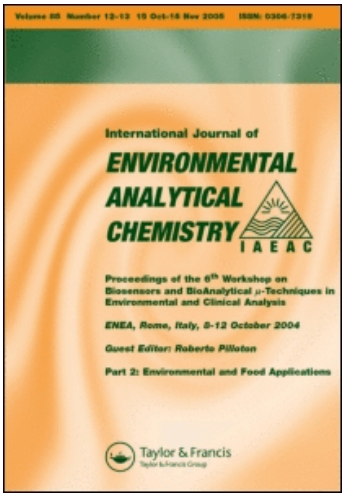

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Development and application of an analytical protocol for evaluation of treatment processes for landfill leachates. I. Development of an analytical protocol for handling organic compounds in complex leachate samples

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Development and application of an analytical protocol for evaluation of treatment processes for landfill leachates. I. Development of an analytical protocol for handling organic compounds in complex leachate samples

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A strategy is presented for evaluation of treatment procedures for landfill leachate with emphasis on organic pollutants. An analytical scheme, the LAQUA protocol, was developed as a guide for the analytical work. The protocol includes organic as well as metals, inorganic ions, water-quality parameters, and toxicity. The proposed strategy considers the behaviour of both polar and non-polar organic substances at trace levels. For polar substances, phenols were chosen as markers and determined with an automated supported liquid membrane extraction device, coupled on-line to HPLC with a diode-array detector. For non-polar substances, PCBs and 10 unidentified compounds were chosen as markers and analysed by solid-phase extraction combined with supercritical fluid extraction with GC analysis. The chosen measurement strategy, based on the use of marker substances, difference measurements, and versatile data-handling procedures, provided essential information about complex systems at relatively low cost.

Keywords: Treatment evaluation strategy; Landfill leachate; Organic pollutants; Polar markers; Non-polar markers

1. Introduction

Leachate water from landfills has a complex composition. High concentrations of salts and heavy metals often occur simultaneously with a vast number of different organic compounds. These include polycyclic aromatic hydrocarbons, phthalates, pesticides, and halogenated aromatic compounds such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDE), a variety of phenolic compounds, and other

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priority pollutants [1–9]. The US Environmental Protection Agency (US EPA) has characterized more than 400 pollutants in leachate from 13 non-hazardous landfills in the USA [5]. Thus, in developing analytical strategies for such complex aqueous samples, there is a need for a methodology which includes measurement of charged species like heavy-metal ions as well as polar organic pollutants like phenols and non-polar persistent organic pollutants such as PCBs. In an analytical perspective, there is a need for high-tech equipment for inorganic analysis, e.g. ICP-MS, as well as for organic compounds, e.g. GC-MS. Since organic compounds widely differ in physico-chemical properties, it is important to incorporate separation steps such as HPLC and GC in the analytical procedure to obtain sufficient information of the organic compounds in contaminated waters.

Strategies for characterization of polar organic compounds in leachate are rare, even though up to 95% of the TOC of some contaminated waters have been reported to be polar organic substances [10]. Castillo and Barcelo have presented an interesting approach, which combines toxicity-based fractionation with a more advanced chemical characterization. Although a good strategy, it incorporates labour-intensive identification steps [6, 11]. For large series of samples in connection with investigation of new treatment steps, work done using this methodology might be very costly. Furthermore, when monitoring a landfill, a strategy to follow both non-polar and polar organic tracers is needed [12].

Concerning evaluation of the efficiency of a certain treatment step for leachate with respect to organic compounds, it is not convenient, or necessary, to measure all the compounds which could ultimately be detected in leachate analysed by HPLC or capillary GC. This would take a tremendous amount of time and money, especially for quantification. Instead, a strategy is needed, whereby groups of compounds or single compounds can be used as markers of the present situation in the leachate, which leads to quantification of a limited number of species. Even with this approach, large data-sets are created. Accordingly, normalization procedures are needed before any comparison can be done in a quick and efficient way.

When evaluating the efficiency of different treatment steps as described in this paper, the analytical procedure can be further simplified by using relative measurements. In this case, often only a rough estimate is needed of the concentrations of pollutants in the system as long as the difference before and after treatment is accurately determined. This is especially true for all substances, known or unknown, with concentrations that tend to approach zero, i.e. the more efficient a treatment step is, the larger the uncertainty that can be accepted in the absolute values. However, before discharging the leachate to a final recipient, one has to make sure that the concentrations of known pollutants are so low that they do not pose any acute or long-term environmental threat. One should also always be aware of the risk of missing unknown but toxic compounds that might originate from the landfill. In fact, a characterization of the leachate composition is included in Annex III in the European Council directive 1999/31/EC on the landfill of waste [13].

In this article, we describe an analytical approach based on the automation of analytical procedures as far as possible combined with efficient data handling. The protocol is especially suitable for comparison between different treatment processes. To our knowledge, this is the first attempt towards a general strategy to handle this analytical problem. The proposed strategy has been applied to the evaluation of a pilot

plant for local treatment of leachate at Härlöv Municipal solid waste (MSW) landfill at the outskirts of Kristianstad, Sweden.

2. Experimental

2.1 *Samples*

Samples used for this investigation were obtained from a pilot plant containing different procedures for treatment of leachate. The leachate treated in this pilot plant was obtained from Härlöv landfill. The leachate passed through the pilot plant starting with pre-treatment (Pretr.) steps consisting of aeration and sedimentation, followed by six parallel treatment steps: ozone oxidation (Ozone) [14], chemical oxidation with Fenton's reagent (Chem. Ox.) [15, 16], bioremediation with a suspended bio film process (Bio) [17], or filtering through geobeds based on peat [18] with or without carbon-containing ash. The geobed filters were named as follows: GeoO with the filter based on peat and the leachate irrigated on top, GeoU with peat and leachate pressed through the filter from below, and finally GeoCO with peat mixed with carbon-containing ash and the leachate irrigated on top. A more detailed description of the pilot plant and the treatment procedures is found elsewhere [19].

