

AC/O₃-BAC processes for removing refractory and hazardous pollutants in raw water

Laisheng Li^{a,b,*}, Wanpeng Zhu^b, Pengyi Zhang^b, Qiuyun Zhang^a, Zulin Zhang^b

^a School of Chemistry and Environment, South China Normal University, Guangzhou Higher Education Mega Center, Guangzhou 510006, China

^b Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China

Received 22 September 2005; received in revised form 13 October 2005; accepted 12 November 2005

Available online 28 December 2005

Abstract

Granular activated carbon (AC)/O₃-biological activated carbon (BAC) process was employed to treat raw water and compared to O₃-BAC process in its optimum parameters (3 mg/L ozone dosage with 15 min oxidation time and 15 min empty bed contact time in BAC). The results showed that the presence of AC improved ozone utilization and biodegradability of the effluent. For dissolved organic carbon (DOC) removal, AC/O₃-BAC was more efficient than O₃-BAC and its synergetic effect could be noticed. It was showed that small molecules with molecular weight (MW) < 3 kDa predominated in the raw water accounting for more than 56% DOC, and their amount increased after oxidation, accounting for more than 64% DOC. Except for organic pollutants with MW > 10 kDa, those of other MW range were decomposed better by AC/O₃ process than by O₃ process alone. GC/MS analysis showed that AC/O₃-BAC process was effective in removing phthalate esters (PAEs) and persistent organic pollutants (POPs). PAEs' removal ratio reached more than 93% and reduced with the increase of the length of the alkyl side chains and the alkyl branch chains. POPs-polybromobiphenyls' removal reached more than 94% except for 2,2',4,5',6-pentabromophenyl and decreased with the substitutional bromines increase except for 2,2',5,5'-tetrabromobiphenyl, which could be completely removed.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Activated carbon; Catalytic ozonation; Biological activated carbon; Dissolved organic compound; Phthalate esters and persistent organic pollutants

1. Introduction

Removal of micro-pollutants in raw water is very important for its safe drinking. However, the organic pollutants remained in raw water are mostly refractory and difficult to be further biologically degraded. Conventional treatment process like flocculation-filtration-disinfection is not effective enough to remove them either.

Ozone is a powerful oxidant, and it is well known that ozonation of water would result in considerable organic pollutants' reduction and biodegradability improvement [1–3]. In general, large ozone dosage was needed for organic pollutants' reduction especially for mineralization, which accordingly impedes its large-scale application. On the other hand, the combination of ozonation and activated carbon (AC) (hereafter referred as AC/O₃) may offer an interesting potential for implementation at industrial scale, since ozonation may destroy adsorbed

molecules and regenerate the adsorption capacity of activated carbon [4–7]. AC can initiate radical-type chain reactions that proceed in solution and accelerate the transformation of ozone into secondary oxidants, such as hydroxyl radical ([•]OH) [8]. It was proved that ozonation of phenols [9], 1,2-dihydroxybenzene [10] and 1,3,6-naphthalene-trisulphonic acid [11] was enhanced in the presence of AC, probably due to catalytic effects provided by active surface groups. AC presents a large surface area where ozone and organic pollutants could be adsorbed and react. The complete mineralization of refractory organic matter in raw waters will also consume a lot of ozone. To increase economical efficiency of ozonation, it was usually combined with biological process for water treatment [12]. Ozonation followed by biological activated carbon (hereafter referred as O₃-BAC) is widely used for drinking water treatment [13]. However, AC/O₃ followed by BAC (hereafter referred as AC/O₃-BAC) process has been not reported.

The objective of this paper was to evaluate the effectiveness of AC/O₃-BAC process for removing organic pollutants in raw water, especially phthalate esters (PAEs) and persistent organic pollutants (POPs).

* Corresponding author. Tel.: +86 20 39310213; fax: +86 20 39310187.

E-mail addresses: llsh99@mails.tsinghua.edu.cn, llsh@scnu.edu.cn (L. Li).

