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Efficiency Assessment of Wastewater Treatment Plant Based on SPMD Sampling

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Abstract: The efficiency of treatment processes forboth municipal and industrial wastewater (treatment plant -Ostrava, Czech Republic) focused on persistent organic pollutants (POPs) was assessed. Semipermeable membrane devices (SPMDs) as a sampling system were applied. Exposed SPMDs were analyzed both for chemical contaminants of POPs and toxicity response. The chemical analyses of PAHs were made by HPLC-FLD, PCDD/Fs and PCBs were analysed by GC/MS/MS on GCQ or PolarisQ (Thermoquest). Ecotoxicity data on chlorococcal alga *Desmodesmus subspicatus (Scenedesmus subspicatus)* and luminescent bacteria *Vibrio fischeri* are presented here. All toxicity data as effective volume Vtox are expressed. The results show good treatment ability of the treatment plant and proved used system as an appropriate tool for efficiency assessment of treatment and/or decontamination processes.

Keywords: Sewage treatment process; Persistent organic pollutants; Bioluminescence inhibition; Algal bioassay, Vtox

1 Introduction

Direct discharge from industrial and municipal wastewater treatment plants into streams has become a growing environmental problem. Most of these wastewaters are complex mixtures containing a lot of inorganic and organic compounds (Fu et al. [3]). Their

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complexity precludes the identification of their potential environmental impact through chemical analyses alone. The best way of approaching the question of risk assessment has been to develop biological test systems which, combined with the chemical analysis, can be useful to evaluate aquatic assessment and to establish relevant water quality criteria (Ciccotelli et al. [1]).

Toxicity is a biological response and thus needs to be taken into account in formulating realistic guidelines on acceptable upper limits on various contaminations of wastewater discharges to the environment [2]. Wastewater treatment plant (WWTP) effluents represent important point sources of organic pollution of residual toxicity in cases of insufficient treatment efficiency. Well operating plants without the nutrient removal can be point sources of the toxicity or eutrophication of receiving streams, dangerous particularly for sensitive areas. Impacts of WWTP effluents on the river water quality can be detected by means of bio monitoring, including preliminary visual field observation, microscopic evaluation of periphyton samples and by the application of selected laboratory and on-site experimental bioassays (Sládeček et al. [18]). Toxicity tests can serve as a good tool for WWTP management. Seasonal shocks caused by toxic substances affect effectiveness of the treatment process (Grau et Da-Rin [5]; Kosmala et al. [13]; Sweet et al. [19]).

Surface waters are used for disposal of industrial and municipal effluents and while regulationslimit effluent concentrations of contaminants to protect rivers and their biota, only low concentrations of various contaminants are usually found in treated effluents but they have often been accumulated over time in sediments. Sediment quality investigations are necessary beside water quality determination for assessment of harmful impacts of discharges on the river (Zagorc et Cotman [20]).

Impacts of WWTP effluents on the river water quality can be detected by means of analytical monitoring and bio-monitoring, including preliminary visual field observation, microscopic evaluation of periphyton samples and by the application of selected laboratory and field experimental bioassays.

Bioassays aimed at the detection of residual toxicity, important from the ecological and hygienic points of view, should be introduced primarily for the testing of industrial WWTP effluents where the presence of toxic substances may be expected.

Many long-term monitoring studies used some aquatic organism to concentrate trace and ultra trace concentrations of persistent organic contaminants in waters in their fatty tissues (bioconcentration). Despite their worldwide use , all of the organism-based samplers exhibit many limitations due to lack of proportionality between concentration in their tissue and exposure concentration.

The organism sampler limitations are influenced by physical stressors. Discussed organisms work as a “contaminant sieve”- accumulated residues are subjected to metabolization or actively depurated. Next, residues accumulated in organisms reflect both dissolved phase of contaminants in environment and in diet. Organisms also cannot fulfill requirements (to be used as suitable method for active water-management) for identification of contaminant sources based on differences in monitoring profiles by both fingerprints and contamination levels.

2 Materials and methods

2.1 Semipermeable membrane devices

Assessment of environmental pollutants exposure, particularly persistent organic compounds (POPs), is closely connected with applications of an in-situ passive sampling approach. Passive dosimeters are mostly applied to monitor water environment. Presence of POPs and heavy metals in waters reflects serious risk to consequent transport to food chain through biota.

Passive sampling technology presents numerous advantages over standard sampling methods: record low levels of contamination (followed by expensive pre-concentration of large volumes of water and analytical technique needed for acceptable detection limits), accidental concentration variation of pollutants, limitations in determination truly-dissolved (bio available) phase - all resulting to high sampling and analytical cost.

One of possibilities is semi-permeable membrane device, SPMD (Huckins et al. [6], [7]; Pety et al. [15]). SPMD is a membrane filled with triolein, substance in properties similar to fish fats. Various persistent organic pollutants are collected in triolein (Huckins et al. [6]; Prest et al. [16]). After exposition triolein is dialyzed and the final dialysate is analyzed then. Various organic solvents are used for preparation of dialysate. Choice of solvent used for preparation of SPMD extract is very important for toxicity analysis, consequently for the choice of exposed organism. SPMD membranes proved to be highly effective dosimeter of hydrophobic, lipophilic organic contaminants in water of very low concentration due to their bioaccumulation ability (Rantalainen et al. [17]).

A passive sampling method represents the measurement of an analyte concentration as a weighted function of the sampling time. The exposure is being considered as integral contaminant response within particular sampling period. SPMD sampling tool is designed for long-term monitoring of lipophilic, hydrophobic contaminants in aquatic and air environment. It has been viewed as a bridge between analytical chemistry and biomonitoring methods. It is based on bioconcentration phenomenon.

