

LANDFILLS WASTE WATER TREATMENT PLANTS PERMEATES AND EUROPEAN UNION DIRECTIVE 2000/60/EC : A CASE STUDY OF PAHs

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SUMMARY : The Directive 2000/60/EC requires that the permeates, from the landfill leachate treatment plants, respect the priority substances emission limit values. This study is performed to determine the adequacy between the requirements of the Directive and the management of 8 leachate treatment plants in Wallonia, divided among 4 sequence processes. For all the plants, the study is only focusing in PAHs reduction treatment and PAHs concentration in the thrown permeates. The concerned PAHs are naphthalene, anthracene and 6-Borneff. The 15 analysed PAHs show good results : the high PAHs reduction rate and the low PAHs concentration of permeates, in respect to the emission limit value, for plants belonging to 3 sequence process plants.

1. INTRODUCTION

The European Directive 2000/60/EC establishes a framework for Community action in the field of water policy. The action settles strategies to prevent pollutions of water. In fact, according to the Directive, “*the European Parliament and the Council shall adopt specific measures against pollution of water by individual pollutants or groups of pollutants presenting a significant risk to or via the aquatic environment, ... For those pollutants measures shall be aimed at the progressive reduction and, for priority hazardous substances, (...) the cessation or phasing-out of discharges, emissions and losses*”. The Decision N° 2455/2001/EC of the European Parliament and the Council established a list of 33 priority hazardous substances and modifies the Directive 2000/60/EC.

Landfilling waste management yields large quantities of leachate. This is a toxic waste water containing hazardous contaminants and some of them are on the list of the 33 priority substances. According to the Directive, produced leachate has to be purified in waste water treatment plants (WWTP) before throwing out as a permeate to surface waters. This permeate shall cope with the “*progressive reduction*” for pollutants and “*cessation or phasing-out of discharges, emissions and losses*” for priority hazardous substances.

The aim of pollutant reduction or cessation is a matter of concern in the leachate treatment plants thus, one can wonder whether the 2000/60/EC Directive and decision n° 2455/2001/EC are threats for leachate treatment plants ? In fact, the permeate, produced in the leachate treatment plants, needs to meet high quality requirements that may involve new investments or cause an increase of leachate treatment costs.

PAHs hold an important place in the list of 33 priority substances, which are divided in 3 groups. 6-Borneff PAHs belong to the group of 10 priority dangerous substances, naphthalene and anthracene to the group of 15 priority substances subjected to revision and fluoranthene to the group of the 8 priority substances. The study will focus on PAHs survey to try to answer this question.

The Directive requires the Member States to ensure establishment and/or implementation of relevant emission limit values for those of the 33 substances which are matter of concern and, that are possibly defined in other European Directives such as the 1999/31/EC (waste directive). In Wallonia, the transposition of the 2000/60/EC gives limit values for the PAHs.

The study focuses on two PAH substances (anthracene and naphthalene), one group of PAHs (6 Borneff) described in the Directive to which the sum of 15 PAHs of the EPA list (acenaphtylene excepted) is added for a global assessment. Assessment is achieved in the reduction rate of PAHs concentration in leachate and in the PAHs concentration of the thrown out permeate. Eight landfill sites were chosen for data collection : Belderbusch (BDB), Cour-au-Bois (CAB), Froidchapelle (FRO), Habay-la-Neuve (HLN), Tenneville (TNV), Happe-Chapois (HCP), Hallembaye-2 (HAL2), and Hallembaye-1 (HAL1).

2. MATERIALS

2.1 Leachates and permeates

Leachate and permeate are sampled on the eight landfill waste water treatment plants. The characteristics are presented in the Table n°1. Because of the various composition of leachate, the plants are equipped with various processes.

Table 1 : Characteristics of the studied landfills and leachate treatment plants in 2004.