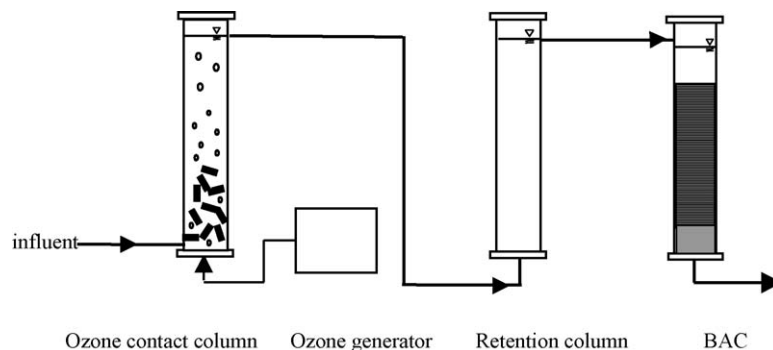


Fig. 1. Schematic diagram of AC/O₃-BAC pilot plant.

2. Materials and methods

2.1. Experimental set-up

Fig. 1 shows the experimental schematic diagram that consists of an ozone contact column, a retention column and a BAC column, all of which had a diameter of 60 mm and a height of 1000 mm except for the oxidation column with a height of 750 mm. There were two sets of parallel experimental set-ups for O₃-BAC and AC/O₃-BAC, respectively. For AC/O₃-BAC, 100 g coal-based granular activated carbon was added in the ozone reactor (fluidized activated beds).

The ozone contact time (empty bed contact time, EBCT) was 15 min. The retention column was used for further reaction and consumption of residual ozone, and its hydraulic retention time (HRT) was 20 min. BAC reactor was generally operated with EBCT of 15 min except specified elsewhere. The ozone gas was continuously bubbled into the water through a porous glass plate. Ozone was produced from pure oxygen using a DHX-SS-001 ozone generator (Harbin Jiujiu Electric Chemical Engineering Ltd.).

2.2. Analytical methods

Dissolved organic carbon (DOC) was analyzed with a TOC analyzer (SHIMADZU TOC-5000). UV₂₅₄ was determined with a Shimadzu UV-250 spectrophotometer. Turbidity was analyzed with Lp2000 turbidity-meter (made in Portugal). The ozone concentration in the ozone gas was determined by iodometry method [14]. Biodegradable dissolved organic carbon (BDOC) was determined following the procedure by Servais et al. [15]. It involves sterile filtration of the sample, reinoculation with a natural assemblage of bacteria from the same origin as the sample, and incubation for at least 10 days in the dark at 20 °C. DOC is followed, until a plateau is reached and the difference between initial and final DOC is taken as a measure of BDOC. Ultrafiltration membrane was employed to determine the change of molecular weight (MW). MW distribution was characterized by a series of ultrafiltration membranes with nominal cutoff values of 1, 3 and 10 kDa, and each fraction were collected for DOC determination.

A Hewlett-Packard 5890 GC with a mass detector (MSD) and Chemstation software, were used. The organic pollutants were

analyzed by scan mode. The capillary columns were HP-5MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The carrier gas was helium. A split-splitless injector in the splitless mode was used and the temperature program was programmed from 60 °C (initial time 3 min) to 120 °C at a rate of 10 °C/min, 120–280 °C at a rate of 5 °C/min and held at 280 °C for 10 min. The injector and mass spectrometer were held at 280 and 280 °C, respectively. The electron impact energy was set at 70 eV.

Before analysis, relevant standards were run to check column performance, peak height and resolution. With each set of samples to be analysed a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. Compounds were identified mainly by their retention times. Selected samples were also analysed by full-scan GC–EI–MS for confirmation.

2.3. Water quality of raw water after sand filter

The experiment for advanced purification of raw waters was carried out in Miyun Reservoir of Beijing City. Water quality is shown in Table 1.

3. Results and discussion

3.1. The optimum parameters in AC/O₃-BAC processes

In AC/O₃-BAC process, ozone dosage, oxidation time and retention time in BAC unit were three key operation parameters. DOC removal efficiency increased with ozone dosage and oxidation time in both AC/O₃ unit and the AC/O₃-BAC process. However, DOC removed per unit ozone consumption decreased with ozone dosage. In our study, 3 mg/L ozone dosage with 15 min oxidation time was much more economical. Although DOC removal efficiency increased with EBCT, 15 min EBCT

Table 1
Water quality of raw water

Parameters	Range
UV ₂₅₄ (m ⁻¹)	4.9–7.4
Turbidity (NTU)	0.65–0.97
DOC (mg/L)	4.94–7.27
BDOC/DOC	0.17–0.19
NH ₄ ⁺ -N (mg/L)	<0.5

