ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 139 (2001) 205–215

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Study of photochemical oxidation of standard chlorinated paraffins and identification of degradation products

In-Ock Koh*, Wolfram Thiemann

Department of Physical and Environmental Chemistry, University of Bremen, PO Box 33 04 40, D-28334 Bremen, Germany

Received 2 November 2000; accepted 7 December 2000

Abstract

The kinetics of the photolytical oxidation of standard chlorinated paraffins by a combination of ultraviolet light and hydrogen peroxide was studied in various diluted aqueous solution. The most efficient degradation of the chlorinated paraffins was found in a 0.1% acetone–water medium in the series of experiments (aqueous solution with H_2O_2 or without H_2O_2 addition). The half-lives of Hordalub 500 and Hordaflex LC 50 in 0.1% acetone aqueous phase were less than 1 h ($t_{1/2} < 1$ h), other chlorinated paraffins (CP 30, CP 40, CP 52 and CP 56) ranged between 2.5 and 5.2 h. Free chloride was determined as a function of progressing degradation. Long-chain alkanes were identified as degradation products of short-chain chlorinated paraffins. The ecotoxicity tests investigated showed that in the green algae test for chlorinated paraffins, no inhibition of cell growth was observed. By means of biological tests of chlorinated paraffins, a significant acute toxicity for Daphnia as well as a chronic toxicity for luminescent bacteria were determined.

Keywords: Chlorinated paraffins; Photooxidation; Intermediate products; Ion chromatography; GC/MS; Biological toxicity test

1. Introduction

Typical commercial "chlorinated paraffins" (CPs) are *n*-chloroalkane mixtures of chain lengths of C10–C30 whose chlorine content ranges between 10 and 72% (by weight). CPs are used on a worldwide scale as plasticizers in PVC, flame retardants, and additives in paints, sealants and cutting fluids [1–4]. As a consequence of their industrial application, their residues may penetrate the primary food chain and ultimately the whole ecosystem. Information concerning environmental distribution, persistence, and ecological toxicity is needed for hazard assessment of CPs. A number of studies are dealing with the toxicity of CPs [1–6] and their concentration determined in environmental samples [8–19]. The assessment of their environmental fate and exposure is rather scarce because of the lack of suitable analytical methods. Further, another reason for this situation is the limited data on degradation studies of photolysis, hydrolysis, oxidation and biodegradation. Photolysis is one of the major transformation processes affecting the fate of CPs in the aquatic environment.

Friedman and Lombardo [20,21] published photochemical degradation of CPs in aliphatic hydrocarbon solvents by applying ultraviolet (UV) irradiation with 550 W mercury vapor lamp. In this paper, they prove to be rather poor absorbers of UV light and as a consequence, no direct photochemical decomposition was observed. It is assumed that CPs take part in no gas reactions for degradation in the troposphere, but indirect photolysis was suggested by oxidizing radicals [2]. Half-lives of CPs in the atmosphere, based on Atkinson's OH radical mechanism, were calculated to range from 0.85 to 7.2 days [1,3].

CPs are assumed to contribute only little to hydrolysis and oxidation in the aqueous phase at ambient temperature. Nevertheless, photolytic reactions of hydrolysis or oxidation by involving free radicals or catalysts can be induced in the aquatic environment [2]. However, no experimental data on this subject for the chemical stability under environmental conditions have been reported.

Bergman et al. [22] examined thermal degradation of polychlorododecane containing 59 and 70% chlorine, and other commercial CPs by GC/MS. Their pyrolytic decomposition products were aliphatic hydrocarbons, unchlorinated or less chlorinated aromatics such as polychlorinated biphenyls, naphthalenes and benzenes. These by-products were formed by different reaction mechanisms dependent on the degree of chlorination of the CPs.

* Corresponding author. Tel.: +49-421-218-2372/3518; fax: +49-421-218-7382.
E-mail address: koh@uni-bremen.de (I.-O. Koh).

1010-6030/01/$ – see front matter
PII: S1010-6030(00)00427-5

However, a study of the photodegradation products in aquatic environment had not been undertaken before. An investigation of the photoproducts formed was not available, neither for the reaction paths of fragmentation of CPs, nor for the estimation of accumulation rates and exposures in environmental compartments, especially in sediment, atmosphere, and soils.

CPs are practically unaffected by microbial degradation processes [1–4] and have a bioaccumulative and cancerogenic potential [1–4,7,8]. Therefore, the toxic effects of CPs are particularly relevant for environmental organisms. They prove to be harmful to aquatic and terrestrial organisms.

In this study, the photooxidation of standard CPs in aqueous phase by UV radiation was investigated. First, it was studied how UV irradiation influenced the chloride cleavage from the CPs. For this purpose, CPs in a diluted aqueous medium (acetone served partially as a solubilizer) were irradiated with UV emitted from a middle pressure mercury lamp. In order to observe the reaction rates depending on the type and amount of added oxidizing agents, the UV irradiation of CPs was carried out in the presence of various amounts of hydrogen peroxide. The photolysis products formed were determined in order to search for the main photodegradation pathways of CPs in water samples.

Biological tests were run in order to check for reduction of toxicity as a result from UV/H_2O_2 treatment of CPs. For the evaluation of ecotoxicity, the standard CPs and their degradation products were tested for their effect on aquatic biological organisms such as luminescent bacteria, algae and Daphnia m. organisms.

2. Materials and methods

2.1. Chemicals

The solvents used were acetone, *n*-hexane for residue analysis (Riedel de Haen), and diethylether, p.a. quality from Merck. Saturated straight chain hydrocarbons (C8–C30) of 99% (GC) quality were obtained from Sigma. Cyclododecane (>99%) was of synthesis quality (Merck). The solutions of hydrogen peroxide were prepared from a concentrated and nonstabilized solution at 35% by weight of p.a. quality (Fluka). Silica gel (1 g/6 ml isolute) cartridge used as a sorbent for solid phase extraction was purchased from Baker.

2.2. Standard chlorinated paraffins

All standard CPs were gratefully supplied by Hoechst AG. Their corresponding chain length which was determined according to our own methods [23], and chlorine content is given in Table 1.

Table 1
Composition of the standard CPs

CPs (trade names)	Chain length	Chlorine content (%)
CP 30	C17–C24	35
CP 40	C17–C20	44
CP 52	C12–C18	52
CP 56	C10–C13	56
Hordalub 500	C10–C13	62
Hordaflex LC 50	C17–C20	52

2.3. Sample preparation of chlorinated paraffins in acetone and water

The photodegradation of the CPs was examined in 0.1% acetone–water medium as well as in pure water. Because CPs have a low solubility in water [1–4], water–acetone solutions were partially employed. Stock solutions were prepared by adding 60 mg of standard CPs (Hordalub 500, Hordaflex LC 50, CP 30, CP 40, CP 52 and CP 56) in 10 ml acetone in a concentration of 6 mg/ml. The individual stock solutions were diluted with distilled water to a final concentration of 6 mg/l. The sample solution was stirred at room temperature for 48 h.