Landfill sites	Starting year	Waste capacity (ton)	Filling stage	Treatment processes	Leachates in 2004 (m ³)
BDB	1992	445 000	Closed in 1998	MBR/ACA	6 222
CAB	1989	5 321 249	5 cells closed, 1 in filling	MBR/ACA	26 621
FRO	1979	991 000	1 cell of 6 in filling	MBR/ACA	8 206
HLN	1980	1 500 000	1 cell of 2 in filling stage	Clarif-floccul/ACA	51 453
TNV	1980	1 700 000	1 cell of 2 in filling stage	Clarif-floccul/ACA	59 110
HCP	1986	719 025	1 cell of 2 in filling	MBR/O ₃ oxidation	18 202
HAL2	1999	1 085 343	In filling stage	Reverse osmosis	13 648
HAL1	1989	1 640 000	Closed in august 1999	Reverse osmosis	15 611

MBR/ACA consists of biological degradation and microfiltration stage which includes nitrification/denitrification process and microfiltration process (MBR), and a completion process stage with activated carbon absorption (ACA).

Reverse osmosis process consists of a concentrating of leachate four times in a two sections plant and a evacuation of the concentrated leachate out of the site for more advanced treatment. Biological Aerated Filtration System is a biological submerged filter containing a fixed, dense granular bed with influent wastewater flowing in an upward direction. The system uses a proprietary media that serves as a biological contactor as well as a filter, eliminating the need for separate clarification and saving space.

2.2 Automatic sampler

For permeate sampling, we used fixed automatic samplers, generally installed at the exit of the sites treatment plants (legal obligations). Only Happe-Chapois and Belderbusch are not equipped with such tools. These samplers are for all the sites of “Endress + Hauser” mark and are provided with a vacuum pump and a cooled compartment for samples conservation. In Happe-Chapois and Belderbusch, we used a portable automatic sampler “Isco Glacier” also comprising a cooled compartment for sample conservation.

2.3 Analysis instruments

The system is composed of HPLC Beckman System Gold 126 model coupled with a Fluorometer 122 Gilson with variable wavelength.

2.4 Sampling bottles

For the collecting of the samples collection, “Scott/Duran” brown glass bottles of 5 liters (primary sampling) or of 1 liter analysis sample were used.

3. EXPERIMENTAL STUDY AND METHOD

3.1 Samples collection an experiment procedure

Leachate and permeate samples were collected in September 2003, March 2004, September 2004 and March 2005 at the entrance (leachate) and exit (permeate) of each leachate treatment plant. The permeates were collected in a 5 liters bottle in brown glass using automatic samplers. The sampling base was a rate of 50 ml every 15 minutes during 24 hours. One liter is collected from the sample and sent for analysis.

The leachates were collected manually (instantaneous sample), generally in leachate basin before each entrance. The samples were collected and freeze-stored during a maximum of 3 days before a liquid-liquid extraction. After this, the extraction was analysed as described above in a maximum of 7 days after the operation. While waiting for analyse, the extraction was kept in freeze conservation.

3.2 Leachates and permeates samples analysis method

The analysis is carried out in accordance with standard NBN EN ISO 17993. The protocol consists of liquid-liquid extraction of 1 liter leachate / permeate with 50 ml cyclohexan. Drying of extract with Na_2SO_4 , follow-up of extract concentration on turbovap ; concentration and solvent (acetonitril) exchange with turbovap ; separation of PAHs by HPLC according to the following chromatographic conditions : Vydac column 201 TP54 25 cm X 4.6 mm I.D. Mobile

phase: acetonitril/water 50/50 during 5 minutes, from 50/50 to 100/0 in 20 minutes and 100/0 during 10 minutes. Injected volume: 20 µl. Flow: 1.5 ml/min. Detection by fluorescence. According to this method, the 16 PAHs of the EPA list are determined excepted acenaphthylene as it does not absorb in fluorimetry.

4. RESULTS AND DISCUSSION

The obtained results are PAHs concentration in ng/l unit and are presented in the three following stages. The first stage is a quantitation of the PAHs concentration at the entrance of leachate treatment plants by measuring the 15 PAHs of EPA list. The second stage presents reduction rate of the PAHs concentration in the leachate, by assessment of 15 PAH, of 6-Borneff PAHs, of naphtalene, and of anthracene reduction in the permeates. The third stage assesses residual PAHs concentration in the permeate of leachate treatment plants.

Before presenting the results, any considerations about substances and presented values are developed hereafter.

4.1 Consideration about substances and minimal values determination

The minimal values presented are determined by the lab quantification limit. As a consequence, there is not a zero level concentration as the minimal concentration will be the quantification limit for the substance analyzed. Here are the quantification limits for the studied PAHs.

