

**DISTRIBUTION AND LEVELS OF BROMINATED FLAME
RETARDANTS IN SEWAGE SLUDGE**

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ABSTRACT

One hundred and sixteen sewage sludge samples from 22 municipal wastewater treatment plants in Sweden were analysed for brominated flame retardants.

Polybrominated diphenyl ethers (PBDEs) were in the range n.d.-450 ng/g wet weight, tetrabromobisphenol A (TBBPA) varied between n.d.-220 ng/g wet weight, 2,4,6-tribromophenol was in the range n.d.-0.9 ng/g wet weight and polybrominated biphenyls were not detected (except for a possible analytical interference). There was a significant variation in the samples among plants. Influence from industries and other local sources can therefore be assumed. The correlation pattern indicated contribution from three different types of technical products; composed of either low-brominated PBDEs, deca-BDE or TBBPA

Keywords: BFRs, brominated diphenyl ethers, PBDE, TBBPA, waste water treatment, principal component analysis, ANOVA

INTRODUCTION

Brominated flame retardants (BFRs) are widely distributed in the environment, and their persistence and/or potential for bioaccumulation have caused concern (WHO, 1997).

The content of BFRs in sewage sludge from wastewater treatment plants gives an indication of the general exposure and use of these compounds. Several investigators have reported findings of the most widely used BFRs in this matrix, and other parts of the wastewater disposal system (Antusch, 1999, Hagenmaier et al, 1992, Hellström, 2000, Kuch et al, 2001, Nylund et al, 1992). In this study we will give a general overview of distribution and levels of BFRs in sewage sludge from Swedish plants.

METHODS

Samples

Sewage sludge samples from Swedish wastewater treatment plants are frequently analysed for various pollutants. Results are here reported for 116 sewage sludge samples, from 22 municipal wastewater treatment plants, which arrived to the ALcontrol laboratory in Nyköping, Sweden, between October 1999 and September 2000. The sludge samples were collected by the plant owner's staff and sent directly to the laboratory.

Chemical analysis

Sample preparation, extraction and clean-up procedures were adapted with minor modifications from Nylund et al (1992) and Sellström et al (1995 and 1998). Chemicals used are listed in Table 1.

The samples were analysed for brominated flame retardants (BFRs) by high-resolution gas chromatography/mass spectrometry (HRGC/MS) with negative chemical ionisation (NCI). A HP 5973 mass spectrometer was used for all analyses and the ion source temperature was kept at 150 °C and the electron energy at 133 eV. The gas chromatographic separations were carried out using J&W DB5MS columns, with (5%-Phenyl)-methylpolysiloxane as stationary phase. 30 m x 0.25 mm i.d. columns were used for all analyses except for decabromodiphenyl ether and decabromobiphenyl where a 15 m x 0.25 mm i.d. column was used instead. The temperature programmes were run from 80 °C to 325 °C and helium (AGA, Stockholm, Sweden) was used as carrier gas.

Quantification was done by the internal standard method relative to a multilevel calibration for all components. 3,3',4,4'-Tetrabromodiphenyl ether, ¹³C-2,3,3',4,4',5'-hexabromobiphenyl and pentabromophenol were used as internal standards.

Analytical data were originally reported in either ng/g wet weight (n=94) or ng/g dry weight (n=22), but for comparison all values have here been recalculated to wet weight.

Data analysis

The analytical data were described and evaluated using exploratory data analysis (EDA), analysis of variance (ANOVA), linear regression and principal component analysis (PCA). Tukey (1977) review the EDA-methods. Ståhle and Wold (1989) describe ANOVA, and Draper and Smith (1981) describe regression analysis. PCA is reviewed by Jackson (1991) and Martens and Næs (1989), together with other bilinear methods for multivariate data analysis.

The software Statistica (StatSoft, Inc., USA) was used for EDA, ANOVA, linear regression and descriptive statistics. The principal component analysis was carried out with the software Unscrambler (CAMO ASA, Norway).

RESULTS

The analytical results are summarised in Table 2. Medians, quartiles and ranges are better suited as measures of location and spread than the arithmetic means and standard deviations, since the distributions for all analytical variables were highly skewed.

In Figure 1 the distributions of the sum of PBDEs for the different wastewater treatment plants are shown with Box-Whisker plots. Here the data is also summarised as medians, quartiles and ranges.