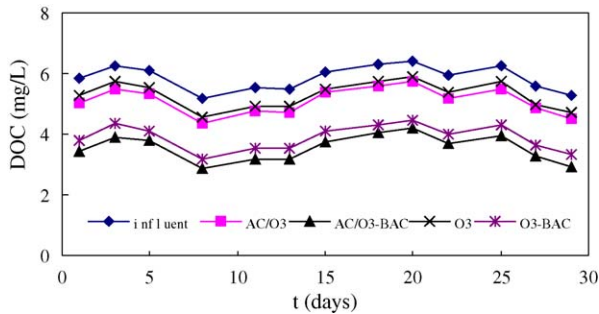


Fig. 2. Comparison of the effluent DOC between two processes.

was necessary and enough to obtain relatively higher BDOC removal efficiency in the subsequent BAC and much more economical.

3.2. Comparison between AC/O₃-BAC and O₃-BAC processes

Before the run of AC/O₃-BAC and O₃-BAC, DOC removal comparison by two BAC filters alone was conducted. The BAC matured and the treatment efficiency for raw water kept stable after 6 months operation. Their DOC average removal was about 11.6%. After the treatment efficiency of two processes reached the steady state, DOC removal comparison by two processes was listed in Fig. 2. It was clearly seen that AC/O₃-BAC process was more efficient than O₃-BAC in removing DOC.

The DOC removal efficiency in two processes was listed in Table 2. The results showed the synergetic effect in AC/O₃-BAC process was more than that in O₃-BAC process.

AC/O₃-BAC process led to a higher reduction of DOC than O₃-BAC process did. In the presence of AC, the higher ozone utilization was obtained in the ozone contact column. At 3 mg/L ozone dosage, 54% of added ozone was on average consumed or reacted in the presence of AC, while it was only on average 48% in the absence of AC. DOC removed per unit ozone consumed (mg DOC/mg O₃) was also higher than in the presence of ozone. It was 0.47 and 0.4 mg DOC/mg O₃ in the presence and absence of AC, respectively. After 2 months operation, the higher ozone utilization in AC/O₃ could not be contributed to adsorption of AC. As previously reported [8], the presence of AC could transform ozone into secondary radicals such as hydroxyl radical to initiate a radical-type chain reaction in the aqueous phase, so that the reaction of organic pollutants with ozone was accelerated. Besides, the higher DOC removal in oxidation unit due to higher ozone utilization, the biodegradability of AC/O₃ effluent (0.464) was also some higher than that of O₃ process (0.423),

Table 2
Comparison of DOC removal rate in different processes

Processes	DOC removal rate (%)		The whole process (%)	Δ (%)
	BAC alone (%)	Oxidation alone (%)		
AC/O ₃ -BAC	11.6	12.9	39.5	15.0
O ₃ -BAC	11.6	9.7	33.4	11.1

Δ = the whole process – BAC alone – oxidation alone.

Table 3
Influent BDOC and its removal in subsequent BAC unit

Process	BDOC (mg/L)	BDOC removal values (mg/L)
BAC alone	1.12	0.76
O ₃ -BAC	2.31	1.56
AC/O ₃ -BAC	2.45	1.75

which accordingly resulted in higher DOC removal by BAC in AC/O₃-BAC process than that in O₃-BAC process as shown in Table 3. After oxidation either by O₃ or AC/O₃, the ratio of BDOC/DOC significantly increased, BDOC removal in their subsequent BAC increased more than the BAC process alone. The presence of AC improved the biodegradability of ozonation effluent, which was beneficial to microorganism growth in the subsequent BAC. The higher biomass concentration was beneficial to obtaining higher DOC removal.

