaluate the influence of the acidification step over the extraction yield of other endocrine disruptor like di(2-ethylhexyl)phthalate and di-n-butylphthalate.

ACKNOWLEDGEMENTS

National Council of Research and Technological Development (CNPq), University of Caxias do Sul.

V. REFERENCES

[1] T. Yamamoto, A. Yasuhara, et al., "Bisphenol a in hazardous waste landfill leachates," *Chemosphere*, vol. 42, no. 4, pp. 415 – 418, 2001.
[2] G. Zeng, C. Zhang, et al., "Adsorption behavior of bisphenol a on sediments in xiangjiang river, central-south china," *Chemosphere*, vol. 65, no. 9, pp. 1490 – 1499, 2006.
[3] Z. Zheng, P.-J. He, et al., "Phthalic acid esters in dissolved fractions of landfill leachates," *Water Research*, vol. 41, no. 20, pp. 4696 – 4702, 2007.
[4] K. J. D., S. R. L., and F. A. A., "Landfill leachate treatment," *Journal - Water Pollution Control Federation*, vol. 56, no. 1, pp. 27–33, 1984, eng.
[5] J. Li, B. Zhou, et al., "Influence of the coexisting contaminants on bisphenol a sorption and desorption in soil," *Journal of Hazardous Materials*, vol. 151, no. 2–3, pp. 389 – 393, 2008.
[6] M. Bauer, and R. Herrmann, "Estimation of the environmental contamination by phthalic acid esters leaching from household wastes," *Science of The Total Environment*, vol. 208, no. 1 - 2, pp. 49 – 57, 1997.
[7] V. E. Forbes, H. Selck, et al., "Does bisphenol a induce superfeminization in marisa cornuarietis? Part I: Intra- and inter-laboratory variability in test endpoints," *Ecotoxicology and Environmental Safety*, vol. 66, no. 3, pp. 309 – 318, 2007.
[8] Q. Huang, and W. J. Weber, "Transformation and removal of bisphenol a from aqueous phase via peroxidase-mediated oxidative coupling reactions: Efficacy, products, and pathways," *Environmental Science & Technology*, vol. 39, no. 16, pp. 6029–6036, 2005.
[9] A. Mantovani, A. Stazi, et al., "Problems in testing and risk assessment of endocrine disrupting chemicals with regard to developmental toxicology," *Chemosphere*, vol. 39, no. 8, pp. 1293 – 1300, 1999.
[10] P. Nelson, "Epidemiology, biology, and endocrine disrupters," *Occupational and Environmental Medicine*, vol. 60, no. 8, pp. 541–542, 2003.
[11] N. Suzuki, and A. Hattori, "Bisphenol a suppresses osteoclastic and osteoblastic activities in the cultured scales of goldfish," *Life Sciences*, vol. 73, no. 17, pp. 2237 – 2247, 2003.
[12] G. Ghiselli, and W. F. Jardim, "Endocrine disruptors in the enviroment," *Química Nova*, vol. 30, pp. 695 – 706, 06 2007, Title and abstract in English.
[13] D. Zalko, C. Jacques, et al., "Viable skin efficiently absorbs and metabolizes bisphenol a," *Chemosphere*, vol. 82, no. 3, pp. 424 – 430, 2011.
[14] J. M. Braun, A. E. Kalkbrenner, and A. M. Calafat, "Variability and predictors of urinary bisphenol a concentrations during pregnancy," *Environmental Health Perspectives*, vol. 119, pp. 131–137, 2010.
[15] T. Wintgens, M. Gallenkemper, and T. Melin, "Occurrence and removal of endocrine disrupters in landfill leachate treatment plants," *Water Science and Technology*, vol. 48, no. 3, pp. 127–134, 2003.
[16] T. Wintgens, M. Gallenkemper, and T. Melin, "Removal of endocrine disrupting compounds with membrane processes in wastewater treatment and reuse," *Water Science and Technology*, vol. 50, no. 5, pp. 1–8, 2004.
[17] M. Fernandez, T.-N. Noguerol, et al., "Toxicity identification fractionation of environmental estrogens in waste water and sludge using gas and liquid chromatography coupled to mass spectrometry and recombinant yeast assay," *Analytical and Bioanalytical Chemistry*, vol. 393, no. 3, pp. 957–968, 2009.
[18] P. Fauser, J. Vikelsøe, et al., "Phthalates, nonylphenols and LAS in an alternately operated wastewater treatment plant—fate modelling based on measured concentrations in wastewater and sludge," *Water Research*, vol. 37, no. 6, pp. 1288 – 1295, 2003.
[19] D. Azevedo, S. Lacorte, et al., "Occurrence of nonylphenol and bisphenol-A in surface waters from portugal," *Journal of the Brazilian Chemical Society*, vol. 12, no. 4, pp. 532–537, 2001.
[20] S. K. Marttinen, R. H. Kettunen, et al., "Removal of bis(2-ethylhexyl) phthalate at a sewage treatment plant," *Water Research*, vol. 37, no. 6, pp. 1385 – 1393, 2003.
[21] R. Länge, T. Hutchinson, et al., "Effects of the synthetic estrogen 17α-ethinylestradiol on the life-cycle of the fathead minnow (pimephales promelas)," *Environmental Toxicology and Chemistry*, vol. 20, no. 6, pp. 1216–1227, 2001.