Clear-cut spatial trends were not evident, but samples from the northern part of Sweden generally showed lower levels of the analysed compounds. The samples with the highest concentrations of decabromodiphenyl ether and tetrabromobisphenol A were collected in wastewater treatment plants with possible contribution from textile respectively electronics industry. The short time-span (12 months) covered by these samples does not permit us to evaluate possible temporal trends.

The variations of the sum of PBDEs among and within the wastewater treatment plants were evaluated with analysis of variance (ANOVA). The measurement results were log-transformed in order to fulfil the normality assumption (see Dean, 1981). The variation among plants was statistically significant, Table 3.

The correlation pattern between the different PBDEs and TBBPA was evaluated using principal component analysis. The measurement results for deca-BDE and TBBPA were log-transformed prior to the data analysis, and all variables were auto-scaled (55 samples analysed for all PBDEs and TBBPA). The low-brominated PBDEs did not require any transformations, since their distributions were only slightly skewed within this subset. A model with three significant components (cross validated) could explain 93 % of the variance. The 3D-loadings plot in Figure 2 show how the different analytical variables correlate. Tetra-, penta- and hexabrominated diphenyl ethers correlate well, while decabromodiphenyl ether and tetrabromobisphenol A show other distribution patterns distinctly separated from each other. The correlation coefficients between the different lower-brominated diphenyl ethers vary between 0.92-0.98. The linear relationship between PBDE #47 and #99 is shown in Figure 3.

The congener pattern for tetra-, penta- and hexabrominated diphenyl ethers is stable as shown in Table 4. This corresponds well with the composition reported for the commercial product Bromkal 70-5DE (Huber and Ballschmiter, 2001, Sjödin et al, 1998, Sundström and Hutzinger, 1976).

DISCUSSION

The results presented show that there are considerable variations in the concentrations of brominated flame retardants in sewage sludge, and that there is a statistically significant variation among municipal waste water treatment plants. Influence from local sources can therefore be assumed. Two examples of industries that can give specific contributions are the electronics (TBBPA) and textile industries (deca-BDE), and the highest concentrations of each pollutant were indeed found in samples with such

a connection. Similar observations regarding TBBPA were also made by Kuch et al (2001). The correlation pattern of BFRs in the analysed samples indicates that there are three major constituents, i.e. contribution from three distinctly different types of technical products, composed of either low-brominated PBDEs, deca-BDE or TBBPA.

Norris et al (1973), later confirmed by Watanabe and Tatsukawa (1987), showed that decabromodiphenyl ether can undergo photolytic debromination. There are however no indications in this study that the bromination pattern for PBDEs is changed during wastewater treatment, and only weak or non-significant correlations were found between the low-brominated PBDEs and deca-BDE. This is not to be expected either since significant UV-exposure can only occur after the sewage sludge has left the treatment plant.

BFRs are only one example of the many hundreds of organic pollutants that occur in sewage sludge. Analyses of this matrix are therefore attractive as a monitoring tool for the current usage and emissions of persistent organic pollutants prior to environmental transformations and degradation. Spatial and temporal variations may give an indication of local and general sources as well as the effectiveness of product control measures.

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Table 1: Chemicals used

| Chemicals | Supplier / quality |
|-------------------------------------------------------|-----------------------------|
| Acetic anhydride | Merck p.a |
| Dichloromethane | Rathburn, HPLC Grade |
| n-Hexane | Merck LiChrosolv |
| Methyl tertiary butyl ether (MTBE) | Merck p.a |
| Potassium hydroxide KOH | Merck p.a |
| Pyridine | Fluka GC quality |
| Sodium chloride NaCl | Merck p.a |
| Sulfuric acid H ₂ SO ₄ conc. | Merck p.a. |
| Toluene | Distilled in the laboratory |
| PBDE: | |
| 2,2',4,4'-Tetrabromodiphenyl ether | CIL 50 µg/ml in nonane |
| 2,2',3,4,4'-Pentabromodiphenyl ether | CIL 50 µg/ml in nonane |
| 2,2',4,4',5-Pentabromodiphenyl ether | CIL 50 µg/ml in nonane |
| 2,2',4,4',6-Pentabromodiphenyl ether | CIL 50 µg/ml in nonane |
| 2,2',3,4,4',5'-Hexabromodiphenyl ether | CIL 50 µg/ml in nonane |
| 2,2',4,4',5,5'-Hexabromodiphenyl ether | CIL 50 µg/ml in nonane |
| 2,2',4,4',5,6'-Hexabromodiphenyl ether | CIL 50 µg/ml in nonane |
| Decabromodiphenyl ether | Fluka purum |
| 3,3',4,4'-Tetrabromodiphenyl ether (IS) | CIL 50 µg/ml in nonane |
| PBB: | |
| Firemaster BP-6 | Accu Standard tech. |
| Decabromobiphenyl | Chem Service |
| ¹³ C-2,3,3',4,4',5'-Hexabromobiphenyl (IS) | CIL 40 µg/ml in nonane |
| TBBPA: | |
| Tetrabromobisphenol A | Aldrich 97% |
| 2,4,6-Tribromophenol | Aldrich 98% |
| Pentabromophenol (IS) | Aldrich 99% |