3.3. The change of molecular weight distribution in AC/O₃ and O₃ processes

As well known, ozone generally reacts with macromolecules quickly and is able to decompose them into particles lower in molecular weight. The MW distribution of raw water and oxidized water with ozone dosage of 3 mg/L was presented in Table 4. It was shown that small molecules with MW < 3000 Da predominated in the raw water, accounting for more than 56% DOC, and it was increased after oxidation, accounting for more than 64% DOC. It was interesting that only the fraction with molecule weight of 1000–3000 Da increased after ozonation either by O₃ or AC/O₃. The accumulation of this fraction was due to decomposition of higher in molecular weight fractions and further degradation was slowed down within oxidation process. Except for molecules with MW > 10,000 Da, the fractions with other MW range decomposed better by AC/O₃ than by O₃, which was probably owed to the effect of selective adsorption by AC. As well known, AC is prone to adsorb natural organic matters with small molecules. In the AC/O₃ process, low molecules like MW < 10,000 Da was easily adsorbed to AC, and the adsorbed molecules decomposed faster than that in O₃ process due to AC initiated radical-type chain reactions. Though ozone in the AC/O₃ process also reacted quickly with large molecules, the addition of AC decreased the ozone amount for direct reacting with large molecules. As a result, smaller amount of large molecules like MW > 10,000 Da was decomposed by AC/O₃.

Table 4
MW characteristics of untreated and ozonated water

MW range	DOC concentration (mg/L)			DOC weight ratio (%)		
	Influent	AC/O ₃	O ₃	Influent	AC/O ₃	O ₃
<1000	2.649	2.401	2.430	44.2	45.2	44.0
1000–3000	0.734	1.000	1.172	12.2	18.8	21.2
3000–10000	1.084	0.990	1.024	18.1	18.6	18.5
>10000	1.526	0.925	0.902	25.5	17.4	16.3

3.4. AC/O₃-BAC process for removing PAEs and POPs

PAEs are a class of chemical compounds primarily used as plasticizers and additives in special paints and adhesives [16]. As a consequence, they are released into the natural environment during manufacture, use, disposal and leaching from plastic materials. They are found to accumulate in the environment and to be toxic to a variety of aquatic organisms, which are at the base natural food chain in both marine and fresh environments [17]. Their toxic properties are even more important considering their high bioaccumulation rate (range from 100 to 3000 times) in different organisms [18]. The United States Environmental Protection Agency and its counterparts in several other countries have classified the most commonly occurring PAEs as priority pollutants and endocrine disrupting compounds. PAE concentrations have been reported in the range of 0.1–300 µg/l for surface marine waters and freshwater sites, and 0.1 ng/g to 100 µg/g for river sediments [19,20].

Polybrominated biphenyls (PBBs) are persistent, lipophilic substances that have structural conformity similar to that of polychlorinated biphenyls (PCBs) and share many of the same biological and toxicological properties, but are even more resistant to degradation [21]. PBBs have been detected in the marine food chain in the Baltic Sea, the North Sea and in the North Atlantic Ocean [22]. PBBs have been detected in a human population in Michigan due to an accident where food products were contaminated [23]. PBBs have also been detected in two sediment samples from the River Calder and one from the River Ribble in the UK [24]. But PBBs are still manufactured for use as flame-retardants in electronic equipment, plastics, building materials, and carpets around the world. Their production scale and use are increasing, and their emission is diffuse and difficult to control [25]. For example, in the Netherlands, the annual consumption has been up to 250 t/year [26]. Reported effects of PBBs have been cancer, neurotoxicity and immunotoxicity [23,26,27].

In this study, the raw water in Beijing Miyun reservoir is better, no PAEs and PBBs are detected. PAEs and PBBs were added to raw water at known starting concentration and thoroughly mixed. The added PAEs were dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP), respectively. The added POPs were hexachlorobenzene (HCB), 4-bromobiphenyl (PBB003), 2,6-dibromobiphenyl (PBB10), 2,2',6-tribromobiphenyl (PBB18), 2,2',5,5'-tetrabromobiphenyl (PBB52) and 2,2',4,5',6-pentabromobiphenyl (PBB103).

PAEs in water were analyzed by GC/MS before and after AC/O₃-BAC treatment, the removal of PAEs was listed in Table 5, which showed that AC/O₃-BAC process was effective in removing PAEs. The removal ratios are more than 93%, but they reduced with the increase of the length of the alkyl side chains and the alkyl branch chains. The short-chain PAEs, such as DMP and DEP, were degraded at higher rate than the long-chain PAEs, such as DBP and DEHP. In the degradation process of PAEs, the nature of the identified by-products gives evidence for a major attack on the aliphatic chain, which is a general enough finding in the previous works [16]. The increase of the length of the alkyl