Standard SPMD consist of lay-flat thin-walled nonporous tube with transient pores approximately 10^{-9}m, manufactured from low-density polyethylene (LDPE) filled inside by 1 ml of synthetic lipid – triolein (1,2,3-tri-[cis-9-octacenoyl]glycerol) of high purity. General dimension of the standard SPMD is: width 2.5 cm (lay-flat), overall length 91 cm, and thickness approx. 75 μm.

2.2 SPMD sampling

Tested samples were obtained from different places of a wastewater treatment plant (Ostrava, Czech Republic). The presumption was that some substances on inlet could influence the effluent toxicity. Capacity of this particular treatment plant is approximately 184 300 m^3/day with load equal to 638.850 equivalent inhabitants. The inputs to the WWTP are of two kinds: sewage water from the big industrial city and wastewater

from coking plants. Both of these inputs consist of two different inlets. One municipal inlet represents only sewage water, the second one represents joint sewage and industrial wastewater. Two inlets from coking plants are from different sources: "Svoboda" and "Sverma" coking plant. It was important to monitor the WWTP in different places through a course of treatment. Monitored profiles, see Figure 1, were selected according to the experience and predicted parameter changes with key contribution to quality of produced sewage sludge. These places were chosen: municipal sewage inlet, municipal and industrial wastewater inlet, inlet from coking plant Svoboda, inlet from coking plant Sverma, activation, sludge and sludge centrifugate and effluent from WWTP into recipient – Cerny creek. Detailed description of condition during sampling is summarized in Table 1. Figure 1 is to give an overview of WWTP.

SPMD sampling was performed according to recommended good SPMD practice: immersed in hexane to remove monomers and others impurities for 24 hours, then placed in clean airtight steel cans and transported to sampling places with transport-trip and field blanks. On the sampling point were SPMDs placed in a perforated stainless steel container to protect the membranes against mechanical damage and to restrict water flow velocity at the membrane. Numbers of exposed SPMDs per one site were given to tested parameters and QA/QC aspect; in this research were used 5 membranes per a site. With the SPMDs set deployed another SPMDs were exposed to ambient air during the deployment (trip/field blanks) at the sampling places to monitor possible contamination from the air. Each container equipped with a temperature logger (Tiny-Loggers, Intab, Stenkullen, Sweden) which registered water temperature every 15 minutes.

After being sampled, each sampler was rinsed by drinking water; the SPMDs were placed in a clean airtight steel can. Periphyton, minerals and rough particulates were then removed from membrane surface with clean cloth and then rinsed by clean water. Exposed membranes were preserved frozen at –18^{o}C until analyzed.

2.3 Chemical analysis

Following these chemical parameters was monitored: 17 of WHO recommended (WHO I-TEF [9]) polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs); all detectable tri-deca polychloriated biphenyls (PCBs) and 12 of 16 US EPA monitored polyaromatic hydrocarbons (PAHs): phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluorantene, benzo[k]fluorantene, benzo[a]pyrene, benzo[g,h,i]perylene, dibenzo[a,h]anthracene, indeno[1,2,3,-c,d]pyrene.

Exposed SPMDs were dialyzed with hexane (suprapure quality, MERCK) for 3 days including 2 solvents exchange resulting 200 ml fraction. After dialysis the ^{13}C-labelled isotopic internal standards (PCDD/Fs, PCBs – Wellington laboratories) or deuteriated (PAHs) were added to the extract and analyzed with accordance of laboratory available (accredited) methods. Solvent of aliquot for determination of PAHs was changed to methanol and analysed by HPLC-FLD. PCDD/Fs and PCBs were analyzed by GC/MS/MS on GCQ or PolarisQ (Thermoquest). Clean-up method and optimisation of MS/MS de-

tection are described in (Grabic et al 2000 [4]). Multiortho PCBs were analyzed in 2% DCM in hexane fraction from Al_2O_3 column. Nonortho PCBs and PCDD/Fs were analyzed in 50% DCM in hexane fraction from same column after clean up on activated carbon column.

All results from analysis were evaluated as concentration per SPMD. Then evaluation was performed from knowledge uptake rates for particular condition (temperature) and compound.

This calculation was performed according equation 1, derived from the complex equation describing uptake kinetics (Huckins et al. [6], [7]).

$$C_W = \frac{C_{SPMD} \cdot V_{SPMD}}{R_S \cdot t} \tag{1}$$

C_W is ambient truly dissolved contaminant concentration in water, C_{SPMD} is concentration in SPMD, V_{SPMD} is overall volume of the SPMD, R_S effective sampling rate, t is time of exposure (sampling time). The effective sampling rates (R_S) were used according to Kathleen and Gale [11].

For bioassays testing dialysates were transferred into acetone-DMSO (1:1) mixture [10]. This offers good solubility and low background toxicity. By this way prepared samples were used for grounding of dilution series for bioassays next.

2.4 Bioluminescence test

Tests with bioluminescent bacterium were carried out following the standard procedures (ISO 11348). The samples were tested in a medium containing 2% of NaCl and about 10^7 cells of bacteria reconstituted from the lyophilized reagent (Bruno Lange, *Vibrio fischeri* NRLL-B-11177). Control samples (i.e., bacterial suspensions to which 2% NaCl was added instead of a test samples) were always run parallel to the test sample. Tests were performed at 15°C, pH of all dissolved samples in this study was 5-8, it was not adjusted. Each test was run in duplicate 6 to 10 sample concentration and a negative control. The luminescence was measured with the LMZ II tube luminometer (Immunotech, A Beckman Coulter Company) at 5-, 15- and 30- min exposure times. The concentration of the original SPMD triolein (mg/L/day), which caused a 50% reduction in light production after exposure for 5 (or 15) minutes, was designated as the 5 (15) – min EC50. This value was used for determination of Vtox then. Potassium dichromate ($K_2Cr_2O_7$) was used as a reference toxicant, corresponded with the ISO 11348 guideline the EC50 (30min) the inhibition caused 4 mg/l of dichromate was within recommended range specified in the test guideline.