For the ecological tests, each stock solution was diluted with distilled water to prepare the individual standard solutions of 250 μg/l of CP 30, CP 40 and CP 56, and 125 μg/l of CP 52, Hordalub 500 and Hordaflex LC 50 in water.

In another experimental series, no organic solvent was used for the preparation of sample solutions in order to avoid solubilizer effects. The individual CPs were added to pure distilled water and prepared in a concentration of 6 mg/l as in the case of acetone–water medium described above. (In this case, the risk was accepted that the CPs would possibly not “dissolve” in the pure sense, but build a sort of emulsion in water only.)

2.4. Experimental apparatus (middle pressure mercury lamp)

The photolysis experiments for CP were carried out in a cylindrical photoreactor consisting of a reaction chamber, a cooling jacket and a UV lamp. A middle pressure mercury lamp (TQ 150) which was utilized as the radiation source was provided by Heraeus Noblelight (Hanau).

The main lines of the radiation spectrum are found at wavelengths of $\lambda = 254$, 302, 313, 366, 405/408 and 436 nm. The intake of power was 150 W and the radiation output was 6.2 W in UV-C, 3.6 W in UV-B and 4.5 W in UV-A. All radiation experiments were carried out in batch operation. The lamp was covered with a cooling jacket in order to inhibit the heating of solution during the operation and keep the temperature constant. A magnetic stirrer was used for good mixing of the aqueous solution in the reaction chamber. The volume of a reaction solution was 700 ml. Hydrogen peroxide (0.02 or 0.002%) was added

to the reaction chamber just before the beginning of the photolytical experiment.

2.5. Ion chromatography

Chloride ions result from the cleavage of CPs during the irradiation. A 5 ml aliquot of irradiated solution was sampled at each 30 min reaction times and filled into polyethylene vials.

The determination of chloride ions was performed by ion chromatography based on DIN 38405 unit 19 [28]. The ion chromatography (DIONEX DX-100) consists of a conductivity detector, an anion suppressor, an auto sampler and columns as given below:

- Input column: IONPAC® AG4A-SC (4 mm × 50 mm) guard column.
- Separation column: IONPAC® AG4A-SC (4 mm × 250 mm) analytical column.

The flow rate was operated at 2 ml/min and injection volume was 25 μl. The used eluents were 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ in twofold distilled water. The operation of the system was performed with DIONEX AI-450 software.

2.6. Sample preparation with solid phase extraction

For the identification of decomposition products, a solid phase extraction of irradiated solution was performed similar to procedure described in [8]. A microcolumn (cartridge) of silica gel (1 g/6 ml isolute) in a Baker spe-12 G system was rinsed with 3 ml of hexane and flushed with 10 ml of distilled water for cleaning and conditioning.

The 700 ml irradiated solution was drawn through the silica gel cartridge by using a water jet pump, while vacuum was controlled at about 600 mbar. At the end of the adsorption process, the column was again rinsed thoroughly with pure water and then dried at room temperature with air by using the vacuum. The silica gel cartridge was dried by purging with nitrogen. The column with the adsorbed residues was rinsed with 4 ml hexane and eluted with 4 × 1 ml hexane/diethyl ether 90/10% (v/v). Finally, the total extracts were concentrated to 1 ml with a jet of nitrogen. Internal standard cyclododecane was added to the extracts at final concentration of 100 μg/l. It was used as correcting factor for the quantitative analysis of CPs by GC/MS measurement.

2.7. GC/MS technique

A Shimadzu GC-17A gas chromatograph was equipped with a 60 m DB5-MS capillary column (0.25 mm ID, d_1 = 0.25 μm (film thickness)). QP-5000 MS detector (quadrupole type) coupled to GC was operated with electron impact (EI) ionization at 70 eV. Injector temperature was 260°C and the injection volume was 1 μl in the split mode. Detector block and transfer line were held at 320°C. Helium was used as carrier gas at a rate of 30 cm/s. The data processing of mass spectra was performed in both TIC and SIM (selected ion monitoring) modes.

- Temperature program: 40°C for 2 min isothermal, with 30°C/min up to 110°C, then with 9°C/min up to 300°C for 15 min.
- Carrier gas program (controlled by pressure): 148.6 kPa for 2 min isothermal, with 16 kPa/min increase up to 188 kPa, then with 5 kPa/min up to 295 kPa for 15 min.

3. Results and discussion

3.1. Recovery of chlorinated paraffins with solid phase extraction

The efficiency of solid phase extraction with silica gel column and the elution behavior were investigated with standard CPs in hexane according to [23]. As indicated in Table 2, the recovery rates of CPs were between 76 and 96%. CP 30 showed a lower recovery rate, because CP 30 was already eluted in the first hexane fraction due to similarity to alkane behavior.

3.2. Photochemical oxidation of standard chlorinated paraffins in aqueous solution

The photodegradation of CPs was examined at a total irradiation time of 5 h in the following media:

- in 0.1% acetone–water solution,
- in pure aqueous solution, and
- in aqueous solution with hydrogen peroxide (0.02 as well as 0.002%).

The added concentration of hydrogen peroxide as an oxidizing agent was set from the equimolar concentration related to the CP's structure of a given alkane chain length. The hydrogen peroxide doses in 700 ml test solution were set to 1 equivalent (0.002%, v/v) and 10 equivalents (0.02%, v/v).

The photolytical degradation rate of standard CPs was calculated by means of a conversion of the bound Cl-substituent to free Cl^- ions, which were determined by ion chromatography, i.e. the advancing degradation rate of CPs corresponded with the formation of chloride ion.

Table 2
Recovery rate of standard CPs with solid phase extraction on silica gel column [23] (elution solution: hexane/diethyl ether; 90/10% (v/v))

	CP-type					
	CP 30	CP 40	CP 52	CP 56	Hordalub 500	Hordaflex LC 50
Recovery (%)	60	70	81	96	93, 91[a]	79

[a] Ref. [8].

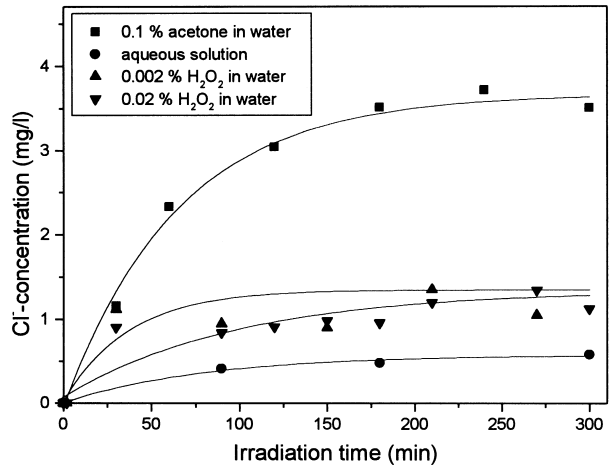

Fig. 1. Cleavage of Cl^- ions of Hordalub 500 in aqueous medium as a function of irradiation time.