Table 5

Removal of phthalate esters in AC/O₃-BAC process

PAEs	Influent (µg/L)	Effluent (µg/L)	Removal (%)
DMP	593.2	0.071	99.98
DEP	753.9	0.153	99.97
DBP	106.8	2.28	97.9
DEHP	23.0	1.51	93.4

Table 6

POPs removal in AC/O₃-BAC process

POPs	Influent (ng/L)	Effluent (ng/L)	Removal (%)
HCB	220.9	7.7	96.5
PBB003	165.4	4.9	97.0
PBB10	90.1	3.8	95.8
PBB18	55.9	3.2	94.3
PBB52	185.7	No	100
PBB103	150.5	31.3	79.2

side chains and the alkyl branch chains may inhibit interaction with oxidative species produced in the aqueous phase.

POPs in water were analyzed by GC/MS before and after AC/O₃-BAC treatment. The removal of POPs was listed in Table 6. The results showed that AC/O₃-BAC process was effective in removing POPs. PBBs' removal rate reached more than 94% except for PBB103. The lower brominated congeners show greater levels of disappearance than those with more brominated did. Since PBBs have structural conformity similar to that of PCBs, hydroxylation is an important initial step in the PBB degradation pathways, because lower brominated congeners may be more susceptible to advanced oxidation processes (AOPs) destruction due to the greater number of sites available for hydroxylation. Alternatively, the lower solubility of more highly brominated congeners may inhibit interaction with oxidative species produced in the aqueous phase. In either case, the negative correlation between the extent of congener disappearance and bromination may have important practical implications for PBB destruction by AOPs.

4. Conclusions

AC/O₃-BAC process was employed to treat raw waters. The results showed that its optimum parameters are 3 mg/L ozone dosage with 15 min oxidation time and 15 min EBCT in BAC unit. The presence of AC improved ozone utilization and biodegradability of the effluent. AC/O₃-BAC was more efficient than O₃-BAC for DOC removal. Use of ultrafiltration membrane revealed that organic pollutants with MW < 10,000 Da were decomposed better by AC/O₃ than by O₃ process alone.

GC/MS analysis showed that AC/O₃-BAC process was effective in removing phthalate esters and persistent organic pollutants. DMP, DEP, DBP and DEHP removal rate reached more than 93%, but they reduced with the increase of the length of the alkyl side chains and the alkyl branch chains. POPs-polybromobiphenyls' removal rate reached more than 94% except for 2,2',4,5',6-pentabromobiphenyl and decreased

with the substitutional bromines' increase except for 2,2',5,5'-tetrabromobiphenyl, which can be completely removed.

Acknowledgements

The authors are grateful for the financial support from the National High Technology Research and Development Program of China (contract no. 2002AA601250) and National Natural Science Foundation of China (contract no. 50238020).