2.5 Algal bioassay

The experiments utilized *Desmodesmus subspicatus (Scenedesmus subspicatus),* strain Brinkmann 1953/SAG 86.81 (obtained from Culture Collection of Autotrophic Organisms, Institute of Botany, Czech Acad. Sci., Trebon). The alga was kept and cultivated

in suspension condition and medium recommended in ISO 8692 guideline. Due to a small amount of SPMD dialysate 50ml Erlenmeyer flasks with 25ml of suspension were used. Monospecific algal cells were cultured for several generations in a defined medium containing a range of concentrations of the tested SPMD dialysate, prepared by mixing appropriate quantities of nutrient concentrate, demineralizated water and an inoculum of exponentially growing algal cells. 10^4 cells per millilitre as initial cell density were used. The test solutions were incubated for a period of 96 hours, at a light intensity of $60\mu\mathrm{E}\cdot\mathrm{m}^{-2}\cdot\mathrm{s}^{-1}$, fluorescent tubes-day, and temperature 23^oC, cell density in each suspension was measured every 24 hours, counting chamber was used to measure the cell density. Inhibition was measured as a reduction in growth and growth rate, relative to control cultures grown under identical conditions (Lukavský [14]). The results, values of 72hEC50, were counted for inhibition of algal growth rates.

2.6 Vtox

The parameter *Vtox* allows comparing toxicity of samples obtained from SPMDs with different duration of its exposition, different sites, projects and laboratories. *Vtox* represents a volume of media which is theoretically needed for dilution of all toxicants absorbed in one membrane during one average day of deployment to obtain solution with chosen effective concentration, for example EC50 (Kočí et al [12]). The higher *Vtox* is the bigger volume of toxicants was absorbed and thus the higher contamination of sampled site is. Following formula define *Vtox*, where (m) is concentration of extracted membranes in solvent mixture expressed as number of membranes in ml of solvent mixture ($\mathrm{pcs.ml}^{-1}$), (d) is duration of deployment of membrane during a sampling (days) and ECXX is an effective concentration of extract on chosen organism, for example EC50 ($\mathrm{ml.L}^{-1}$).

$$Vtox(50) = \frac{1}{m \cdot EC50 \cdot d} \qquad (L \cdot d^{-1}) \tag{2}$$

Similarly like toxicological unit TU, one of the benefits of *Vtox* is its property of easy demonstration of contamination level – the higher *Vtox* the higher ambient contamination.

3 Results and discussion

Bioassays are important tools for monitoring the quality of surface and ground water. They can allow simple and sensitive measurement of the biological acceptability of water quality, and test results can identify suspicious localities, which require more detailed and more expensive analysis. Enormous quantities of inorganic and organic compounds, in waters, and their synergistic effects complicate the forecasting of biological effects from chemical analysis alone.

3.1 Chemical analysis

All 88 detectable PCB congeners, 12 of 16 US EPA monitored PAHs and 17 WHO recommended PCDD/Fs identified in SPMD samples from WWTP at each deployment site are summarized in Tables 2, 3 and 4. From observed water concentrations and flow rates were calculated efficiencies of individual contaminants from the wastewaters during the treatment process. A total quantity of pollutants in inlet into WWTPwas comp-ared with the effluent. Concentrations of all the compounds are presented as water concentrations, not concentrations in the triolein.

The major pollutants in all monitored sites were PAHs. The concentration (μg/L) was three orders greater than concentration of PCBs (ng/L) and even six orders greater than overall concentration of PCDD/Fs (pg/L). Main sources of PAHs were inlets from both coking plants (299 and 399 μg/L in inlet from Sverma and Svoboda respectively), the concentrations were two orders higher than those in sample from "sewage wastewater", sample from sewage and industrial wastewaters" and in sample "effluent from WWTP" as well (Figure 2). In spite of such high concentrations in the inlet into WWTP, i during the treatment process from 90 to 99 % of all detectable PAHs (excluding fluoranthene and pyrene with the efficiency 58.9 and 86.4 % respectively)were removed.. However, PAHs were most likely only removed from the water, not biodegradeted and lately deposited in waste sludge. Analysis of stabilized sludge confirmed absorption of high amount of PAHs (67.8 mg/kg dw) on sludge particles without any change.

Concentrations of individual PCDD/Fs in most of the profiles were under determination limits and therefore it was not possible to determine elimination of individual contaminants, but only for the sum of whole group. The major pollutant from group of PCDD/Fs were OCDDs. Its concentration represented 68-88 % of overall concentration of PCDDs and 60-80 % of overall concentration of PCDD/Fs, depending on sampling site.

Contrary to PAHs, PCDD/Fs were found mainly in sewage wastewaters and sewage and industrial wastewaters. The PCDD/Fs contamination of wastewaters from coking plants was very low or even not determinable (PCDDs in wastewaters from coking plant Sverma). Only 4 PCDFs above determination limit and no PCDDs appeared in outlet from WWTP. The overall concentration of PCDD/Fs in outlet was 0.69 pg/L. It is only 2 % of total inlet into the WWTP, 98 % was removed. Also here was the major part of pollutants adsorbed on the sludge and not biodegraded. The sum concentration of PCDDs and PCDFs in the sludge was 1110 ng/kg and 648 ng/kg dw respectively.