Table 2: Brominated flame retardants in sewage sludge, ng/g wet weight

| Analyte | n | Min | Lower quartile | Median | Upper quartile | Max |
|----------------------------------------------------|-----|------|----------------|--------|----------------|------|
| 2,2',4,4'-Tetrabromodiphenyl ether (PBDE #47) | 105 | <0.3 | 4.9 | 7.0 | 10.5 | 48 |
| 2,2',3,4,4'-Pentabromodiphenyl ether (PBDE #85) | 105 | <0.3 | <0.3 | 0.42 | 0.61 | 2.7 |
| 2,2',4,4',5-Pentabromodiphenyl ether (PBDE #99) | 105 | <0.3 | 6.7 | 10 | 14 | 320 |
| 2,2',4,4',6-Pentabromodiphenyl ether (PBDE #100) | 105 | <0.3 | 1.0 | 1.7 | 2.5 | 11 |
| 2,2',3,4,4',5'-Hexabromodiphenyl ether (PBDE #138) | 105 | <0.3 | <0.3 | <0.3 | <0.3 | <1 |
| 2,2',4,4',5,5'-Hexabromodiphenyl ether (PBDE #153) | 105 | <0.3 | 0.54 | 0.86 | 1.2 | 5.5 |
| 2,2',4,4',5,6'-Hexabromodiphenyl ether (PBDE #154) | 105 | <0.3 | 0.42 | 0.72 | 0.99 | 5 |
| Decabromodiphenyl ether (PBDE #209) | 114 | <0.6 | 5.2 | 11 | 21 | 390 |
| Tetrabromobisphenol A (TBBPA) | 57 | <0.3 | 0.51 | 2.0 | 4.0 | 220 |
| 2,4,6-Tribromophenol | 57 | <0.3 | <0.3 | <0.3 | 0.36 | 0.9 |
| 2,3',4,4',5-Pentabromobiphenyl (PBB #118) | 21 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 |
| 2,2',3,4,4',5'-Hexabromobiphenyl (PBB #138) | 21 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 |
| 2,2',4,4',5,5'-Hexabromobiphenyl (PBB #153) | 21 | <0.3 | <0.3 | <0.3 | 0.78* | 1.1* |
| 2,3',4,4',5,5'-Hexabromobiphenyl (PBB #167) | 21 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 |
| 2,2',3,4,4',5,5'-Heptabromobiphenyl (PBB #180) | 21 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 |
| Decabromobiphenyl (PBB #209) | 21 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 |

* Incomplete separation from PBDE#154.

Table 3: ANOVA table, sum of PBDEs in 103 samples with complete analyses

| Source of variation | df | Sums of squares (SS) | Mean squares (MS) | F | p |
|---------------------|-----|----------------------|-------------------|------|-------|
| Among plants | 21 | 8.85 | 0.421 | 1.90 | 0.021 |
| Within plants | 81 | 17.94 | 0.222 | | |
| Total | 102 | 26.79 | 0.263 | | |