Table 2 : Quantification limit value and number of aromatic cycles of the studied PAHs molecules.

PAHs	Naph	Acen	Fluo	Phen	Anth	Fluot Pyr	BaA, Chry	BbF	BaP, BkF, DahA	Bper, IP
Nb of Cycles	2	3	3	3	3	4	4	5	5	6
Quant. limit	40	30	10	15	1	5	2	2	1	5

4.2 Initial PAHs concentration in leachate

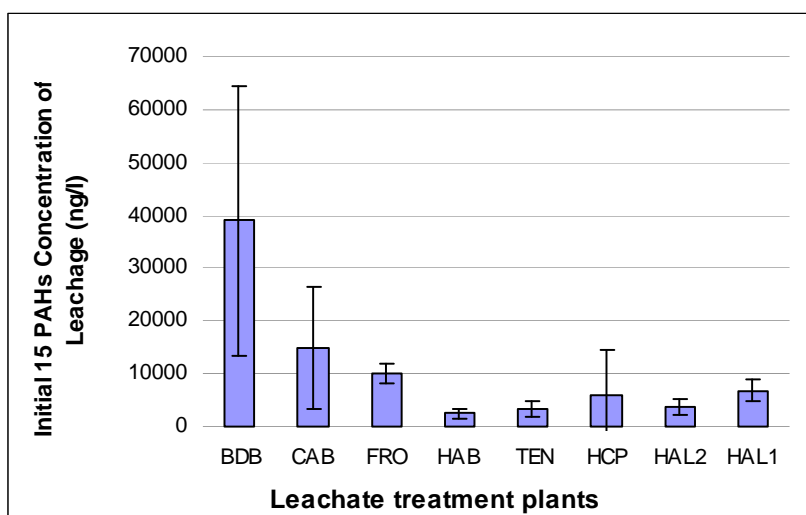


Figure 1 : Initial 15 PAHs concentration of Leachate at the entrance of treatment plants.

Total PAHs concentration in leachate is determined by the sum of 15 PAHs listed in table 3.

The values for the leachates, recorded during four observing campaigns, are in general lower than those described by Andréotola (1997) except the naphthalene which is sometimes in the range. Andréotola gives leachates values in the range of 4 600 – 186 000 ng/l for naphthalene, 13 900 – 21 300 for acenaphthene, 9 560 – 723 000 for fluoranthene, 21 000 – 32 600 ng/l for fluorene, 8 100 – 1 220 000 ng/l for phenanthrene and 9 560 – 723 000 ng/l for fluoranthene. PAHs concentration in leachate from each site present a low variability in time, except for the leachates from Belderbusch and Cour-au-Bois where the concentrations, obtained for the second campaign, are more than 2 times as high than the average of the three others compaigns. This is why there is a large dispersion for the results in these two sites. Another exception is observed in Happe-Chapois because of high PAHs concentration, PAHs with 2 to 4 carbon cycles, for the first campaign. Is this a matter of leachate quality variation as the site is still in exploitation ? It should not be a matter of sampling as this has been taken as usual in a storage basin.

4.3 PAHs reduction rate in leachate treatment plants

4.3.1 Results and discussion of 15 PAHs reduction rate in the leachate treatment plants

We observed the reduction of PAHs in different leachate treatment plants. This was undertaken on four levels. The first level is total 15 PAHs reduction rate. The second level is the 6-Borneff PAHs reduction. The third level is naphthalene reduction and the fourth, anthracene reduction. These substances and groups of substances are included in the Parent Directive on water policy as priority hazardous substances or hazardous substances to “reduce, cease or phase out emission”. The comparison between the leachates and permeates is not stated on the same liquid. In fact, the analyzed permeate does not exactly result from the considered leachate. This can undoubtedly bring a skew in our analysis such a sometime reduction rate over 100 %. But, this is relatively weak because the leachates are generally sampled in collecting and storage basins. This strongly limits leachate variability in the time of 24 hours which is necessary for permeate sampling.