Concentrations of all 88 detectable PCB congeners are summarized in 1 and the concentrations of PCBs with the equal number of chlorine substituents are added up at the end of the table. The main source of PCBs was inlet consisting of sewage + industrial wastewater (70 ng/L), the major part of all PCBs represented hexaCB, heptaCB and partially pentaCB. The second most contaminated input was the sewage wastewater (7.6 ng/L) . The less polluted were wastewaters from coking plants Sverma and Svoboda containing 1.8 ng/L and 0.84 ng/L respectively. These concentrations were even lower

than in the outlet from WWTP (3.4 ng/L). Otherwise, the efficiency of treatment process was quite high, 85 % of total PCBs. The efficiency of WWTP varied for PCBs with different number of chlorine substituents. The higher number of substituents, the higher the elimination efficiency. OktaCB and heptaCB were removed approximately from 97 % but triCB and tetraCB from 43.8 and 32.4 % respectively, pentaCB were eliminated from 84.4 %. This effect can be explained by a dechloration of polychlorinated molecules. Some of chlorine atoms were cleaved away and consequently the concentration of less chlorinated molecules increased. It could even enhance above the initial one, what is in the final evaluation of the treatment efficiency demonstrated by negative values (see 1).

Concentration of PCBs in the sludge differed with different number of substituents too. The lower thenumber of chlorine atoms bonded to the molecule, the higher the concentration in the sludge (excluding pentaCB). This can be explained by dechloration of polychlorinated molecules during the treatment process that caused an increase of the concentration in the water and consequent adsorption on the sludge (2.66 mg/kg dw).

SPMD monitoring of inlets and outlet confirmed good treatment efficiency of the WWTP. However, high amount of classified pollutants was adsorbed on the activated sludge and not biodegradated. Therefore it is important to devote great attention to the waste management. SPMD passive sampling is an effective tool for monitoring of POPs especially for determination of very low levels of contamination.

3.2 Bioassays

Toxicity of POPs contaminated effluents depends on the amounts and types of the individual compounds present; however, even for pure compounds, concentration-toxicity relationships are generally nonlinear. Mixtures of compounds pose bigger problems because toxicity of a mixture is not easily linked to individual toxicities of components in the mixture. Thus, for predicting the impact of a wastewater stream on the ecology of a receiving surface water body, the toxicity of contaminated water needs to be determined.

A main addition of toxicity to alga and bacterium was caused by PAHs. The basic reason was in their dominant concentration, more than 98% of overall POPs concentration in all tested samples. This is especially evident in samples from coking plants, where these substances dominated in more than 99.999%. The contribution to overall toxicity of samples caused by PCDD/Fs and PCBs in pg/L or ng/L respectively seems to be important, too. This is to be seen, in comparison of toxic response of sample “sewage and industrial wastewater” to “sewage wastewater” and “effluent form WWTP”, where the concentration of PAHs is by order similar. The increase of toxic response in this sample is apparently caused by higher level of PCDD/Fs and PCBs concentration. We do not compare these values to results obtained from “water after sludge centrifugation” sample, because the character of this sampling point was very different and presence of other non-analysed toxic pollutants is expected here. The SPMD method together with algal bioassay seams to be effective for monitoring even such trace concentration of organic pollutants like pg/L for PCDD/F or ng/L for PCBs.

The SPMDs method proved to be suitable for purposes of monitoring, bringing high effectiveness with combination qualitative/quantitative profile monitoring, and toxicity testing as well. All mentioned advantages are results of long-term continual, integral sampling. This method has not shown any limitation for application remarkable contaminated samples. This method seems to be effective for sludge management of WWTP where strong POPs contamination can involve the quality of produced sewage sludge. Results confirmed presumption that the input of POPs influences the final environmental properties of treated water.

Although the efficiency of WWTP determined by chemical parameters was higher than 90%, higher level of decrease of total toxicity in the end of wastewater treatment process was expected because the level of PAHs in effluent was low. The presence of toxic metabolites of biological degradation was confirmed primary by toxicity assessment and consequently by chemical analysis. Both bioassays demonstrated their usefulness for determination of the level of contamination of evaluated samples. The toxicity reduction evaluation (TRE) must be carried out at wastewater treatment plants whose effluents fail toxicity standards. The TREs require numerous and repeated toxicity assays, thus favoring application of microbioassays. Presently, no single microbioassay can detect all categories of environmental toxicants with equal sensitivity. Therefore, a battery of tests approach is recommended. The differential sensitivity of alternative tests may, in fact, be exploited. Further research is needed to construct strains of genetically engineered microorganisms or isolate microorganisms or enzymes that respond to specific classes of toxicants. These can be combined into batteries appropriate for different environments or test objectives included evaluation of SPMD membranes.

Resulted data demonstrate extremely high sensitivity of algae as a test organism for evaluation of SPMD dialysates. Algal cultures were able to meaningfuly rank heavy and low contaminated sites. That means that SPMD method of passive sampling is a very good tool for assessment of water environment especially from the aspect of monitoring substances inhibiting aquatic species.

Algal and bacterial bioassays are very sensitive to microbial contamination. The dialysates from SPMD membranes are of course after extraction and dialysis sterile and simultaneously represent, thanks to defined procedure, conditions during environmental sampling. For this reasons the use of sterile SPMD dialysates for toxicity analysis of POP with algal tests seems to be good solution. There was examined that previously in introduction mentioned disadvantages of associated with the use of alga organisms for assessment of environmental samples is not limiting factors for SPMDs use. SPMDs can rank even such samples, where alga cannot survive. This fact can be useful for prevention of environmental hazards.