[22] N. Vieceli, E. Lovatel, et al., “Study of bisphenol a in sanitary landfill soil,” *WIT Transactions on Ecology and the Environment*, vol. 154, pp. 225–231, 2011.

[23] N. Viecelli, E. Lovatel, et al., “Quantitative analysis of plasticizers in a wastewater treatment plant: Influence of the suspended solids parameter,” *Journal of the Brazilian Chemical Society*, vol. 22, no. 6, pp. 1150–1155, 2011.

[24] C. A. Staples, P. B. Dome, et al., “A review of the environmental fate, effects, and exposures of bisphenol A,” *Chemosphere*, vol. 36, no. 10, pp. 2149 – 2173, 1998.

Nathalia Cristine Viecelli Bacharel em Engenharia Ambiental pela Universidade de Caxias do Sul, é atualmente aluna do programa de doutorado em Engenharia do Ambiente da Universidade Técnica de Lisboa, Instituto Superior Técnico.

Ricardo Perazzoli Baldasso Possui graduação em Química pela Universidade de Caxias do Sul (2011). Tem experiência na área de Ciências Ambientais. Atuando principalmente nos seguintes temas:Extração em Fase Sólida (SPE), Farmácos, Cromatografia a Gás (GC). Mestrando do Programa de Pós-Graduação em Engenharia e Ciências Ambientais da Universidade de Caxias do Sul.

Irajá do Nascimento Filho Graduação em Licenciatura Plena Em Química pela Pontifícia Universidade Católica do Rio Grande do Sul (1984), mestrado em Química pela Universidade Federal do Rio Grande do Sul (1998) e doutorado em Química pela Universidade Federal do Rio Grande do Sul (2002). Atualmente é professor adjunto da Universidade de Caxias do Sul. Tem experiência na área de Química, com ênfase em Análise de Traços e Química Ambiental, atuando principalmente nos seguintes temas: gcmsd, spe, gc/msd, fenóis e landfill lechate. inascimf@ucs.br

Kira Lusa Manfredini Bióloga pela Universidade de Caxias do Sul (2009), Mestranda do Programa de Pós-Graduação em Engenharia e Ciências Ambientais da Universidade de Caxias do Sul. Atualmente é técnica no Instituto de Saneamento Ambiental da Universidade de Caxias do Sul. Tem experiência no Saneamento Ambiental, direcionado ao gerenciamento (caracterização, avaliação do sistema atual e proposta de gestão) de resíduos sólidos, avaliação de impactos ambientais e para Plano Ambientais Municipais e Licenciamento Ambientais. klmanfre@ucs.br