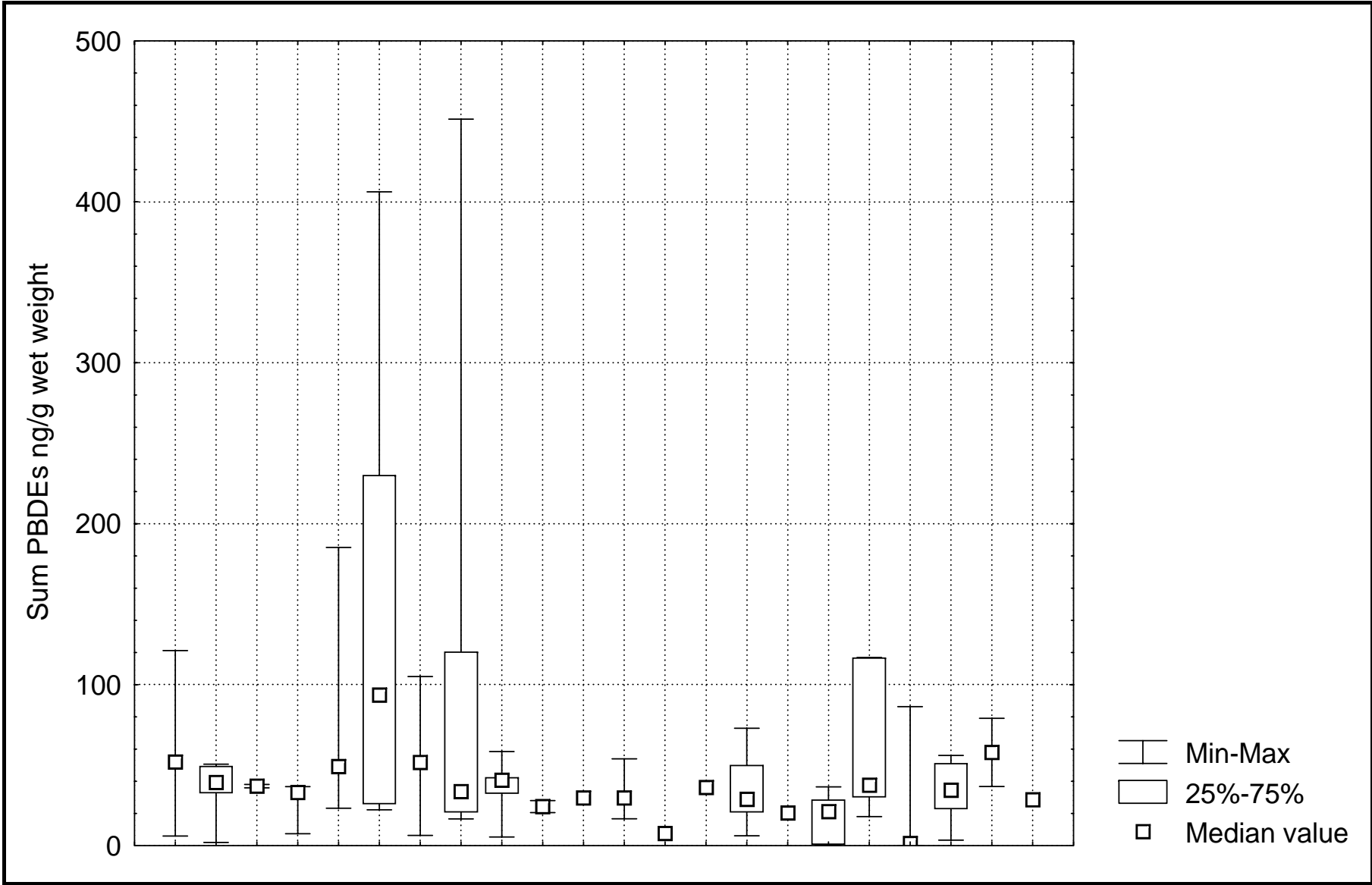
Table 4: Congener pattern for Br₄-Br₆DEs (%) in 71 samples with concentrations above the detection limit

| | BDE #47 | BDE #85 | BDE #99 | BDE #100 | BDE #153 | BDE #154 |
|------|---------|---------|---------|----------|----------|----------|
| Mean | 34 | 2.1 | 48 | 8.2 | 4.3 | 3.4 |
| Sdev | 3.3 | 0.37 | 3.0 | 0.65 | 0.70 | 0.44 |