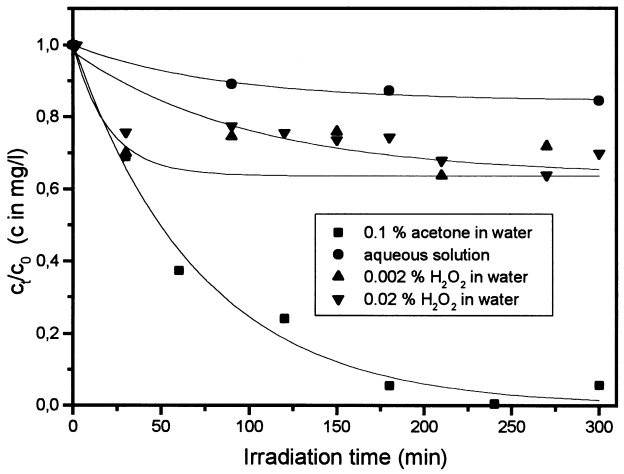

Fig. 2. Photodegradation of Hordalub 500 by UV irradiation (c_t: residual concentration of Hordalub 500, c_0: initial concentration of Hordalub 500).

The degradation of CP was calculated by the following equations [23]:

$$^{de}\mathrm{CP} = \frac{X}{K} \times 100\% \quad (1)$$

$$D = \frac{^{de}\mathrm{CP}}{^{in}\mathrm{CP}} \times 100\% \quad (2)$$

where ^{de}CP is the degraded concentration of CP at irradiation time t, X the concentration of chloride ion (mg/l) at irradiation time t, K the chlorine content (0.3, 0.4, 0.52, 0.56 and 0.62), ^{in}CP the initial concentration of CP at irradiation time $t = 0$ (6 mg/l), and D the degradation (%).

The photolysis curves for Hordalub 500 in four aqueous solutions are shown in Fig. 1, where the observed chloride concentrations are plotted versus irradiation times.

As the concentration of CPs decreased, the concentration of chloride ion and the CP's degradation rate increased (Fig. 1). The curves show a quite fast degradation of Hordalub 500 at the irradiation time up to 60 min, at which point the molecule broke up only at a slow rate until the end of the experiment.

In Fig. 2, the ratio of residual concentration (c_t) to that of initial Hordalub 500 (c_0) is presented graphically as a function of irradiation time.

The largest reaction rate of the Hordalub 500 was observed in the case of 0.1% acetone–water medium within this series (diluted medium with H_2O_2 or without H_2O_2 addition). After 240 min of reaction time, a complete (100%) destruction of the initial CP concentration was achieved. This case can be explained through the condition that the decomposition rate of the investigated CPs was strongly dependent on their complete "solubility". Additionally, acetone in the aqueous phase as sensitizer can promote the rapid oxidation and decomposition of CPs.

The rates of degradation increased with the addition of hydrogen peroxide compared to the pure water solution without H_2O_2 addition. However, the increase of the hydrogen peroxide by factor 10 up to 0.02% influenced only slightly the destruction rate.

More hydroxyl radicals ($^{\bullet}$OH), generated by the irradiation of H_2O_2, can lead again to a regeneration of H_2O_2 by the recombination reaction. Very large hydrogen peroxide or organic substances quantities may shield the UV efficiency. This is certainly one of the reasons why H_2O_2 did not affect so much the oxidation efficiency. Further, it can be considered that the formation of hydroxyl radicals inhibited the action of the middle pressure mercury lamp, because the molar absorption coefficient of hydrogen peroxide lies in the absorption spectrum from 200 to 280 nm [24] and UV radiation of a wavelength of $\lambda < 280$ nm is necessary for an effective split of the hydrogen peroxide into OH radicals. In the absence of H_2O_2, the pure aqueous solution resulted in the lowest decomposition rate of Hordalub 500.

The logarithm of the ratio of the concentrations is plotted in Fig. 3. As expected, the semi-log plots are

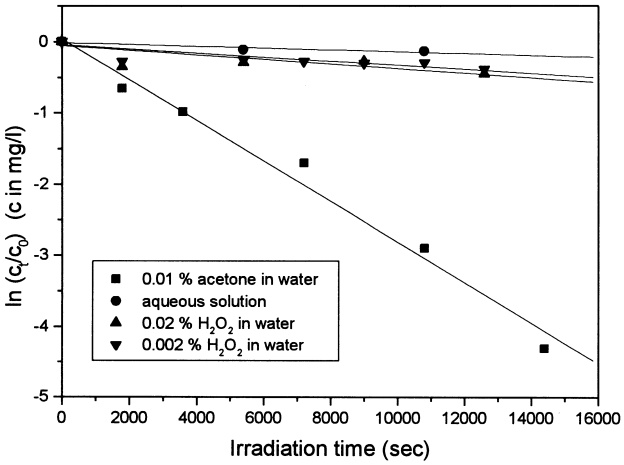

Fig. 3. Kinetics of UV degradation for Hordalub 500 ($\ln(c_t/c_0)$ to irradiation time t).

Table 3
Kinetics of standard CPs from the UV degradation investigations after 300 min irradiation time and calculated half-lives of reaction

CPs	k (s^{-1})	Correlation coefficient (r^2)	$t_{1/2}$ (h)
Aqueous solution with 0.1% acetone			
Hordalub 500[a]	28.5×10^{-5}	0.99164	0.7
Hordaflex LC 50[b]	23.3×10^{-5}	0.944	0.8
CP 40	7.2×10^{-5}	0.95564	2.7
CP 30	6.2×10^{-5}	0.94052	3.1
CP 56	5.1×10^{-5}	0.95771	3.8
CP 52	3.7×10^{-5}	0.96461	5.2
Aqueous solution with 0.02% H_2O_2			
Hordalub 500[a]	3.3×10^{-5}	0.94772	5.8
Hordaflex LC 50[b]	2.5×10^{-5}	0.86125	7.7
CP 40	2.7×10^{-5}	0.91803	7.1
CP 30	3.5×10^{-5}	0.81007	5.5
CP 56	2.4×10^{-5}	0.87881	8.0
CP 52	2.5×10^{-5}	0.90834	7.7
Aqueous solution with 0.002% H_2O_2			
Hordalub 500[a]	2.8×10^{-5}	0.94496	6.9
Hordaflex LC 50[b]	1.6×10^{-5}	0.69336	12.0
CP 40	2.2×10^{-5}	0.87154	8.8
CP 30	2.4×10^{-5}	0.89384	8.0
CP 56	2.1×10^{-5}	0.79499	9.2
CP 52	1.7×10^{-5}	0.81876	11.3
Aqueous solution			
Hordalub 500[a]	–	–	–
Hordaflex LC 50[b]	–	–	–
CP 56	–	–	–
CP 40	1.8×10^{-5}	0.82024	10.7
CP 30	2.0×10^{-5}	0.96029	9.6
CP 52	1.5×10^{-5}	0.7853	12.8