4 Conclusion

Screening of wastewater with SPMD dialysates, where bioassays can serve as a first and inexpensive step and chemical analysis as detailed evaluation of the very situation, may

be a powerful tool for wastewater management. Additional advantage of SPMD method is the possibility of long-time storage of exposed samples/dialysates for additional evaluation at a later time.

Cleaning efficiency of WWTP was proved by the decrease of POPs concentration on effluent compare to all inputs. Low concentrations of POPs in effluent but high concentrations in stabilized sludge show that main way of elimination is not biodegradation caused by activated sludge of secondary treatment step of WWTP, but adsorbtion on its particles (glycogalyx). High amount of toxic substances in stabilized sludge was proved by toxicity bioassays. All used bioassays exhibit strong response to effluent from sludge centrifugation.

The SPMDs method proved to be suitable for purposes of monitoring, bringing high effectiveness with combination qualitative/quantitative profile monitoring, and toxicity testing as well. All mentioned advantages are results of long-term continual, integral sampling. This method has not shown any limitation for application remarkable contaminated samples. This method seems to be effective for sludge management of WWTP where strong POPs contamination can involve the quality of produced sewage sludge. Results confirmed presumption that the input of POPs influences the final environmental properties of treated water.

The Vtox parameter of SPMD biological evaluation combined with chemical analyses proved to be a valuable monitoring tool for persistent organic pollutants in aqueous conditions and sampling profiles.

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Abbreviations

POP	– persistent organic pollutants
SPMD	– semi-permeable membrane device
EC50	– concentration of toxic substance causing 50% positive effect
PCB	– polychlorinated biphenyls
LDPE	– low-density polyethylene
WWTP	– wastewater treatment plant
WHO	– World Health Organisation
PCDD/Fs	– polychlorinated dibenzo-p-dioxins/furan
PAH	– polyaromatic hydrocarbons
HPLC	– high performance liquid chromatography
Vtox	– toxic volume causing choosed positive effect

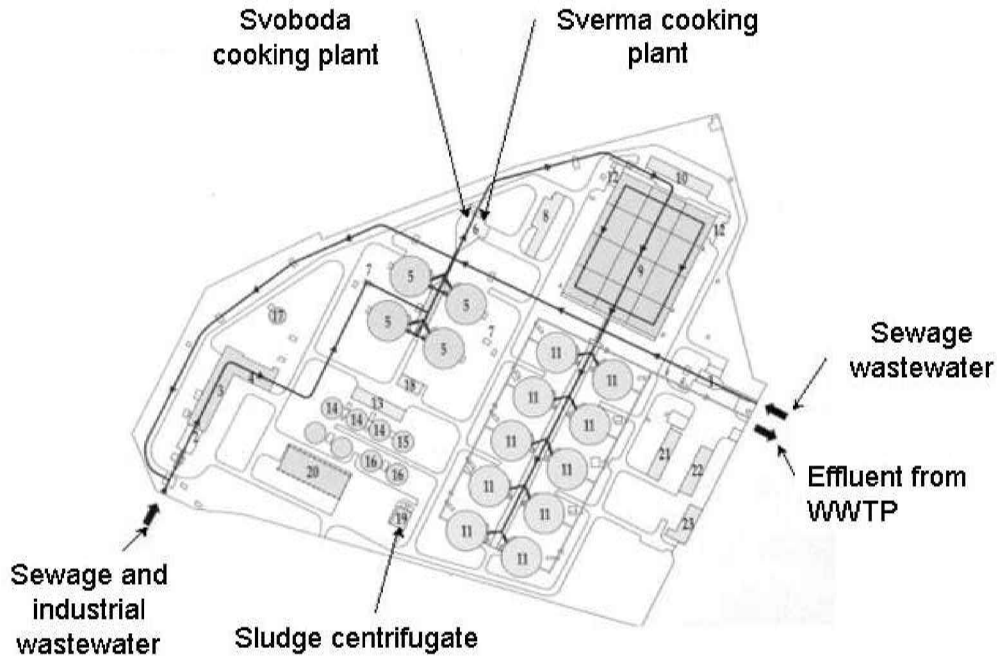

Fig. 1 Scheme of WWTP Ostrava.