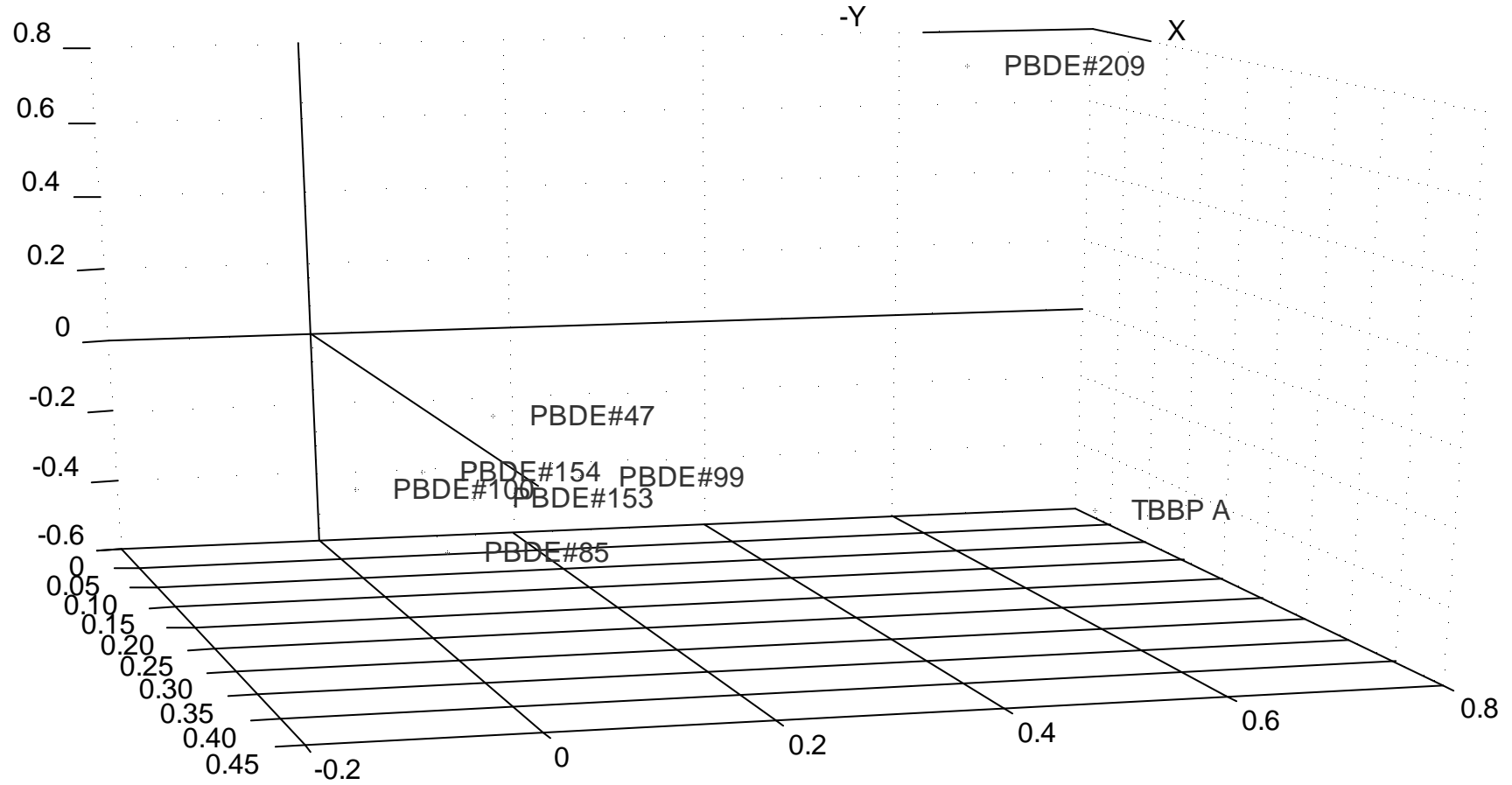
Figure 1: Box-Whisker plots for each wastewater treatment plant (22 plants and 1-13 samples from each)

Figure 2: Loadings plot for PBDEs and TBBPA (55 samples analysed for all PBDEs and TBBPA)

Figure 3: PBDE #99 vs. PBDE #47, ng/g wet weight in 104 sewage sludge samples ($r^2=0.94$)



X-loadings



BFR-model, X-expl: 68%,14%,11%