[a] Reaction time: 240 min.
[b] Reaction time: 210 min.

rather linear and the degradation of Hordalub 500 obeyed pseudo-first-order kinetics. The first-order rate constants and respective half-lives of each standard CPs are summarized in Table 3. In the pure water sample, the reaction rate of CPs could not be calculated because of the extremely small degradation rate.

Hordalub 500 and Hordaflex LC 50 in aqueous solution with 0.1% acetone generally showed a faster degradation rate than the other standard CPs. While the half-life of Hordalub 500 and Hordaflex LC 50 was less than 1 h ($t_{1/2} < 1$ h), the half-lives of other CPs ranged between 2.5 and 5.2 h.

The high decomposition rate of Hordalub 500 could be interpreted on the base of its larger chlorine content. The bond energy of C–Cl is lower than that of C–C bond, the Cl ions formed from bond breakage were traced effectively with ion chromatography.

In other standard CPs with low chlorine contents, the photolysis can occur mostly via C–C bond breakage and as a consequence, a slower reaction rate resulted, judged by ion chromatography only.

Physicochemical degradation rates of CPs in water are to be compared with the results of Madeley and Birtley [6] for the biodegradation of CPs. Half-lives of $C_{12}H_{20}Cl_6$ and $C_{16}H_{24}Cl_{10}$ in water were 60 and 100 days, respectively [2]. Consequently, the UV irradiation can be successfully applied for the elimination of refractory CPs in the aqueous phase.

3.3. GC/MS investigation of irradiated chlorinated paraffins

After UV irradiation of CPs and enrichment of the fractions, identification was made by GC/MS. In Figs. 4–6, three typical GC/MS chromatograms depict the photolytic oxidation of Hordalub 500 in terms of irradiation times. The EI mass spectra of the decomposition components were detected with the "full-scan technique" in combination with the "SIM mode". Both techniques were used for the identification of the characteristic peaks for CPs. For the identification of individual decomposition products, the SIM mode was operated at a first window of the retention time period ($t_R \leq 12$ min) for the mass numbers at $m/z = 71$, 85 and 99, which were ascribed to the characteristic C_5H_{11}, C_6H_{13} and C_7H_{15} alkane fragments ($C_nH_{2n+1}{}^+$). In the second window ($t_R > 12$ min), the typical molecular ions for CPs were observed by the mass numbers of $m/z = 75$, 105, 107 and 115 following Junk [25]. The ions of $m/z = 105$ and 107 were classified as the chlorinated alkyl fragments. Junk [25] suggested that the ion at $m/z = 105$ was identical with the fragment $C_5H_{10}{}^{35}Cl$, while its chlorine isotope fragment, $C_5H_{10}{}^{37}Cl$, was found at $m/z = 107$. The significant ions of $m/z = 69$, 83 and 97 were assigned to cyclododecane as internal standard.

After 30 min irradiation time, the decomposition products were identified as the more separated single peaks (Fig. 5), while the initial compound peaks could not be separated, resp., unresolved from each other (Fig. 4). The concentration of Hordalub 500 decreased with further irradiation duration. After a irradiation time of 300 min, no fragment of CP could be detected and ensured the complete degradation (Fig. 6).

3.4. Determination of degradation rate by GC/MS in combination with ion chromatography

The quantification of the irradiated CPs was performed with GC/MS by using cyclododecane as a calibration factor [23]. The results of photodegradation rates of CPs are given in Table 4, which were determined independently by ion chromatography as well as GC/MS.

The photochemical oxidation of Hordalub 500 in 0.1% acetone–water solution determined by GC/MS after 300 min irradiation time agreed rather well with the result of the ion chromatography. The most effective degradation rate of Hordalub 500 in 0.1% acetone–water solution was confirmed under the given test conditions (300 min irradiation) in both experimental series. In the other photolysis experiments, larger deviations occurred between both results.

In general, the degradation values measured by the ion chromatography were lower than their corresponding

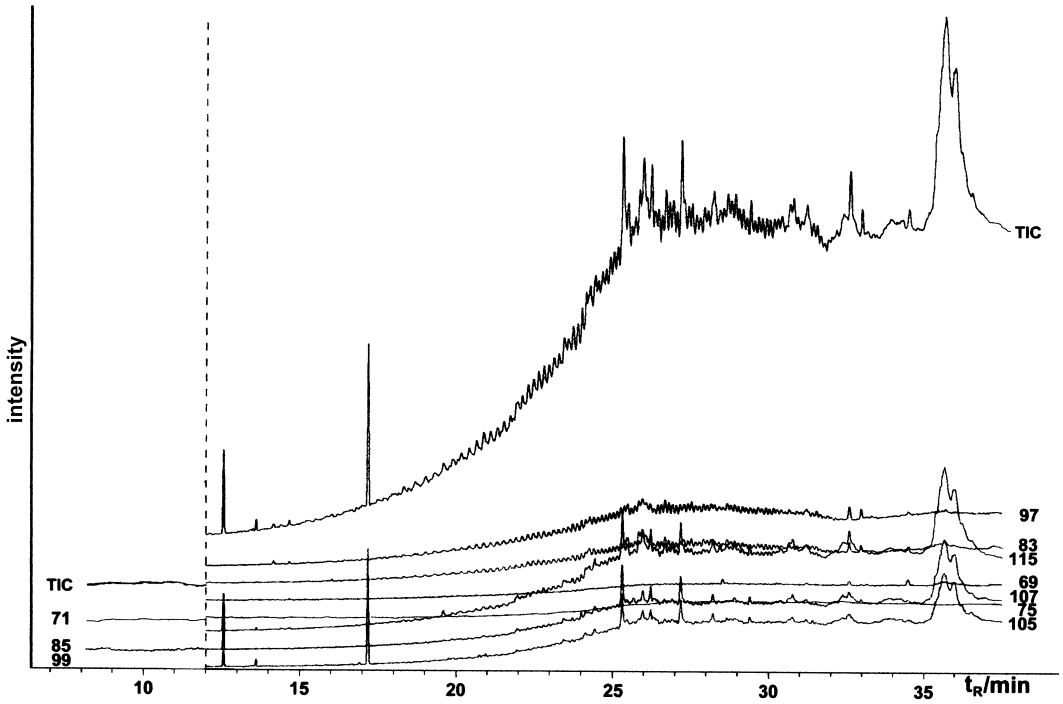

Fig. 4. GC/MS chromatogram of Hordalub 500 at 0 min irradiation time (SIM — $t_R \leq 12$ min: $m/z = 71$, 85 and 99; $t_R > 12$ min: $m/z = 105$, 107, 115, 75, 69, 83 and 97).