Time-integrated weekly samples were obtained with timer-controlled sampling pumps (Iwaki Co. Ltd, Tokyo). Aliquots were collected intermittently each hour, resulting in sample volumes of about 5 l per day stored in a temporary vessel. Each day, an aliquot of 1 L was taken from this vessel and stored in a collection vessel in a refrigerator at the pilot plant. Every week, samples were taken from these vessels, transported, and stored in a refrigerator before analysis, which normally was performed within one week. Before taking out aliquots from the vessels, these were thoroughly shaken to ensure that the aliquots taken were representative.

The samples taken were divided into three sub-samples used for investigation of organic pollutants, inorganic and water-quality parameters, and toxicity, respectively. The organic pollutant sub-samples were acidified by adding hydrochloric acid (HCl), using 5 mL of 37% HCl per litre leachate, giving a pH of ca 2. This preserves the samples and dissolves the large amount of Fe_2O_3 and carbonates present in the leachate water. An aliquot of 0.5 L of each of the organic sub-samples was used for investigation of polar substances, and 1 L aliquots were used for non-polar substances.

2.2 *Chemicals*

Unless stated otherwise, all chemicals used were of p.a. grade, obtained from VWR (Darmstadt, Germany). All buffers and standard solutions were prepared in reagent water purified by equipment from Elga Labwater (High Wycombe, UK) or by a MilliQ/RO4, Millipore (Bedford, MA).

2.3 *Development of analytical procedures*

In this article, development of analytical procedures was directed toward organic pollutants. The determination of inorganic and water-quality parameters based on

existing standard methods is not discussed any further here. Results from these determinations are presented by Mårtensson *et al*. [19]. The developed methodology for determining acute toxicity has previously been described by Svensson *et al*. [20].

2.3.1 Polar markers and their analysis. Five phenols, found to be commonly present in preliminary experiments, were chosen as representative markers. These phenols were phenol, *p*-cresol, *o*-cresol, 2,4-dimethylphenol, and 3-methyl-4-chlorophenol. 4-Chlorophenol was chosen as a surrogate standard (SS). These six phenols were used to optimize the extraction system. Standard solutions of each phenol were prepared by weighing and dilution in methanol to a concentration of $1.00\,mg\,mL^{-1}$. A mixture of the six phenols, generally at a concentration of $100\,ng\,mL^{-1}$ each, was used for the optimization experiments. To 100 mL of acidified (pH 2) sample, $100\,\mu L$ of $100\,\mu g\,mL^{-1}$ of 4-chlorophenol (SS) in methanol was added, resulting in a concentration of $100\,ng\,mL^{-1}$.

An automated analytical system, with sample work-up using supported liquid membrane (SLM) extraction combined with HPLC–DAD was developed for the determination of phenolic markers (see figure 1).

SLM is a three-phase extraction in a flow system, where two aqueous phases are separated from each other with a porous membrane with the pores filled with an organic liquid. The phenolic compounds were made uncharged in the aqueous sample (donor) by choosing a pH of 2 and then extracted into the organic liquid in the pores of the membrane. At the other side of the membrane, the conditions were chosen so that the analytes were charged and irreversibly trapped in the aqueous solution (acceptor). The acceptor was kept stagnant, and the analytes were thus enriched in the acceptor, while pumping the sample on the donor side. The enriched and cleaned up phenolic compounds were then transferred to an SPE pre-column at the inlet valve of an HPLC, where the analytes were further focused before injection on the HPLC column. A similar set-up has previously been described by Knutsson *et al*. for determination of chlorinated phenols in natural waters [21]. However, the use of different analytes and a re-designed automated set-up necessitated a new optimization of the extraction parameters, as described below. A thorough description of the basis for SLM-extraction is given elsewhere by Jönsson and Mathiasson [22–24].

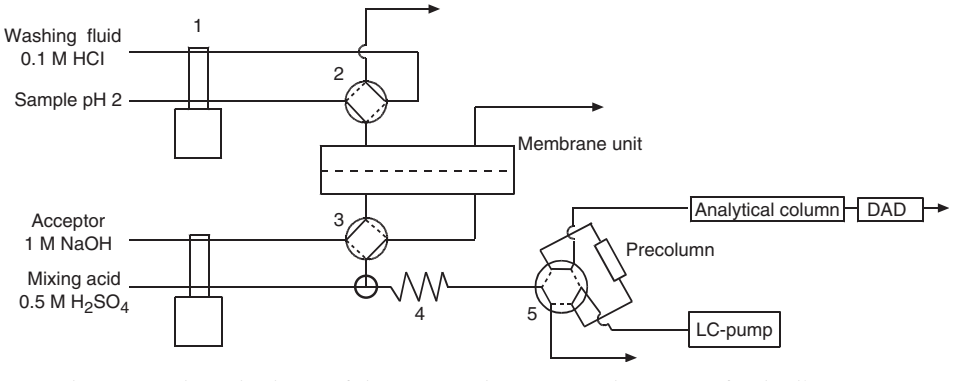

Figure 1. Schematic picture of the automated SLM extraction system; for details see text.