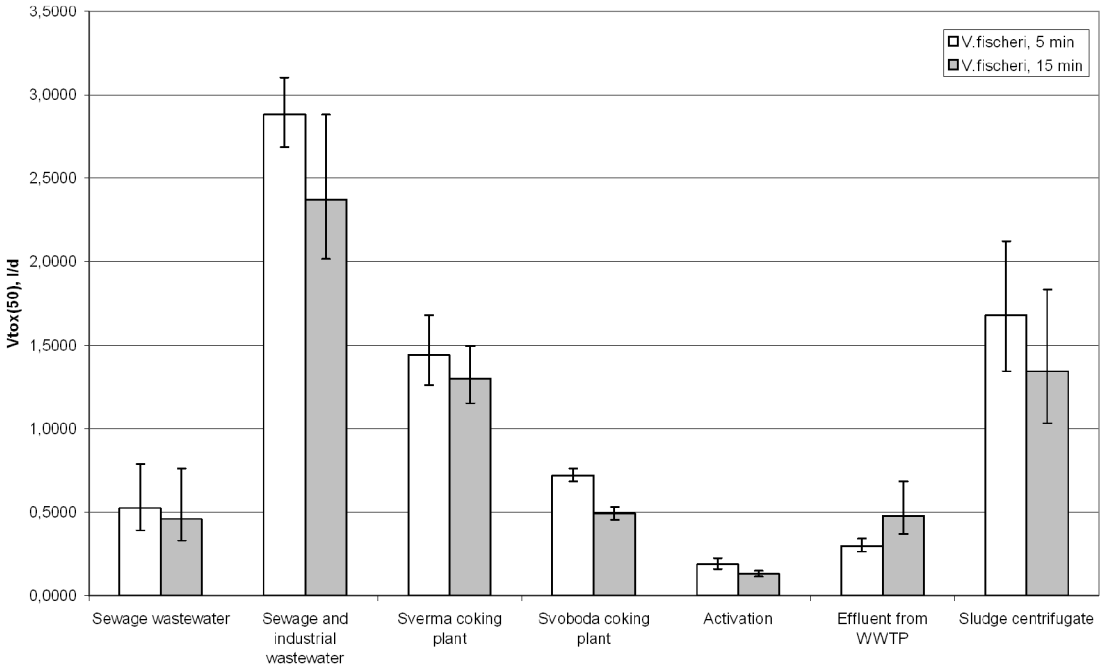

Fig. 2 Toxicity of SPMD samples from monitored profiles in WWTP to Vibrio fischeri.

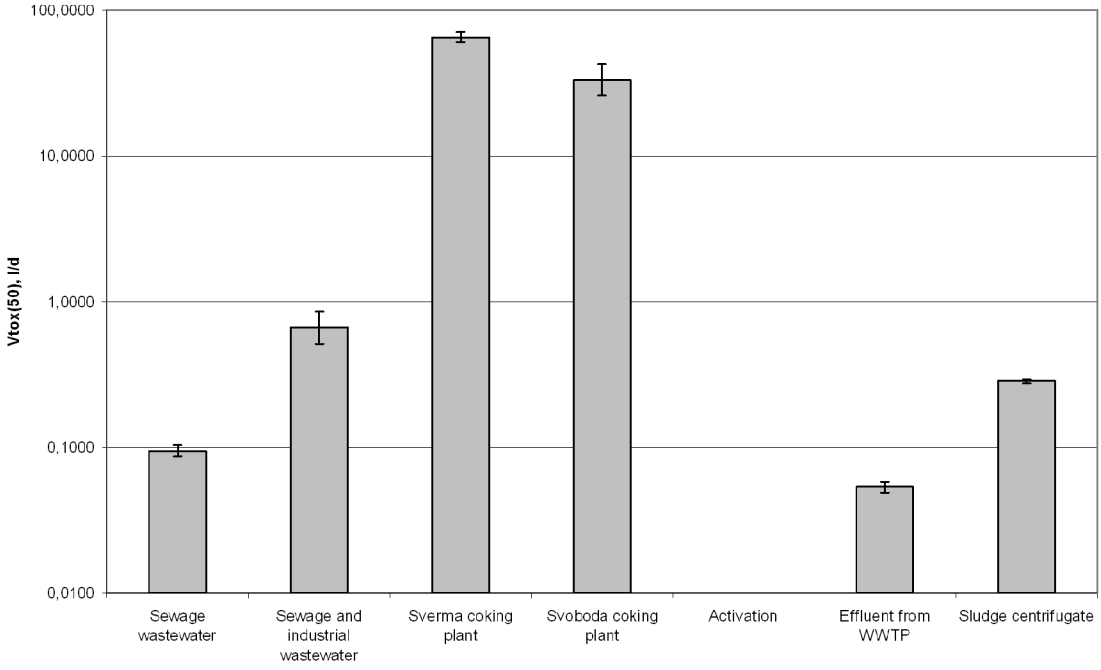

Fig. 3 Toxicity of SPMD samples from monitored profiles in WWTP to Desmodesmus subspicatus.

	Sewage wastewater	Sewage and Industrial	Coking plant Sverma	Coking plant Svoboda	Effluent from WWTP	Activation	Sludge centrifugate
Flow rate [a] [m^3/day]	74468	22026	926	757	98176	98176	94400
Temperature [C]	16.4	16.8	39.9	33.4	16.9	17.0	16.8
Duration [days]	31	31	31	31	31	31	31

Table 1 Primary parameters of SPMD sampling.

	Sewage wastewater	Sewage and industrial wastewater	Sverma coking plant	Svoboda coking plant	Activation	Effluent from WWTP	Sludge centrifugate	Elimination [%]
Phenanthrene	2.9	1.8	117	73.0	0.17	0.044	1.5	99.0
Anthracene	0.44	0.21	12.1	21.6	0.025	0.010	0.10	98.5
Fluoranthene	0.84	0.67	35.4	128	1.2	0.90	0.36	58.9
Pyrene	0.42	0.50	14.1	82.6	0.25	0.17	0.17	86.4
Benzo[a]anthracene	0.11	0.22	31.3	39.3	0.075	0.036	0.062	95.3
Chrysene	0.077	0.20	20.8	27.8	0.028	0.019	0.051	96.4
Benzo[b]fluorantene	0.053	0.13	23.4	10.6	0.074	0.030	0.040	92.2
Benzo[k]fluorantene	0.024	0.059	10.2	4.3	0.034	0.014	0.018	91.6
Benzo[a]pyrene	0.040	0.13	19.5	7.6	0.055	0.021	0.035	93.3
Benzo[g,h,i]perylene	0.019	0.12	6.3	1.8	0.018	0.007	0.012	94.1
Dibenzo[a,h]anthracene	0.004	0.020	3.3	0.91	0.003	0.001	0.003	97.9
Indeno[1,2,3,-c,d]pyrene	0.018	0.079	5.8	1.8	0.010	0.006	0.009	94.2
Sum of PAH	4.9	4.1	299	399	1.9	1.3	2.4	89

Table 2 Estimated water concentrations of PAHs in different processes in the WWTP (pg/L).