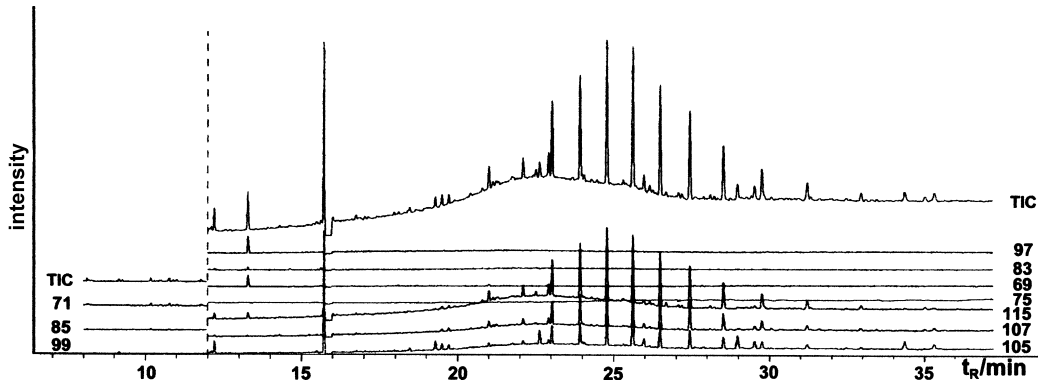

Fig. 5. GC/MS chromatogram of Hordalub 500 at 30 min irradiation time (SIM — $t_R \leq 12$ min: $m/z = 71$, 85 and 99; $t_R > 12$ min: $m/z = 105$, 107, 115, 75, 69, 83 and 97).

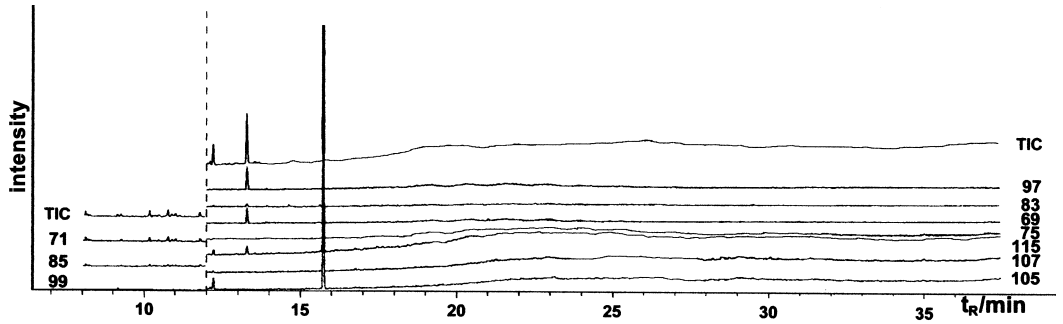

Fig. 6. GC/MS chromatogram of Hordalub 500 at 300 min irradiation time (SIM — $t_R \leq 12$ min: $m/z = 71$, 85 and 99; $t_R > 12$ min: $m/z = 105$, 107, 115, 75, 69, 83 and 97).

Table 4
The degradation rate of CPs determined by GC/MS and ion chromatography

CPs	Irradiation time (min)	Ion chromatography (%)				GC/MS 0.1% acetone (%)
		Aqueous solution	0.002% H_2O_2	0.02% H_2O_2	0.1% acetone	
Hordalub 500	30	11	30	22.8	31.1	58
	300	16	28–36	30–36	100	99.5
CP 56	30	22	26.8	25.5	22	22
	300	30	37	42	62–64	88
CP 52	30	8.4	23.4	21.4	24.4	35
	300	25–27	32	40	56	65
Hordaflex LC 50	30	3	22.3	22	49.6	–
	300	10.4	27	35.1	93–99	–
CP 30	30	16.1	32.8	37.3	35.7	–
	300	32.1	44.6	55.1	67–75	–
CP 40	30	5.7	25.8	25.6	20	–
	300	24	41	46	71–75	–

GC/MS values. In the technique of the ion chromatography, "degradation" is defined only as a formation of Cl^- ion. In the GC/MS method, degradation is interpreted from the "disappearance" of the initial substance only and does not mean necessarily that Cl^- ions are already formed by cleavages of the C–Cl bond.

In a 0.002% H_2O_2 aqueous solution of CP 52 at 300 min irradiation time, a TOC (total organic carbon) value of 2.360 mg/l was determined, of which the initial value ($t = 0$) was 3.544 mg/l. Therefore, the degradation rate could be calculated as 33% and corresponded very well with the degradation rate (32%) determined with ion chromatography (see Table 4).

3.5. Identification of the chlorine content of the chlorinated paraffins

The described procedure with ion chromatography allowed the quantification of the chlorination degrees of the examined chloroparaffins. The chlorine contents were calculated from the ratio of the concentration of chloride ions at 300 min irradiation time divided by initial concentration of CP before the irradiation [23]. Chlorination degrees of investigated standard CPs are shown in Table 5.

Table 5
Chlorination degrees of investigated standard CPs

CPs	Chlorination degrees (percent by weight in w/w)	
	This work (ion chromatography) (%)	Manufacturer's specification (%)
CP 30	23.5–26.4	35
CP 40	32.8	44
CP 52	30.0	52
CP 56	40.2–41.2	56
Hordalub 500	61.2–63.0	62
Hordaflex LC 50	49.2–52.5	52

In the case of Hordalub 500 and Hordaflex LC 50, the "chlorination degrees" determined here correspond very well to the manufacturer's specifications, while the chlorination degrees of the remaining chloroparaffins had a larger deviation from the manufacturer's specifications.

It cannot be excluded that ion chromatography is not sensitive enough to detect minor Cl^- ions in the case of the lower CPs. The shown deviations can be explained also by the fact that higher CPs are generally better soluble in the water phase than those containing lower chlorine amounts. Therefore, the irradiation could be more efficient.

3.6. Identification of photoproducts by GC/MS

The identification of the intermediate products was performed with GC/MS. In order to identify specific structures to the decomposition products, a standard *n*-alkane mixture (C10–C30) was subjected to GC/MS in a separate analysis. In mass spectra of the alkane monitored with SIM mode, molecular ions are presented at $m/z = 71$, 85 and 99. The stable fragment ion ($m/z = 71$) is the basic peak in this mass spectrum.