The final total analytical procedure was performed as follows: acidified sample was pumped, for 10 min at 0.63 mL min^{-1}, by a peristaltic pump (1) (Minipuls 2; Gilson Medical Electronics, Villiers-le-Bel, France), through the donor side of the membrane unit. The latter was built in-house and consisted of one PTFE and one PEEK block with milled spiral grooves, each with a volume of 200 μL and mirror images of each other and thus forming donor and acceptor channel, respectively. The channels were separated with a PTFE membrane (TE 35, 0.2 μm pore size, 190 μm thickness, Schleicher & Schuell, Dassel, Germany) that was impregnated with membrane solvent, forming a SLM extraction unit. During the extraction, the acceptor (1.0 M NaOH with 0.4% acetic acid) was kept stagnant. The acetate acts as a displacement to minimize adsorbtion of phenols in the flow system. After extraction, both sides were kept stagnant for 2 min for equilibration. The acceptor solution was then pumped out and mixed with 0.5 M H_2SO_4 in a mixing coil (4) to pH 4, where the phenols became uncharged and thus could be trapped on a PLRP-S pre-column (20 μm; Polymer Laboratories Ltd, Shropshire, UK, i.d. 2.1 mm, length 20 mm; Upchurch Scientific, Oak Harbor, WA). Thereafter, the two-position six-port pneumatic actuated valve (5) (Valco, Houston, TX) was switched and the analytes on the pre-column were transferred to the C_{18} analytical column (ACE-5C18, i.d. 4.6 mm, length 250 mm, Hichrom Ltd, Reading, UK). The flow rate was 1.0 mL min^{-1} with a mobile phase consisting of 20 mM phosphate buffer prepared with Na_2HPO_4 and NaH_2PO_4 to pH 3.3, mixed with methanol (VWR, Darmstadt, Germany, gradient grade) 55/45 (v/v). For detection and spectral analysis, a diode-array detector (DAD) (SPD M10AVP, Schimadzu, Kyoto, Japan) was used. The phenolic compounds were quantified at 280 nm. The two valves (2,3) used in the SLM system were pneumatically actuated, four-way Kel-F slider valves (Cheminert; Laboratory Data Control, Riviera Beach, FL). The entire system was controlled by an in-house developed control system, consisting of a pneumatic control box and an electronic control unit with simple Windows™-based software, thus yielding an automated analytical system. After completed extraction, an extensive washing programme was performed by pumping washing fluid (0.1 M HCl) on the donor side and acceptor buffer on the acceptor side of the membrane, respectively. Every day, quality-control samples (QC) were run and the response of the SS monitored during every analysis.

For the first time, the membrane was impregnated off-line by soaking the membrane in the membrane fluid, before mounting it in the membrane unit. Re-impregnation of the membrane was done with the membrane still mounted by first rinsing both channels with reagent water, then flushing with air. After that, several 100 μL portions of membrane fluid were allowed to pass the acceptor channel in the membrane unit. Then, the membrane unit was flushed again with air to remove excess solvent and finally washed with reagent water and acceptor buffer before recalibration of the system.

For the work-up procedure with SLM, four different membrane fluids were tested: pure di-*n*-hexylether (Sigma-Aldrich, Steinheim, Germany), di-*n*-hexylether with 10 or 15% (w/v) concentration of tri-*n*-octylphosphine oxide (TOPO) (Sigma, St. Louis, MO, ≥99%) and undecane (Sigma, ≥99%).

2.3.2 Non-polar markers and their analysis. For the analysis of non-polar markers, the following chemicals were used; methanol, *n*-heptane, acetone (Pestanal grade,

Riedel-de Haën, Seelze, Germany) and undecane (>99.0% Sigma). As a PCB standard for GC-MS analysis, the certified reference material, NIST 2262 (US National Institute of Standards and Technology, Gaithersburg, MD), containing 29 PCB congeners was used. Standard solutions were prepared in *n*-heptane and PCB 35 (Larodan, Malmö, Sweden) was used as internal standard. PBDE standards of decaBDE and 4,4′ diBDE (>99%) were purchased from Sigma Aldrich. A technical mixture of an octa-BDE product, OCTA-LM, was obtained from Dead Sea Bromine Group (Bromine Compounds Ltd, Israel). Carbon dioxide (>99.998%, AGA Gas AB, Sundbyberg, Sweden) was used for SFE extraction, and nitrogen (>99.996%, AGA Gas AB) for the reduction in sample volume by evaporation.

For the determination of non-polar markers, a 1000 mL sample was first filtered through 1.2 μm-pore size GF/C glass-fibre filters (Whatman plc, Kent, UK), using a standard glass vacuum filtration device for 47-mm disks and filters (Millipore, Bedford, MA). The eluate obtained was then passed through C_{18} discs (ENVI-18 DSK, 47 mm, 0.6 mm thickness, Supelco, Bellefonte, PA) in the same set-up, and the analytes were trapped on the C_{18} packing. The C_{18} discs and glass-fibre filters were then air-dried, rolled, and placed in separate 10 mL extraction cells, for supercritical fluid extraction (SFE) on an ISCO, model SFX 3560 (Isco Inc. Lincoln, NE) extraction unit. By separately extracting the glass-fibre filters containing particle bound analytes, and SPE discs containing dissolved analytes, a rough estimation of these two fractions can be obtained. This question has been further outlined by Zorita and Mathiasson [25]. However, in this work, we were interested in the total concentration of PCB and PBDE, which was obtained by adding the results from the two fractions together. In fact, it is also possible to modify the extraction procedure by placing the glass-fibre filter and SPE discs in the same extraction cell and directly determining the total concentration. The conditions for the extractions were; pressure 355 bar, extraction temperature 80°C, restrictor temperature 80°C, collection temperature 10°C, static extraction for 1 min and dynamic extraction during 30 min at a flow rate of 2.0 mL min^{-1} with carbon dioxide as supercritical fluid. The analytes were collected in a tube containing 15 mL of acetone. After the SFE procedure the extract was spiked with 50 μL internal standard (IS) solution, 540 ng mL^{-1} PCB 35 in *n*-heptane, and 1 mL of undecane was added. The acetone was evaporated under a mild stream of nitrogen. The undecane was then transferred to a 2 mL vial. The reason for adding the IS at this point was to correct for any possible losses during acetone evaporation and sample transfer, and for changes in detector sensitivity with time. The samples were then run on a GC equipped with autosampler, μ-electron capture detector (μECD) (GC 6890, Agilent, Palo Alto, CA) and an HP-5 column (5% phenylmethylsiloxane, 30.0 m × i.d. 320 × 0.25 μm film thickness, Agilent). The GC-ECD system was optimized with respect to high-boiling-point brominated diphenyl ethers, which were expected to be found in the leachate. The same set of samples was also run on a GC-MS system (Trace MS, Thermo Electron Corp., Waltham, MA) with an HT-5 column (5% phenylpolycarboran-siloxane 30 m × i.d. 250 μm, 0.25 μm film thickness, Scientific Glass Engineering Europe, Milton Keynes, UK) for SIM analysis of 29 PCB congeners with varying degrees of chlorination from 1 to 10 chlorine atoms (PCB: 1, 8, 18, 28, 29, 44, 50, 52, 66, 77, 87, 101, 104, 105, 118, 126, 128, 138, 153, 154, 170, 180, 187, 188, 194, 195, 201, 206, and 209).