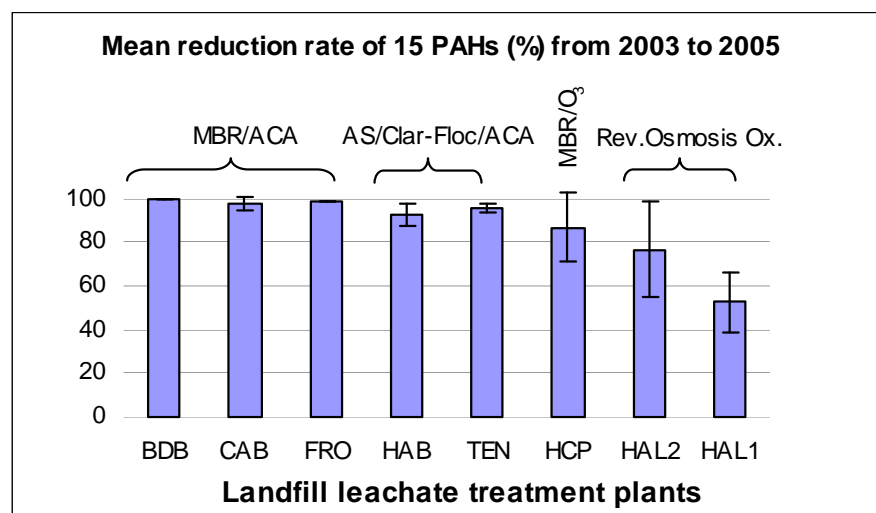


Figure 2 : Mean 15 PAHs reduction ratio in leachate treatment plants.

The eighth leachate treatment plants can be divided in four types of plants :

- the first is MBR/activated carbon absorption (ACA) ;
- the second combined activated sludge as biological process/clarification-flocculation /Biological Aerated Filtration System/ and ACA for completion ;
- the third is composed of MBR and ozone oxidation process for completion ;
- the fourth is composed of a single reverse osmosis process.

The best results of PAHs reduction rate (> 98 %) are reached, with a low dispersion, by the three leachate treatment plants coming from the first type of plants (MBR/ACA) : There are Belderbusch, Cour-au-Bois and Froidchapelle.

Next, we find the second type of plants, composed of Tenneville and Habay-la-Neuve. The results of these plants involve good reduction rates of the 15 PAHs (respectively 96 and 93 %) with a low dispersion.

The third type of plant (Happe-Chapois site) has average results : reduction rate of 15 PAHs at 87 % with an high dispersion. The gap, between these results and the results of the BRM process completed with activated carbon absorption, is explained by the ozone oxidation process itself or a non-optimal functioning.

The fourth type of plant yields poor reducing rates of the 15 PAHs (53 % for Hallembaye-1 and 78 % for Hallembaye-2) and a high variability. The reason is mainly a low reduction rate of PAHs with 2 carbon cycles. The gap between the two Hallembaye may also suggest a non-optimal functioning.

4.3.2 Results and discussion of 6-Borneff PAHs reduction rate in the treatment plants

As seen on the figure 3, the reduction rate of 6-Borneff PAHs is higher than 96 % with a low dispersion. Only Happe-Chapois, Hallembaye 1 and 2, which belong to the third and the fourth plant types, have average reducing rate around 93 % with a higher variability. The reduction rates for the fourth plant type, better for 6-Borneff PAHs than the 15 PAHs, can be explained by the big size of the PAHs molecules gathered in the 6-Borneff PAHs. This is why the reverse osmosis process can more easily remove the PAHs molecules containing 4, 5 or 6 aromatic carbon cycles.