Fig. 7 represents a GC/MS chromatogram of an aqueous solution of CP 52 before irradiation, in which no unique alkane peak could be identified by comparing the retention times of the *n*-alkane standard.

In diluted solution of CP 52 after 30 min irradiation time, relative small peaks were specifically classified as the long-chain *n*-alkane ions (>C25) (Fig. 8). As illustrated in Fig. 9, the characteristic *n*-alkanes ranging from $C_{25}H_{52}$ to $C_{33}H_{68}$ were traced in the chromatogram of irradiated CP 56 solution at 300 min. The formation of long-chain *n*-alkanes as photoproducts (>C25) is explained on the basis that short-chain fragments combined to long-chain molecules within certain micelles formed by the insoluble CPs in water.

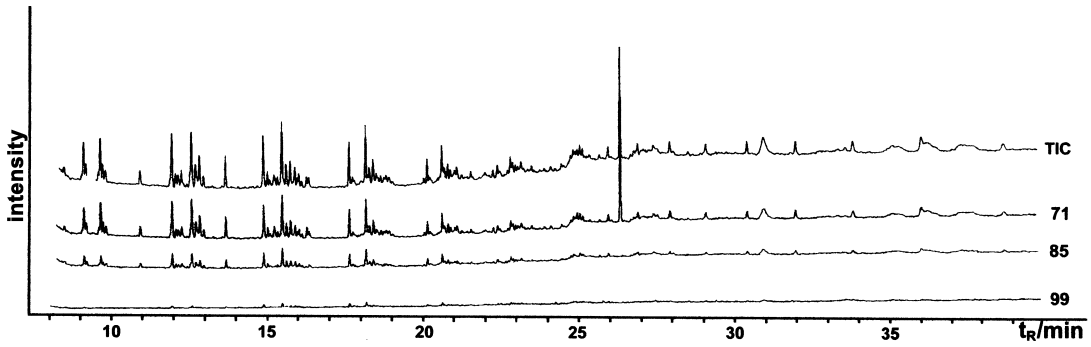

Fig. 7. GC/MS chromatogram of CP 52 at 0 min irradiation time (SIM: $m/z = 71$, 85 and 99).

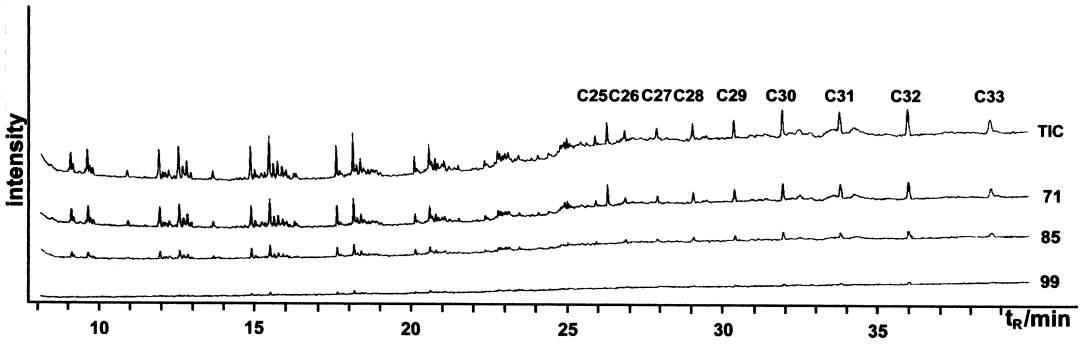

Fig. 8. GC/MS chromatogram of CP 52 at 30 min irradiation time (SIM: $m/z = 71$, 85 and 99), C_n: *n*-alkane with chain length *n*.

Generally in micelles, hydrophobic groups are held inside of two phase structures of surfactant-like molecules. In contrast, hydrophilic groups are located on the surface of large organic molecules in the water phase. Thus, the hydrophobic alkane parts of the molecules stretch inside the spheric micelle, and can combine easily with each other, due to their close vicinity, as soon as they get excited to the radical state!

3.7. Biological toxicity test

The ecotoxicity of chloroparaffin solutions was investigated with the Daphnia, the luminescent bacteria and the algae test. For the sample preparation, acetone as solvent was used to increase the water solubility of CPs. The blank test with 0.1 ml acetone in 1 l water was carried out for Daphnia, luminescent bacteria and algae test. We subjected undiluted concentration of 200 μg/l for CP 30, CP 40 and CP 56, and 100 μg/l for CP 52, Hordalub 500 and Hordaflex LC 50 to the test procedures below.

3.7.1. Daphnia test

The standard CPs were investigated in their action toward Daphnia magna *Straus* in the 24 and 48 h immobilization test, according to standard test protocol of DIN 38412 part

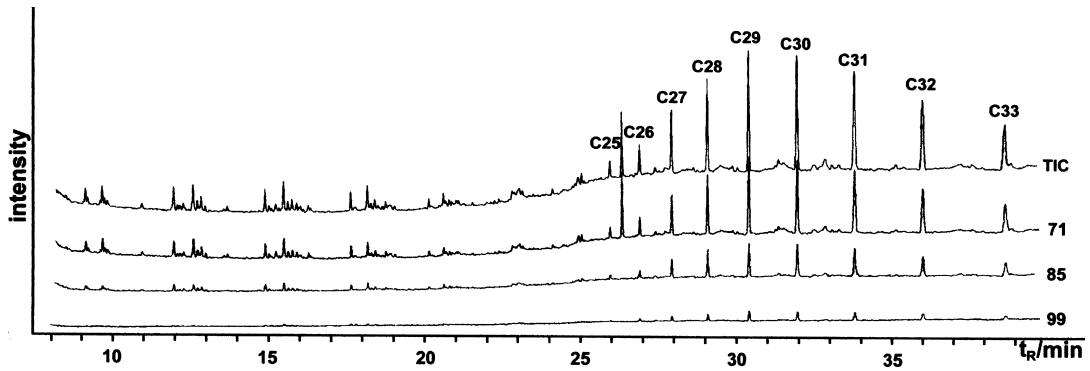

Fig. 9. GC/MS chromatogram of CP 56 at 300 min irradiation time (SIM: $m/z = 71$, 85 and 99), C_n: *n*-alkane with chain length *n*.

Table 6
48 h EC_{50} of the CPs for Daphnia magna

CPs	EC_{50} (μg/l)		EC_0 (μg/l)	
	This work	Literature[a]	This work	Literature[a]
CP 30	152.8	–	130.08	–
CP 40	126.1	–	33.15	–
CP 52	42.0	37.0	<12.5	9.0
CP 56	139.9	138.0	<25.0	28.0
Hordalub 500	74.5	–	65.15	–
Hordaflex LC 50	48.5	–	17.69	≥26

[a] Ref. [31].