2.4 *Data handling*

The data from all identified and quantified compounds, organic as well as inorganic and sum parameters, were treated with a multifactor analysis of variance (ANOVA) with treatment and dates as factors (Statgraphics plus, Statistical Graphics Corp. Rockville, MD). Multiple range tests were done according to Fisher's least significant difference (LSD) procedure, in order to determine significant effects of the treatment procedures. A confidence level of 95% was used for all statistical calculations.

3. Results and discussion

3.1 *Evaluation protocol for landfill leachate (LAQUA protocol)*

Based on our own investigations, and a general literature screening about the composition of different leachate waters from landfills [1–5, 7, 26], the LAQUA protocol was developed. This protocol describes important parameters to be measured in leachate water and includes suitable analytical procedures for these measurements. In some cases, outlined below, we had to develop new procedures or adjust existing procedures to leachate samples. The intention with this work has been to create an analytical methodology for evaluation of treatment processes that could give reliable judgements with relatively small amounts of manual labour, and at reasonable costs. To achieve this, automated procedures, multi-element analysis, use of marker substances and difference measurements have become important features. The LAQUA protocol is described in figure 2.

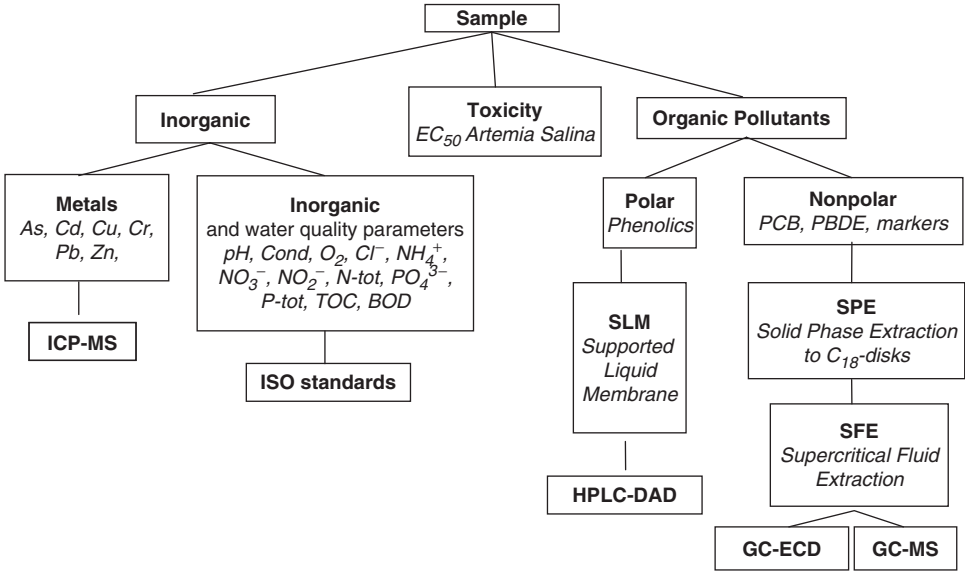

Figure 2. LAQUA-protocol: an analytical strategy for characterization of leachate and evaluation of the efficiency of different treatment procedures.

For polar compounds, preferably determined by HPLC, phenolic compounds were used as markers. Important reasons for this choice are that they are known toxicants at higher concentrations for biota and generally are present in this type of waste water. Four different phenols found in the pilot plant study were selected for monitoring (phenol, *p*-cresol, 2,4-dimethyl phenol, and 3-methyl-4-chlorophenol), identified both by comparison with UV spectra and via retention times of standards. Figure 3 shows typical chromatograms obtained by this procedure.

When analysing non-polar compounds with GC-ECD, many peaks occurred in the same range as the PCB peaks. Ten of these peaks (non-PCBs), which were present in all raw leachate samples examined, were chosen as markers. The chosen markers have similar properties with respect to polarity as PCBs and similar non-polar compounds, and should thus be good markers for PCBs and other non-polar compounds in a treatment system based on geo-filter and/or soil plant irrigation, for example. Here, the efficiency of the treatment depends largely on the physical properties of the compounds. When the concentrations of toxic compounds, such as PCBs and PBDE, approach the background levels, differences in treatment efficiency of different systems might be hard to distinguish. In this case, markers at higher concentrations with similar physical properties might be a good alternative to consider.