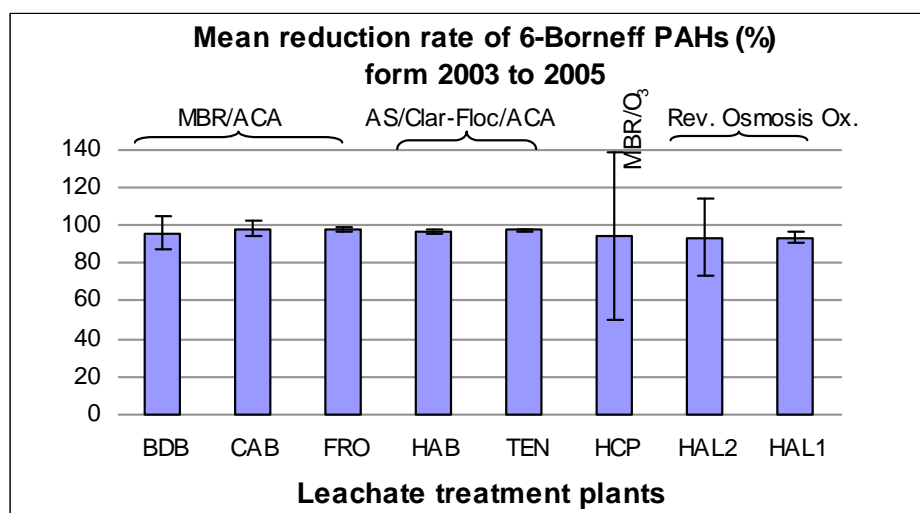


Figure 3 : Mean reduction rate of the 6-Borneff PAHs for leachate treatment plants.

4.3.3 Results and discussion of naphthalene reduction rate in the treatment plants

Naphthalene is obviously the most difficult substance to remove from leachate because of its short molecule size. It involves that the reduction rates of this substance are the lowest for all plants, except those belonging to the first plant type. In the first plant type, the reduction rates of naphthalene are superior to 98 % for Belderbusch and Cour-au-Bois and superior to 94 % for Froidchapelle. The reduction rates are intermediate for the second plant types, 87 % for Tenneville and 85 % for Habay-la-Neuve), and worse for the third and fourth plant types : 66 % for Hallembaye-2, 64 % for Happe-Chapois and 37 % for Hallembaye-1.

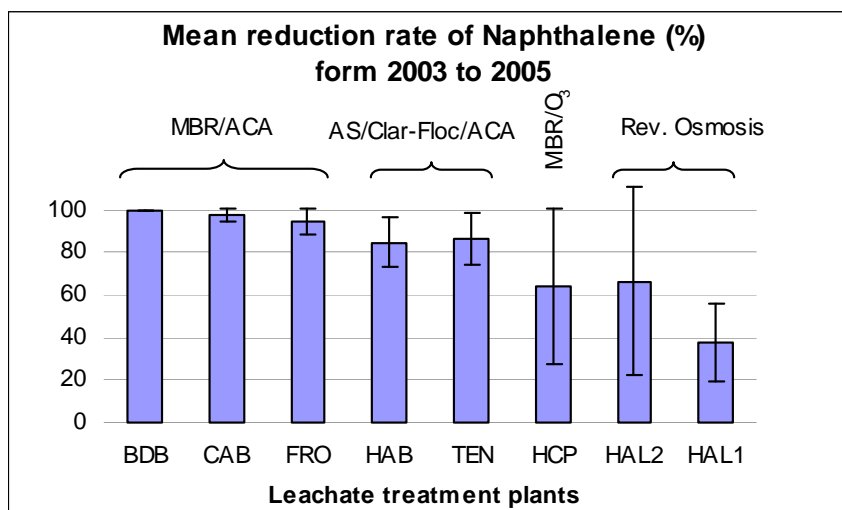


Figure 4 : Mean reduction rate of naphthalene for leachate treatment plants.

4.3.4 Results and discussion of anthracene reduction rate in the treatment plants

All plant types except the fourth present good reduction rate of anthracene, higher than 96 %, with a low variability. The fourth plant type, running the reverse osmosis, has intermediate reduction rate of anthracene with a high dispersion: 82 % and 83 % for respectively Hallembaye-1 and Hallembaye-2.