11 [27]. For the evaluation of the acute Daphnia tests, the respective EC_{50} values were determined and depicted in Table 6.

In the work of Thompson and Madeley [2,3,32], the acute toxicity (LC_{50}–EC_{50}) in the Daphnia was reported to show value in the range of 14–530 μg/l for short-chain CPs. Most of medium- and long-chain CPs have shown low acute effects at concentrations above the water solubility. However, a study by Frank and Steinhäuser [3,31] appeared where medium CP showed a high acute toxicity of Daphnia with EC_{50} of 37 μg/l. In our study, a significant acute toxicity was found in all samples, in which more than 50% of the Daphnia were damaged in all test series. Floating effects at the surface of the water were observed only in individual cases. They resulted from mechanically undissolved oil slick effects [1,2,31]. The toxicity could not be quantified in the case of the longer chain length of CPs.

The aqueous solutions of CP after photochemical oxidative treatment were examined also with the Daphnia test. The solutions of CPs were prepared in the same concentration as above and irradiated at 300 min. The irradiated CP solutions after 30 and 300 min showed no significant immobility of Daphnia, so the intermediate formed led to no acute toxicity of Daphnia. Consequently, the initial toxicity of chloroparaffins toward Daphnia decreased drastically after photooxidative processing.

In long-term tests (21-day reproduction test), the effect of the CPs on Daphnia was confirmed. Here, a NOEC (no-observable-effects) value was 5 μg/l for short-chain [32] and 4.4–8.9 μg/l for medium-chain CPs [31]. The photochemical oxidation had decreased very efficiently the Daphnia related toxicity.

3.7.2. Luminescent bacteria test

The bioluminescent bacteria test, available under the trade name Microtox®, utilizes the halophile microorganism *Photobacteria phosphoreum* as a selected organism of strain, *Vibrio fischeri*. The luminescent bacteria were obtained from Dr. Lange, GmbH. In this study, a short-term as well as a long-term test was carried out according to "Dr. Lange" method [29] based on DIN 38412 part 34 [30]. Light emission of the luminescent bacteria was determined at 585 nm. In the acute toxicity test, the inhibition effect

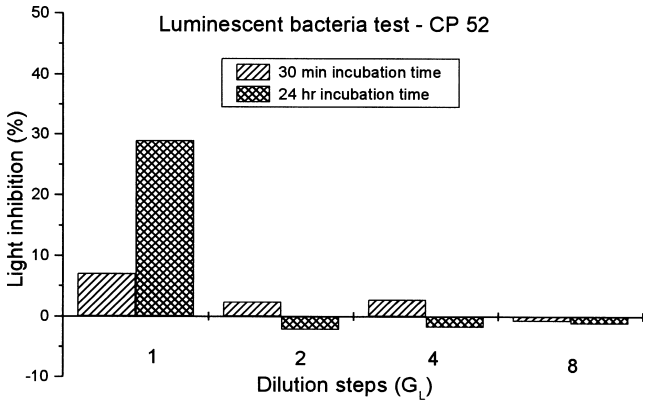

Fig. 10. Luminescent bacteria toxicity of CP 52 after 30 min and 24 h.

of the solution along dilution steps was determined in a contact time of 30 min with the decrease of light intensity compared to the untreated control.

In addition, the chronic toxic effect was determined after a incubation time of 24 h. The result is expressed as G_L-value, describing the necessary dilution step at which an inhibition of less than 20% occurs. As shown in Fig. 10, an acute toxic effect of CP 52 was not observed at 30 min incubation time.

The limited water solubility could play an unknown role here, because the organic molecule could not be absorbed by luminescent bacteria. It is concluded that the luminescent bacteria are relatively little sensitive to CPs as compared to the complex organism Daphnia. Tarkpea et al. [33] report a 30 min EC_{50} as 2.94 mg/l in luminescent bacteria test (*Photobacterium phosphoreum*) with short-chain CP (C10–C13, 49% Cl).

After 24 h incubation to the test, a significant decrease of luminescent emission was observed. In the highest tested concentration (1:1 dilution step), the light intensity was reduced more than 20% as compared to the control.

From these results, it is seen that the chronic toxicity of the CPs is larger than the acute toxicity for luminescent bacteria. For the 24 h long-term test, the undiluted solution of all CP (CP 30, CP 40, CP 52, CP 56, Hordalub 500 and Hordaflex LC 50) showed a G_L-value of 2, while a G_L-value of 1 was determined in the case of the short-term test at 30 min incubation.

After 30 min of incubation time, the photochemically treated samples showed no acute toxicity of CPs at 30 and 300 min irradiation time, so that the various decomposition products of chloroparaffin degradation were obviously of no toxicity for luminescent bacteria.

3.7.3. Algae test

The effect of CPs on the freshwater green alga, *Scenedesmus subspicatus*, was studied according to DIN 38412 part 9 [26]. The cell growth inhibition of algae test was determined by means of a particle counter device. Experiments were run for 72 h. Referring to growth and growth rate, all undiluted and diluted test solution of

chloroparaffins showed no inhibitory effect to algae cells. (Besides an activation of cell growth was observed occasionally against the control culture (inhibition of cell growth <0%).) The "negative inhibition effect" can be interpreted as the effect caused by added nutrients, since the higher nutrient concentration of the test solutions offers favorable conditions for algae growth. Several studies report the toxicity of aquatic plants [1–3]. The calculated EC_{50} values are in milligram/liter range and above its water solubility. In an other investigation, chloroparaffins appeared neither to adsorb on the food algae for Daphnia [31], nor to show a significant toxicity [34]. Nevertheless, a distinct adsorption to the marine alga cells was reported by Thompson and Madeley [35] so that a significant growth inhibition in a marine alga *Skeletonema costatum* was found at 19.6 μg/l of short-chain CPs (C10–C12, 58% Cl). The EC_{50} for cell density were 42.3 and 55.6 μg/l after 4 days exposure, and the EC_{50} for growth rate was 31.6 μg/l after 2 days exposure.

4. Conclusion

Although, in principle, it could be shown here that the UV- and hydrogen peroxide-catalyzed photooxidation proves an efficient method to eliminate the highly refractive chloroparaffins from aqueous samples, a lot of research remains to be undertaken still, before a feasible technology for the large scale application of this method could be developed for practical use: Future research should elucidate the role of potential solubilizer to be added to the rather lipophilic chloroparaffins, like the case described here, where minute amounts of acetone were added. It appears that acetone does not only enhance the solution of the target substances in the water, but does act also as an efficient sensitizer for the photooxidation observed.