For interesting halogenated compounds occurring at very low concentrations and with similar retention times as larger peaks, a direct GC-ECD approach is not sufficient. In these cases, the alternative procedure described in the protocol, using GC-MS in SIM mode, is advised. This approach was used for the PCB determination in leachate from Härlöv. We also think it is important to obtain a more direct measure of the toxicity of the leachate considered; hence, an acute toxicity test based on a

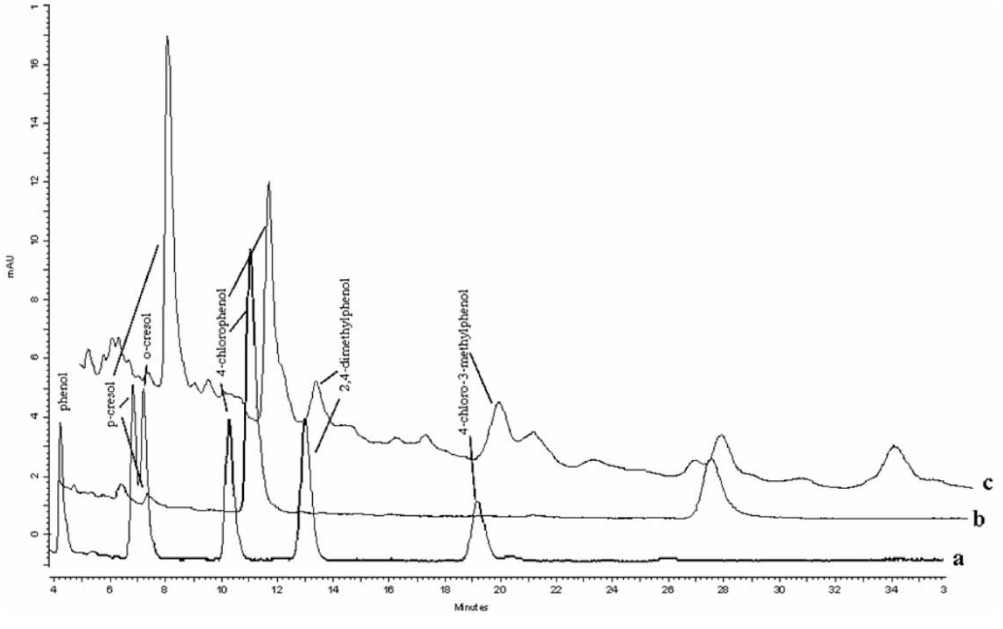

Figure 3. Three overlaid SLM-HPLC chromatograms at 280 nm, containing phenolic markers. Retention time and absorbance is offset for easier visualisation: (a) 50 ng mL^{-1} standard, (b) leachate sample after ozone treatment from the pilot plant, and (c) raw leachate water Härlöv waste deposit, Kristianstad, Sweden.

test species, the salt endurable crustacean *Artemia salina*, is included in the LAQUA protocol. The development of this test is described by Svensson *et al.* [20]

It should be pointed out that the LAQUA protocol is a dynamic product and can easily be extended to include determination of new species, or reduced by excluding parameters that yield little information in the actual situation. For example, we think that there is a general need to incorporate in the LAQUA protocol a chronic toxicity test for evaluation of substances, like oestrogenic disruptors, which are known to have long-term toxic effects. Work along this line is in progress.

3.2 *Development of analytical procedures*

For inorganic species, one can rely on existing analytical procedures; e.g. for heavy metals, ICP-MS or ICP-OES multi-element analyses are the best alternatives. Cost-effective and efficient methods for water-quality parameters and inorganic ions are also available. The large expense, and hence the bottleneck in any evaluation strategy for complex waste water samples, is the determination of organic compounds. The procedures described in this article for polar and non-polar organic compounds are expected to give reliable values at relatively low costs.

3.2.1 Polar markers. The SLM extraction procedure for the phenolic compounds described in the experimental was optimized by investigations of flow rate on the donor side, composition of the membrane liquid, extraction time, composition of acceptor buffer, and of the concentration of the neutralization acid and its flow rate.

In the *acceptor solution*, the phenolic compounds must be charged for efficient trapping. Solutions of Na_3PO_4 and NaOH were tested as acceptor buffers. Although 0.1 M NaOH gives a pH about 3 units above the pK_a values for the phenolic compounds, which should be sufficient for good trapping [22], the best results were obtained using 1 M NaOH. This depends on the fact that when processing leachate water, hydroxide ions are consumed, and the use of 0.1 M NaOH leads to a pH in the acceptor less than 3 units from pK_a at the end of the extraction. The use of Na_3PO_4 gave on average about 20% less enrichment for all phenols. Thus, 1.0 M NaOH was used in further work. Concerning the four *membrane liquids* investigated; undecane, di-*n*-hexylether, di-*n*-hexylether +5% TOPO and di-*n*-hexylether +10% TOPO, the least polar membrane, undecane, had the best long-term stability but gave the lowest enrichment. The addition of TOPO to di-*n*-hexylether gave a markedly better extraction for the more polar phenols, whereas for the less polar phenols, pure di-*n*-hexylether was best. Results are shown in figure 4. RSD values were better than 5% in all measurements.

A compromise between good extraction efficiency and sufficient long-term stability led to the choice of pure di-*n*-hexylether as membrane liquid in further experiments. This membrane liquid is normally stable for more than 4 weeks of normal use, i.e. more than 150 samples can be analysed before the membrane needs to be re-impregnated.

To ensure enough capacity of the PLRP-S pre-column, different volumes of samples, spiked at 50 ng mL^{-1} for each phenol, were processed. A very good linear relation was obtained between sample volume and detector signal for the different phenols up to the largest sample volume investigated, which was 8 mL. No indication of breakthrough