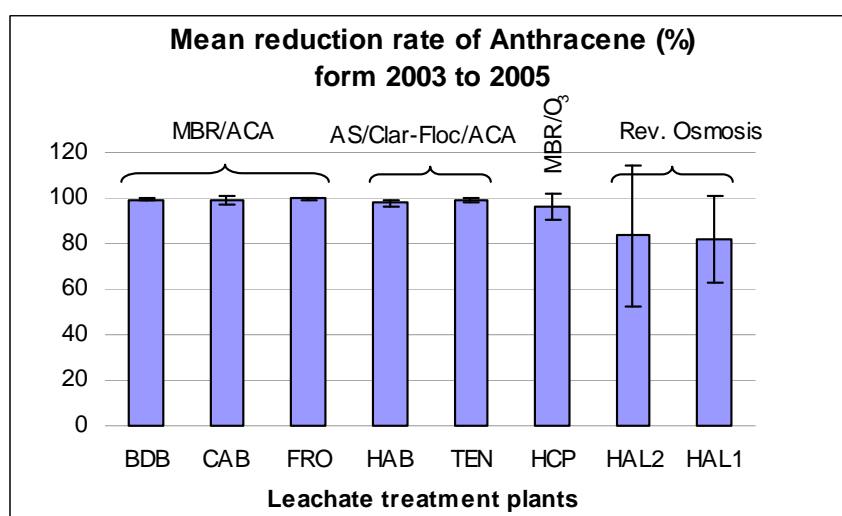


Figure 5 : Mean reduction rate of anthracene for leachate treatment plants.

4.4 PAHs concentration in Permeate

Here is the 10th Article of the Directive : “the Member States shall ensure that all discharges ... into surface waters are controlled” and, for hazardous substances that, “the Member States ensure the establishment and/or implementation of the relevant emission limit values”. In Belgium, the maximum limit values for PAHs emission are : 100 ng/l for the 6-Borneff PAHs, 1000 ng/l for naphthalene and 100 ng/l for anthracene. We can compare the PAHs concentration of the permeates with these limit values.

4.4.1 Naphthalene concentration in permeate

The fourth plant type, running the reverse osmosis process, has the worse results, with a high dispersion. The mean naphthalene concentration for Hallembaye-1 is nearly three times as higher than the limit value (1000 ng/l), while the mean concentration Hallembaye-2 is high without exceeding the limit value. The other processes have very low naphthalene concentration (< 100 ng/l).

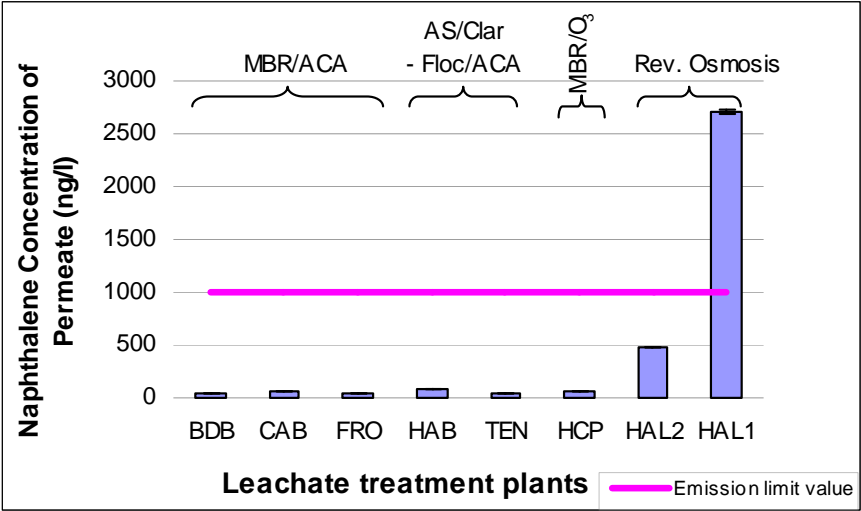


Figure 6 : Mean naphthalene concentration of permeate from leachate treatment plants.

4.4.2 Anthracene concentration in permeate

These results are more satisfying. The mean anthracene concentration of permeate are clearly below the limit value at 100 ng/l for all plants (from 8 to 100 times as lower) as shown on figure 7.