Another interesting phenomenon remains to be studied in more detail: The fact that longer chain alkanes are produced by the photooxidation process as intermediates than the chain lengths of the initial chloroparaffins in question, seems to hint to specific (re-)combination reactions of smaller alkyl radical fragments during the reaction, possibly enhanced by the formation of cluster-micelles of the little water-soluble chloroparaffins in the aqueous medium. Though academically interesting as such, it may pose a specific problem to practical applications of the technology described.

The biological test series showed that chloroparaffins were of significant toxicity toward Daphnia m. organisms, after irradiation toxicity could not be discovered anymore. In the case of luminescent bacteria, only a small long-term toxicity was observed — in contrast with a zero acute toxicity towards these microorganisms! — due to a possible accumulation effect of the chloroparaffins in question in the organisms. Again, before a large scale application, a more detailed investigation should be undertaken, especially submitting the various identified intermediates of photooxidation themselves to the above biological tests.

Acknowledgements

We acknowledge the help of Gerd Lammers from Bremer Unweltinstitut greatefully.

References

[1] Beratergremium für Umweltrelevante Altstoffe (BUA) der Gesellschaft Deutscher Chemiker, Chlorparaffine (Paraffinwachse und Kohlenwasserstoffwachse, chloriert), VCH, Weinheim, 1993.
[2] G.T. Tomy, A.T. Fisk, J.B. Westmore, D.C.G. Muir, Rev. Environ. Contam. Toxicol. 158 (1998) 53–128.
[3] WHO (World Health Organization) Environmental Health Criteria 181: Chlorinated Paraffins, Geneva, 1996.
[4] Chlorparaffin-Untersuchungsprogramm I & II, Greenpeace, 1995.
[5] I. Campbell, G. McConnell, Environ. Sci. Technol. 14 (1980) 1209–1214.
[6] J.R. Madeley, R.D.N. Birtley, Environ. Sci. Technol. 14 (1980) 1215–1221.
[7] Oslo and Paris conventions for the prevention of marine pollution, in: Joint Meeting of the Oslo and Paris Commissions, Karlskrona, June 13–17, 1994.
[8] A. Randegger-Vollrath, Fresen. J. Anal. Chem. 360 (1998) 62–68.
[9] M. Coelhan, Anal. Chem. 71 (20) (1999) 4498–4505.
[10] J.I. Hollies, D.F. Pinnington, A.J. Handley, M.K. Baldwin, D. Bennett, Anal. Chim. Acta 111 (1979) 201–213.
[11] B. Jansson, R. Andersson, L. Asplund, Å. Bergman, K. Litzén, K. Nylund, L. Reutergårdh, U. Sellström, U.-B. Uvemo, C. Wahlberg, U. Wideqvist, Fresen. J. Anal. Chem. 340 (1991) 439–445.
[12] B. Jansson, R. Andersson, L. Asplund, K. Litzén, K. Nylund, U. Sellström, U.-B. Uvemo, C. Wahlberg, U. Wideqvist, T. Odsjö, M. Olsson, Environ. Toxicol. Chem. 12 (1993) 1163–1174.
[13] W. Kraemer, K. Ballschmiter, Fresen. Z. Anal. Chem. 327 (1987) 47–48.
[14] E.S. Lahaniatis, H. Parlar, W. Klein, F. Korte, Chemosphere 2 (1975) 83–88.
[15] R. Rieger, K. Ballschmiter, Fresen. J. Anal. Chem. 352 (1995) 715–724.
[16] W. Rotard, W. Mailahn, S. Kühn, A. Hermeneit, S. Hillebrecht, S. Kemmlein, S. Mentzel, Analyse von Chlorparaffinen in Sediment, Muscheln, Krabben aus der Umgebung einer Produktionsanlage, Umedinfo. 7 (1998) 19–22.
[17] P.P. Schmid, M.D. Müller, J. Assoc. Off. Anal. Chem. 68 (3) (1985) 427–430.
[18] G.T. Tomy, G.A. Stern, D.C.G. Muir, A.T. Fisk, C.D. Cymbalisty, J.B. Westmore, Anal. Chem. 69 (1997) 2762–2771.
[19] V. Zitko, J. Chromatogr. 81 (1973) 152–155.
[20] D. Friedman, P. Lombardo, J. Assoc. Off. Anal. Chem. 58 (1975) 703–706.
[21] P. Lombardo, J.L. Dennison, W.W. Johnson, J. Assoc. Off. Anal. Chem. 58 (1975) 707–710.
[22] Å. Bergman, A. Hagman, S. Jacobsson, B. Jansson, M. Ahlman, Chemosphere 13 (2) (1984) 237–250.
[23] I.-O. Koh, Ph.D. Thesis, University of Bremen, Bremen, 2000.
[24] M.S. Morgan, P.F. Van Trieste, St.M. Garlick, M.J. Mahon, A.L. Smith, Anal. Chim. Acta 215 (1988) 325–329.
[25] S.A. Junk, H.-U. Meisch, Fresen. J. Anal. Chem. 347 (1993) 361–364.
[26] DIN 38412 Teil 9 (EN 28692): Europäische Norm: Wachstumshemmtest mit den Süßwasseralgen *Scenedesmus subspicatus* und *Selenastrum capricornutum*, 1993.
[27] DIN 38412 Teil 11: Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung: Testverfahren mit Wasserorganismen (Gruppe L): Bestimmung der Wirkung von Wasserinhaltsstoffen auf Kleinkrebse (Daphnien-Kurzzeittest), 1982.

[28] DIN 38405 Teil 19: Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung: Bestimmung von 7 Anionen mittels Ionenchromatographie, 1988.
[29] Dr. Lange-Testverfahren LUMIS 24 tox Leuchtbakterientest (LCK 486) nach DIN 38412 L34, L341, Dr. Bruno Lange GmbH (Industriemeßtechnik), Düsseldorf, 1998.
[30] DIN 38412 Teil 34 (341): Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung: Bestimmung der Hemmwirkung von Abwasser auf die Lichtemission von *Photoacterium phosphoreum* — Leuchtbakterien-Abwassertest, 1993.
[31] U. Frank, K.G. Steinhäuser, Vom Wasser 83 (1994) 203–211.
[32] R.S. Thompson, J.R. Madeley, Brixham Report No. BL/B/2358, Imperial Chemical Industries PLC, Devon, UK, 1983, cited in [3].
[33] M. Tarkpea, M. Hansson, B. Samuelsson, Ecotoxicol. Environ. Safety 11 (1984) 127–143.
[34] J.S. Craigie, O. Hutzinger, Chemosphere 3 (1975) 139–144.
[35] R.S. Thompson, J.R. Madeley, Brixham Report No. BL/B/2328, Imperial Chemical Industries PLC, Devon, UK, 1983, cited in [3].