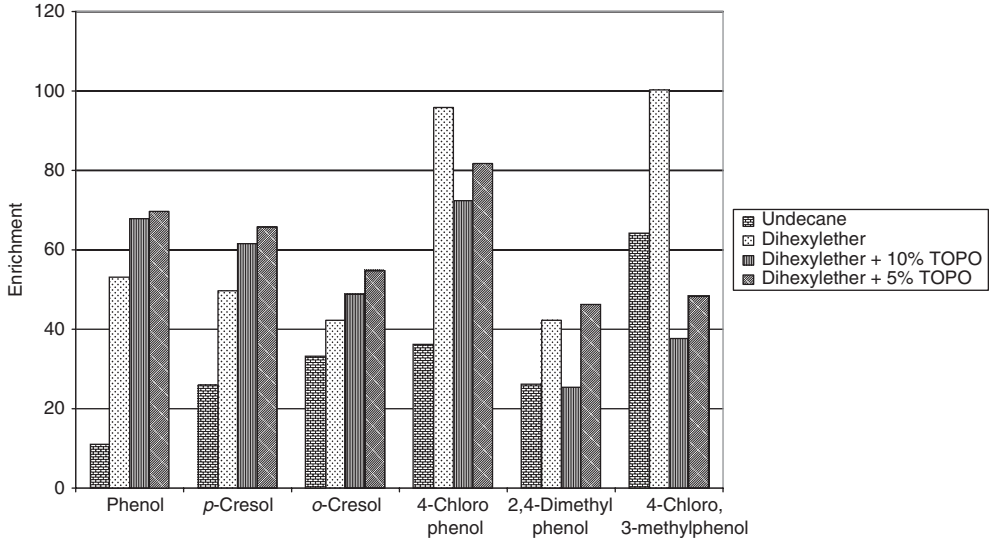

Figure 4. Enrichment factors for different membrane fluids for the investigated phenols, after 30 min extraction at 1 mL min^{-1}.

was observed at 8 mL, which was about double the volume normally loaded on the PLRP-S pre-column. The correlation coefficients (R^2) were in the range of 0.9979–0.9998.

To test the *linearity and RSD of the whole SLM-HPLC system*, calibration curves were obtained based on five concentrations in the range 2.5–100 ng mL^{-1}. Calibration curves for the SLM-HPLC system were linear, with correlation coefficients (R^2) in the range of 0.990–0.999 using an extraction time of 10 min and a sample (donor) flow rate of 0.67 mL min^{-1}. The RSD ($n = 10$) values for the system ranged from 0.9 to 4.8% at concentrations of 25 ng mL^{-1} for the phenolic markers. LOD using 10 min extraction with stagnant acceptors were in the range of 0.2–0.6 ng mL^{-1}.

The long-term stability of the entire system was found to be very good, i.e. the slope of the calibration curves for different phenols, run within a 1.5-year time difference, deviated by an average of only 4.1%. During this time, the membrane was replaced several times, re-impregnation was made occasionally, the peristaltic tubes were replaced several times, and the pre-column was re-packed once.

3.2.2 Non-polar markers. The analytical procedure based on SPE-SFE described previously for PCB determination was used also for the determination of PBDE and the 10 unidentified non-polar markers. Spiked samples (20 ng L^{-1}) gave recoveries close to 100% for all congeners, and the average RSD was 7% (range: 2–15%) for both PCBs and PBDEs. Previous results from sediment extractions using SFE have shown recoveries close to 100% for PCBs [27]. Thus, adding an IS for compensation of incomplete recovery is not needed, but we have added an IS after the evaporation step to account for errors in sample volume and for changes in detector sensitivity with time. However, it could be an even better approach to add an internal standard to the aqueous sample solution, preferably when sampling, to account for adsorption on the

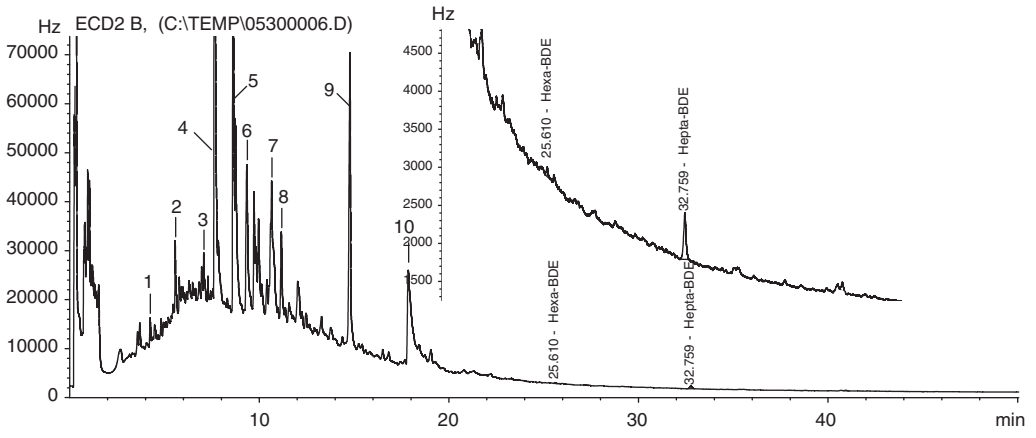

Figure 5. SPE-SFE-GC-ECD chromatogram of leachate water from Härlöv Landfill, Kristianstad, Sweden, with 10 unidentified markers (1–10) and two identified PBDEs. Above the original baseline is the attenuated chromatogram to illustrate that the elution region for higher PBDEs is relatively free from interference. The concentrations of hexa-BDE (PBDE 153) and hepta-BDE (PBDE 183) are ca, 15 and 190 pg mL, respectively.

walls of the sample vessel and extraction equipment. However, this approach is not as straightforward as it seems, since different congeners have widely different characteristics for adsorption on glass, which makes the choice of IS difficult. The difference in adsorption is even more prominent for concentrations at the ppt range [25]. An alternative determination procedure for PCBs could be to elute the analytes from the SPE discs with an organic solvent, combined with a clean-up step on a small adsorbent column, as described by Westbom *et al.* [28]. For PCB analysis, the GC–MS calibration curves, made in SIM mode (range 0.1–100 ng mL^{-1}, nine concentrations), gave R^2 values in the range of 0.9904–0.9995. The average RSD for the GC analysis of different PCB congeners was 2.8% (range: 0.8–5.8%, $n = 10$) at 1.0 ng mL^{-1}. The LOD values for the different PCBs in 1-L samples, after enrichment with a factor of 1000, were between 0.1 and 0.2 pg mL^{-1}.