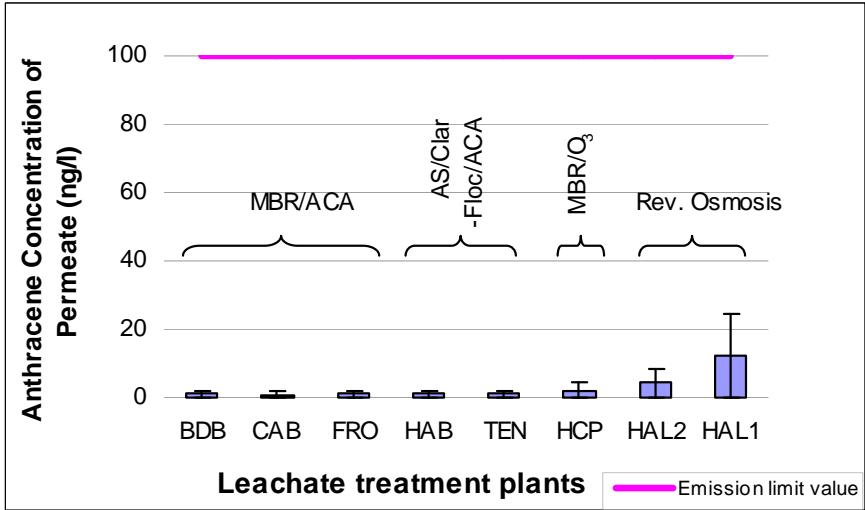


Figure 7 : Mean anthracene concentration of permeate from leachate treatment plants.

4.4.3 6-Borneff PAHs concentration in permeate

For the first and the second plant types, the mean 6-Borneff PAHs concentrations in permeate are very low and generally closed to the quantification limit value at 19 ng/l. For the third plant type (ozone oxidation), the concentration is 56 ng/l for Happe-Chapois and remains exceptional. For the fourth plant type (reverse osmosis), concentrations are respectively 37 and 52 ng/l for Hallembaye-1 and 2. Meanwhile, these results remain below the limit value at 100 ng/l. A very high dispersion is observed for measures from Hallembaye-2 and Happe-Chapois.

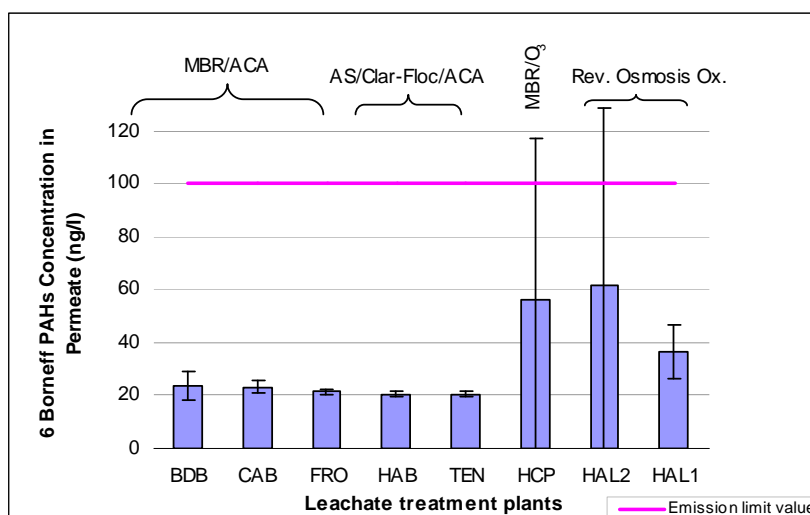


Figure 8 : Mean 6-Borneff PAHs concentration of permeate from Leachate treatment plants.

5. CONCLUSIONS

At the end of this study, we can draw the following conclusions.

The PAHs concentration of leachate from the studied sites is low and variable. In fact, values of the various PAHs components are generally lower than the range described by Andréotola (1997).

The reduction rate of PAHs in the leachate treatment plants is generally high. Indeed, the reduction ratio for the 15 PAHs shows that two leachate treatment plants of the same process (reverse osmosis) reach reduction rates lower than 80 %. The leachate treatment plants, composed of membrane bioreactor process and completion with activated carbon absorption (MBR/ACA), give the best results : the reduction rate is higher than 98 %, by variable according to the considered substances. It was observed that the reduction of naphthalene, more than the other substances, is the most difficult and involves the lowest reduction ratios of naphthalene. This can be explained by the short size of this molecule, the smallest among analyzed PAHs, containing only two aromatic cycles.

The residual PAHs concentration of the permeates shows that, as much for the 6-Borneff PAHs as for the anthracene and the naphthalene, which are the group of substances and the substances that have emission limit values, their concentration are really below the emission limit values applied for three leachate treatment plant types. For the fourth, provided with reverse osmosis unit process, it has values beyond the emission limit value for naphthalene. This can be due to a high threshold of cut of the membrane.

Thus, in conclusion, we can say in the view of this study that the results completely fulfill the quality requirements of DIRECTIVE 2000/60/EC of the European Parliament and Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Finally, this Directive does not imply any heavy changes and investments for leachate treatment plants management in Wallonia.

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