	Sewage wastewater	Sewage and industrial wastewater	Sverma coking plant	Svoboda coking plant	Activation	Effluent from WWTP	Sludge centrifugate	Elimination [%]
2378TCDD	< 0.016	< 0.012	< 0.044	< 0.016	< 0.018	< 0.018	< 0.014	ND[a]
12378PeCDD	< 0.026	0.053	< 0.078	< 0.026	< 0.025	< 0.026	0.022	ND
123478HxCDD	< 0.13	< 0.18	< 0.61	< 0.13	< 0.11	< 0.11	0.11	ND
123678HxCDD	0.148	0.18	< 2.3	< 0.12	< 0.093	< 0.11	0.22	ND
123789HxCDD	< 0.16	0.36	< 0.21	< 0.14	< 0.10	< 0.12	0.13	ND
1234678HpCDD	0.782	1.4	< 0.73	< 0.16	< 0.11	< 0.097	0.26	ND
OCDD	11.0	72.0	< 1.7	1.5	18.4	< 0.72	3.1	ND
2378TCDF	0.076	0.19	< 0.028	0.009	0.086	0.036	0.050	ND
12378PeCDF	0.028	0.056	< 0.028	0.008	0.034	0.007	0.030	ND
23478PeCDF	0.064	0.27	0.047	0.016	0.050	< 0.006	0.034	>94.7
123478HxCDF	0.045	0.18	< 0.082	0.015	0.017	0.017	0.040	ND
123678HxCDF	0.033	0.13	< 0.078	< 0.014	0.022	< 0.014	0.026	ND
234678HxCDF	0.056	0.041	< 0.13	< 0.018	< 0.015	< 0.016	< 0.012	ND
123789HxCDF	< 0.035	0.031	< 0.13	< 0.026	< 0.017	< 0.024	0.034	ND
1234678HpCDF	0.22	0.55	< 0.24	0.065	0.16	0.042	0.099	ND
1234789HpCDF	< 0.023	0.025	< 0.11	< 0.024	< 0.013	< 0.014	0.040	ND
OCDF	< 0.097	< 0.10	< 0.34	< 0.093	< 0.15	< 0.11	0.32	ND
Sum of PCDD	15.9	98.4	ND	2.18	20.8	ND	3.56	ND
Sum of PCDF	2.4	6.9	0.610	0.35	1.97	0.688	1.47	77.9

[a] - Not determined.

Table 3 Estimated water concentrations of PCDD/Fs at different sampling points of the WWTP (pg/L).

	Sewage wastewater	Sewage and industrial wastewater	Sverma coking plant	Svoboda coking plant	Activation	Effluent from WWTP	Sludge centrifugate	Elimination [%]
PCB16+32	124	472	62.8	6.2	255	106	123	49.2
PCB17	129	499	60.0	6.6	201	77.0	104	64.8
PCB18	316	1300	128	14.1	683	296	261	46.6
PCB19	61.5	272	14.6	1.5	155	< 0.6	59.4	>99.5
PCB22	22.6	117	38.0	9.1	154	57.6	94.5	-26.4
PCB24+27	9.0	17.9	3.9	0.5	23.8	9.9	7.4	12.5
PCB25+26	92.3	395	73.4	5.5	186	69.5	66.7	58.1
PCB28+31	562	1170	431	41.1	1440	577	514	20.0
PCB33	173	139	138	10.5	131	50.7	143	70.2
PCB37	0.9	23.4	0.2	< 0.2	2.8	< 0.8	< 0.1	ND[a]
PCB41+64+71+72	74.0	108	32.8	6.8	193	84.0	56.0	-0.1
PCB42	43.7	111	22.5	3.2	110	40.1	32.2	33.8
PCB44	99.4	294	45.6	7.3	227	101	72.7	31.5
PCB45	25.8	79.8	16.1	1.9	71.0	27.8	21.1	29.0
PCB46	17.2	60.7	10.3	1.6	50.7	20.3	16.1	27.1
PCB47+48	86.6	328	54.9	16.9	216	81.5	58.1	44.0
PCB49	108	387	62.7	8.0	268	123	68.8	30.2
PCB51	33.2	116	23.6	2.9	96.1	39.9	25.7	25.4
PCB52	139	635	67.1	16.0	334	124	89.5	52.0
PCB53	10.4	34.2	9.5	3.0	28.8	12.2	8.8	25.2
PCB54	1.0	2.8	1.0	< 0.3	1.5	< 2.3	0.4	ND

[a] - Not determined.
[b] - Not analyse.

Table 4 Chemical analyses of PCBs congeners at different sampling points of the WWTP (pg/L).