For the PBDE compounds, GC-ECD calibration curves, based on five concentration levels, were obtained in the range of 5–100 ng mL^{-1}, resulting in R^2 values of 0.9906–0.9920. Under the GC-ECD conditions used, the chromatograms obtained from real leachate sample are relatively free from interferences in the region where the studied PBDE congeners elute (after hexa-BDE; see figure 5). The LOD values for the PBDE compounds considered in a 1-L leachate sample after enrichment with a factor of 1000, determined as three times the noise level, were 10–20 pg mL^{-1}. The value of Hexa-BDE (15 pg mL^{-1}), one peak in figure 5, is just above the LOD for a 1 L sample. The LOD can be further decreased, since 2-L samples in this case can be used without any risk of breakthrough in the SPE disc extraction step.

3.3 *Sampling procedure*

In the multifactor ANOVA, generally no significant differences were found between sampling dates (weekly intervals) and measured concentrations of organic markers. This shows that the time-integrated sampling levels out any short-term fluctuations

of leachate composition that occur in the incoming leachate to the pilot plant. This fluctuation depends mainly on intermittent pumping from different leachate draining wells in the landfill to the main leachate outlet well, from which the pilot plant was fed with leachate water.

3.4 *Data analysis*

The developed analytical methodology was tested for evaluation of the pilot plant described in section 2. The measurements were done according to the LAQUA protocol. In order to determine whether any treatment had a significant effect, the data were put into a spreadsheet, and a multi-factor ANOVA was run. In order to compare the behaviour of unidentified markers, the response (peak area) was normalized to the response of the same marker in the incoming raw leachate. In this way, it was easy to follow the behaviour in the pilot plant. To minimize data and visualize trends, an average of all 10 unidentified markers was calculated for each treatment. The data obtained were compared with the trends of quantified analytes. In this way, it was possible to identify similarities in behaviour of unidentified analytes with similar physical properties as the quantified PCBs and PBDEs. The unidentified compounds all had good responses with ECD, which implies that they should contain halogens or other electronegative groups, e.g. as the ester function in phthalate esters. Compounds of these types are quite often of environmental concern. Running the samples by GC-MS in scan mode gave a very low response, which made identification very uncertain and hence the quantification impossible. Accordingly, in the present work, we used the more sensitive ECD to follow the effect of the different treatment procedures. The challenge of identifying unknown toxic compounds, occurring at low concentrations, needs more attention in a future perspective.

In the Pilot plant study, organic compounds were analysed in all samples. Figure 6 shows examples of normalized results for the operation of all treatment steps in the pilot plant. From figure 6, it is clear that the unidentified non-polar compounds follow the same trends as the identified and quantified ones with similar physical properties. A surprisingly good correlation was also found when considering the more active treatment methods, as can be seen for PCBs in figure 6(a). Thus, unidentified non-polar markers, with similar physical properties to the identified substances can be used to back up trends. This latter statement is expected to be especially true for treatments based on physical properties, such as the pre-treatment steps described above and geo-filters. Greater care needs to be taken for more active treatment methods, where slight differences in molecular structures might greatly impact the results. Such methods include chemical oxidation with Fenton's reagent, ozone oxidation, and bio-remediation. An example of this can be seen in figure 6 where, especially in the Chem. Ox. and in the bio-treatments, there was a relatively greater decrease for the 10 unidentified markers relative to the PCBs which are more recalcitrant. Another example can be found in figure 6(b) (Bio). In the bio-remediation step, there is a large decrease in *p*-cresol and most of the phenols, but also a large increase in phenol. This implies that phenolic, or other aromatic compounds such as PAHs, might be degraded to phenol or there is some kind of other contamination occurring. This shows that in this case, further polishing steps might be needed before discharging the treated leachate

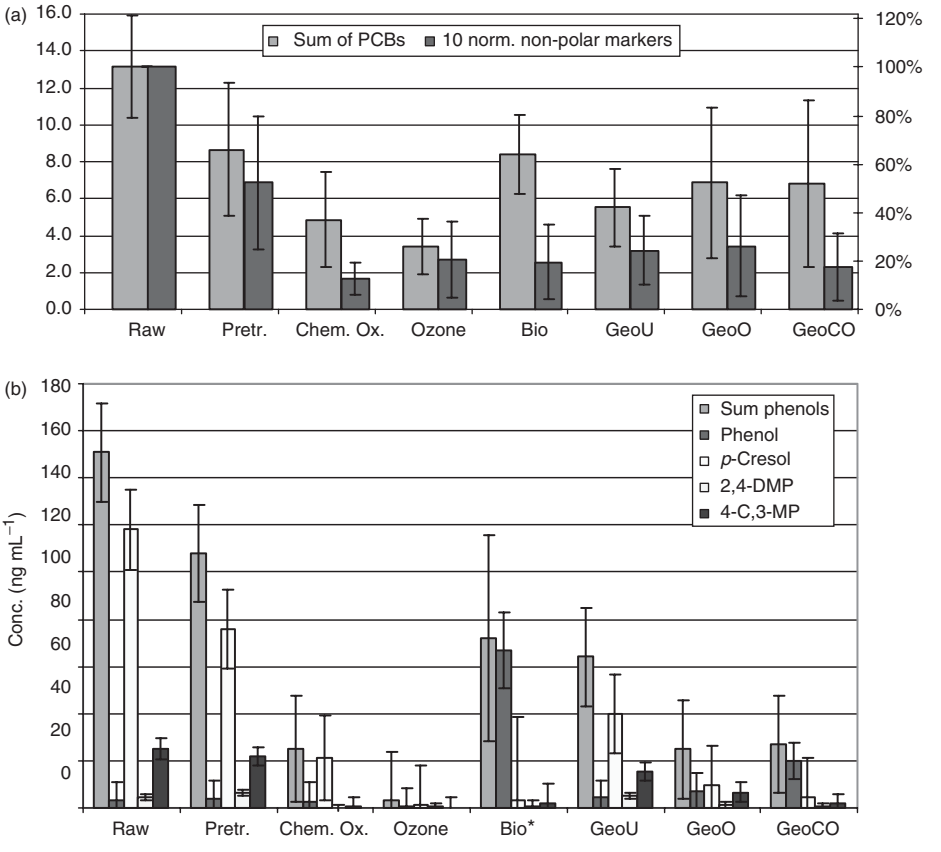

Figure 6. Treatment efficiency with respect to marker substances in different steps of the studied pilot plant. (a) Sum of PCBs (left) and of 10 unidentified non-polar organic compounds (right), normalised according to the text. (b) Results for sum of phenols, and for four major identified phenols. Error bars show the 95% confidence intervals for the average ($n = 8$ except for Bio* where $n = 2$), of samples, obtained from time-integrated sampling at different dates.

to a recipient. It also shows that just monitoring the sum of phenols does not give a full insight into the behaviour of a complex treatment system.