References

- [1] C.D. Adams, R.A. Cozzens, B.J. Kim, Effects of ozonation on the biodegradability of substituted phenols, *Water Res.* 31 (1997) 2655–2663.
- [2] E. Gilbert, Biodegradability of ozonation products as a function of COD and DOC elimination by the example of humic acids, *Water Res.* 22 (1988) 123–126.
- [3] N. Narkis, M. Schneider-Rotel, Evaluation of ozone induced biodegradability of wastewater treatment effluent, *Water Res.* 14 (1980) 929–939.
- [4] S.H. Lin, C.L. Lai, Kinetic characteristics of textile wastewater ozonation in fluidized and fixed activated carbon beds, *Water Res.* 34 (2000) 763–772.
- [5] F.S. Cannon, J. Dusenbury, P.D. Paulsen, D.W. Mazyck, D.J. Maurer, Advanced oxidation regeneration of granular activated carbon for controlling air-phase VOCs, *Ozone Sci. Eng.* 18 (1996) 417–441.
- [6] B.T. Croll, The installation of GAC and ozone surface water treatment plants in Anglian water, UK, *Ozone Sci. Eng.* 18 (1996) 19–40.
- [7] T.K. Kainulainen, T.A. Tuhkanen, T.K. Vartiainen, P.J. Kalliokoski, Removal of residual organics from drinking water by ozonation and activated carbon filtration: a pilot plan study, *Ozone Sci. Eng.* 17 (1995) 449–462.
- [8] U. Jans, J. Hoigne, Activated carbon and carbon black catalyzed transformation of aqueous ozone into OH-radicals, *Ozone Sci. Eng.* 20 (1998) 67–87.
- [9] C.A. Zaror, Enhanced oxidation of toxic effluents using simultaneous ozonation and activated carbon treatment, *J. Chem. Tech. Biotechnol.* 70 (1997) 21–28.
- [10] C. Zaror, G. Soto, H. Valdes, H. Mansilla, Ozonation of 1,2-dihydroxybenzene in the presence of activated carbon, *Water Sci. Technol.* 44 (2001) 125–130.
- [11] J. Rivera-Utrilla, M. Sanchez-Polo, Ozonation of 1,3,6-naphthalene-trisulphonic acid catalysed by activated carbon in aqueous phase, *Appl. Catal. B* 39 (2002) 319–329.
- [12] C. Lin, T. Tsai, J. Liu, M. Chen, Enhanced biodegradation of petrochemical wastewater using ozonation and BAC advanced treatment system, *Water Res.* 35 (2001) 699–704.
- [13] J.D.G. Nigel, Removal of humic substances by oxidation/biofiltration processes—a review, *Water Sci. Technol.* 40 (1999) 141–148.
- [14] H. Bader, J. Hoigne, Determination of ozone in water by the indigo method, *Water Res.* 15 (1981) 449–456.
- [15] P. Servais, G. Billen, H-C. Hascoet, Determination of biodegradable fraction of dissolved organic matter in waters, *Water Res.* 21 (1987) 445–450.
- [16] B. Oliver, M. Gilles, B. Michèle, Degradation of dibutyl phthalate by homogeneous photocatalysis with Fe(III) in aqueous solution, *Appl. Catal. B: Environ.* 33 (2001) 239–248.
- [17] M. Muneer, I. Mazzarino, P. Piccinini, Photocatalytic oxidation of organic acids in aqueous media by a supported catalyst, *Chem. Eng. Sci.* 54 (1999) 3107–3111.
- [18] C.A. Staples, R.D. Peterson, T.F. Parkerton, W.J. Adams, The environmental fate of phthalate esters: a literature review, *Chemosphere* 35 (4) (1997) 667–749.
- [19] K. Hashizume, J. Nanya, C. Toda, T. Yasui, H. Nagano, N. Kojima, Phthalate esters detected in various water samples and biodegradation of the phthalates by microbes isolated from river water, *Biol. Pharm. Bull.* 25 (2002) 209–214.
- [20] S.Y. Yuan, C. Liu, C.S. Liao, B.V. Chang, Occurrence and microbial degradation of phthalate esters in Taiwan river sediments, *Chemosphere* 49 (2002) 1295–1299.
- [21] S. Safe, Polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs): biochemistry, toxicology, and mechanism of action, *CRC Crit. Rev. Toxicol.* 12 (1984) 319–395.
- [22] A.M. Pijnenburg, J.W. Everts, J. de Boer, J.P. Boon, Polybrominated biphenyl and diphenylether flame retardants: analysis, toxicity, and environmental occurrence, *Rev. Environ. Contam. Toxicol.* 141 (1995) 1–26.
- [23] A. Hoque, A.J. Sigurdson, K.D. Burau, H.E. Humphrey, K.R. Hess, A.M. Sweeney, Cancer among a Michigan cohort exposed to polybrominated biphenyls in 1973, *Epidemiology* 9 (1998) 373–378.
- [24] C.R. Allchin, R.J. Law, S. Morris, Polybrominated diphenylethers in sediments and biota downstream, *Environ. Pollut.* 105 (1999) 197–207.
- [25] B. Jansson, R. Andersson, L. Asplund, K. Litzen, K. Nylund, U. Sellstrom, U. Uvemo, C. Wahlberg, U. Wideqvist, T. Odsjo, M. Olsson, Chlorinated and brominated persistent organic samples from the environment, *Environ. Toxicol. Chem.* 12 (1993) 116–1174.
- [26] A. Kristoffersen, Ø.A. Voie, F. Fonnum, *Ortho*-substituted polybrominated biphenyls activate respiratory burst in granulocytes from humans, *Toxicol. Lett.* 129 (2002) 161–166.
- [27] C.C. Capen, Patophysiology of chemical injury of the thyroid-gland, *Toxicol. Lett.* 64–65 (1992) 381–388.