	Sewage wastewater	Sewage and industrial wastewater	Sverma coking plant	Svoboda coking plant	Activation	Effluent from WWTP	Sludge centrifugate	Elimination [%]
PCB56+60	16.4	35.2	6.5	6.3	189	79.9	54.4	-275.7
PCB66+80	128	108	21.7	10.6	269	107	88.9	15.4
PCB70	99.4	425	22.2	8.2	176	82.7	55.2	53.5
PCB74	67.1	262	12.5	5.2	135	54.9	39.0	51.9
PCB84+89+92	74.8	617	10.9	16.1	84.3	33.6	30.6	83.5
PCB87	53.4	446	5.1	11.0	53.5	19.3	19.8	86.8
PCB95	162	1400	20.6	50.7	191	66.9	68.2	85.3
PCB97	4.3	43.1	0.2	0.4	4.8	5.3	1.8	60.6
PCB99+113	28.7	273	3.7	4.3	34.6	8.7	11.0	89.9
PCB101	187	2050	20.6	47.1	191	65.0	66.6	89.6
PCB104	< 0.2	< 0.3	0.2	< 0.2	< 0.2	< 1.4	< 0.1	ND
PCB105	2.3	12.0	2.6	3.4	25.6	10.8	8.5	-131.4
PCB110	142	430	10.5	26.6	135	50.6	54.3	76.2
PCB114	0.5	5.6	< 0.1	< 0.2	1.9	< 1.1	0.6	ND
PCB118	71.8	856	5.6	11.5	73.1	23.9	24.0	90.7
PCB119	2.1	15.3	ND	ND	2.2	ND	0.7	ND
PCB123	1.3	47.5	< 0.2	< 0.2	2.2	29.6	0.4	-144.4
PCB128	15.1	203	2.2	3.8	26.1	5.1	9.4	91.4
PCB130	127	1780	11.9	16.0	105	15.5	38.9	97.0
PCB135+144	84.7	1060	8.7	15.5	86.3	21.6	28.5	93.1
PCB138	346	4500	30.5	41.8	308	67.7	107	94.9
PCB148	55.3	615	6.5	12.5	59.3	16.8	23.4	91.0
PCB149	441	5770	46.4	69.5	405	98.5	129	94.2

Table 4 (continue) Chemical analyses of PCBs congeners at different sampling points of the WWTP (pg/L).

	Sewage wastewater	Sewage and industrial wastewater	Sverma coking plant	Svoboda coking plant	Activation	Effluent from WWTP	Sludge centrifugate	Elimination [%]
PCB151	108	1320	10.9	16.7	103	24.3	34.1	93.8
PCB153+168	822	10900	77.7	107	750	119	242	96.3
PCB155	< 0.2	< 0.4	< 0.2	< 0.2	< 0.2	< 1.3	ND	ND
PCB156	35.2	270	3.6	3.2	34.4	6.9	10.6	92.4
PCB157	1.8	9.3	< 0.4	0.6	3.0	< 1.6	1.3	ND
PCB158	32.9	620	2.5	5.7	46.1	10.4	11.0	93.9
PCB163+164	102	1430	16.8	9.5	78.9	28.9	35.5	93.0
PCB167	16.0	272	1.9	2.0	16.0	3.3	4.8	95.7
PCB170	235	2350	19.5	16.8	130	25.3	41.5	96.6
PCB171	109	1340	9.7	9.6	62.3	6.0	20.2	98.5
PCB174	199	2630	18.8	19.0	114	18.2	38.1	97.6
PCB176	29.3	330	2.6	3.2	16.1	< 1.3	5.3	>98.7
PCB177	59.8	764	4.4	4.8	33.3	12.4	10.7	94.5
PCB178	45.7	486	3.4	3.0	22.6	2.7	7.6	98.2
PCB179	92.7	1070	7.8	11.4	52.8	7.0	17.2	97.8
PCB180	568	7350	46.6	37.5	295	54.7	86.3	97.5
PCB183	136	1690	12.2	12.4	76.8	12.8	23.3	97.4
PCB187	250	2960	21.1	21.3	134	17.8	40.3	98.0
PCB188	< 0.4	< 0.9	< 0.4	< 0.4	< 0.4	< 2.3	< 0.3	ND
PCB189	< 0.4	< 0.7	1.9	< 0.4	4.8	3.6	1.0	ND
PCB191	9.3	148	< 0.4	0.8	6.9	2.0	1.9	~ 95.2
PCB194	188	2470	16.9	8.2	77.7	6.9	17.1	99.0
PCB199	133	1730	11.3	7.0	59.3	7.3	13.6	98.6

Table 4 (continue) Chemical analyses of PCBs congeners at different sampling points of the WWTP (pg/L).

	Sewage wastewater	Sewage and industrial wastewater	Sverma coking plant	Svoboda coking plant	Activation	Effluent from WWTP	Sludge centrifugate	Elimination [%]
PCB201	21.0	303	< 0.5	2.2	10.4	NA[b]	2.2	ND
PCB202	22.6	314	2.0	1.6	10.6	NA	2.7	ND
PCB205	12.2	111	< 0.7	0.7	< 0.7	26.3	< 0.5	ND
PCB206	104	1520	4.3	< 5.4	< 5.4	< 30	3.2	93.1
PCB209	14.0	65.6	< 2.2	11.8	14.0	< 11	7.5	ND
[ng/L]								
TriCB	1.5	4.4	0.95	0.095	3.2	1.2	1.4	43.8
TetraCB	0.95	3.0	0.41	0.098	2.4	0.98	0.69	32.4
PentaCB	0.73	6.2	0.080	0.17	0.80	0.31	0.29	84.4
HexaCB	2.2	29	0.22	0.30	2.0	0.42	0.68	95.0
HeptaCB	1.7	21	0.15	0.14	0.95	0.16	0.29	97.4
OktaCB	0.38	4.9	0.030	0.020	0.16	0.041	0.036	97.2
NonaCB	0.10	1.5	0.0043	ND	ND	ND	0.003	ND
DekaCB	0.014	0.066	ND	0.012	0.014	ND	0.008	ND
Sum of PCB	7.6	70	1.8	0.84	10	3.2	3.4	85.8

Table 4 (continue) Chemical analyses of PCBs congeners at different sampling points of the WWTP (pg/L).