3.5 *Concluding remarks*

We have shown that analytical procedures with a high degree of automation for determination of organic pollutants at trace levels is a good approach for investigation of changes in complicated systems. Trends found by using identified and quantified marker substances can be supported by measuring typical but unidentified components in the leachate. Knowledge about the magnitude of pollutant reduction can, as demonstrated in this article, be achieved by quantification of a limited number of markers in a limited number of samples.

As a basis for the measurements, a protocol, the LAQUA protocol, has been developed and used for evaluating complex samples from a pilot plant for

leachate treatment. More details about the efficiency of different treatment steps in this pilot plant, using this protocol for organics and also including effects on inorganic and water-quality parameters, is presented by Mårtensson *et al*. [19].

The methodology and the LAQUA protocol described here have formed a basis also for subsequent applications. For example, it has been used in a study dealing with the performance of a full-scale natural treatment system [29] and in a recent study of the emission of volatile organic compounds in baled household waste [30].

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References

[1] N. Paxeus. *Water Sci. Technol*., **42**, 323 (2000).
[2] C. Öman, M. Malmberg, C. Wolf-Watz. *Handbook for Leachate Judgement. Methodology for Characterisation of Leachate from Landfills* (in Swedish), B-1354, IVL Swedish Environmental Research Intstitute, Stockholm (2000).
[3] C. Öman, P.-Å. Hynning. *Environ. Pollut*., **80**, 265 (1993).
[4] C. Öman, M. Malmberg, C. Wolf-Watz. *Development of Methods for Characterisation of Leachate from Landfills—Final Report* (in Swedish), B-1353, IVL Swedish Environmental Research Institute, Stockholm (2000).
[5] Environmental assessment for final effluent limitations guidelines and standards for the landfills point source category, EPA-821-B99-006, US EPA (2000).
[6] M. Castillo, D. Barcelo. *Anal. Chim. Acta*, **426**, 253 (2001).
[7] P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.H. Christensen. *Crit. Rev. Environ. Sci. Technol*., **32**, 297 (2002).
[8] C.A.d. Wit. *Chemosphere*, **46**, 583 (2002).
[9] M. Osako, Y.-J. Kim, S.-i. Sakai. *Chemosphere*, **57**, 1571 (2004).
[10] L.D. Betowski, D.S. Kendall, C.M. Pace, J.R. Donnelly. *Environ. Sci. Technol*., **30**, 3558 (1996).
[11] M. Castillo, D. Barcelo. *Anal. Chem*., **71**, 3769 (1999).
[12] E. Benfenati, E. Porazzi, R. Bagnati, F. Forner, M.P. Martinez, G. Mariani, R. Fanelli. *Chemosphere*, **51**, 677 (2003).
[13] European Council Directive 1999/31/EC on the landfill waste. *Off. J. Eur. Commun*., **L182**, 1 (1999).
[14] J. Jerry, W. Chih-Chao, M. Hong-Wen, C. Chia-Chi. *Chemosphere*, **54**, 997 (2004).
[15] E. Neyens, J. Baeyens. *J. Hazard. Mater*., **98**, 33 (2003).
[16] A. Lopez, M. Pagano, A. Volpe, A. Claudio Di Pinto. *Chemosphere*, **54**, 1005 (2004).
[17] U. Welander, T. Henrysson. *Water Environ. Res*., **70**, 1236 (1998).
[18] M. Heavey. *Waste Manage*., **23**, 447 (2003).
[19] L. Mårtensson, S. Bergström, B.-M. Svensson, L. Mathiasson. *Int. J. Environ. Anal. Chem*., **87**, 17–27 (2007).
[20] B.-M. Svensson, L. Mathiasson, L. Mårtensson, S. Bergström. *Environ. Monit. Assess*., **102**, 309 (2005).
[21] M. Knutsson, L. Mathiasson, J.Å. Jönsson. *Chromatographia*, **42**, 165 (1996).
[22] J.Å. Jönsson, L. Mathiasson. *J. Chromatogr. A*, **902**, 205 (2000).
[23] J.Å. Jönsson, L. Mathiasson. *Trends Anal. Chem*., **18**, 318 (1999).
[24] J.Å. Jönsson, L. Mathiasson. *Trends Anal. Chem*., **18**, 325 (1999).
[25] S. Zorita, L. Mathiasson. *Int. J. Environ. Anal. Chem*., **85**, 531 (2005).

[26] T.H. Christensen, P. Kjeldsen, P.L. Bjerg, D.L. Jensen, J.B. Chistensen, A. Baun, H.-J. Albrechtsen, G. Heron. *Appl. Geochem*., **16**, 659 (2001).
[27] T. Nilsson, S. Bowadt, E. Björklund. *Chemosphere*, **46**, 469 (2002).
[28] R. Westbom, L. Thörneby, S. Zorita, L. Mathiasson, E. Björklund. *J. Chromatogr. A*, **1033**, 1 (2004).
[29] L. Thörneby, L. Mathiasson, L. Mårtensson, W. Hogland. *Waste Manage. Res*., **24**, 183 (2006).
[30] D.R. Nammari, L. Mathiasson, L. Mårtensson, M. Marques, L. Thörneby, W. Hogland. *Waste Manage. Res*. (In press).