# DETERMINATION OF CHLORINATED PARAFFINS IN WATER SAMPLES

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**Abstract**
Wastewater treatment plant influents, effluents and river water samples were analyzed for chlorinated paraffins (CPs). CPs were not detected in filtered water samples. Middle chain chlorinated paraffins were mostly present in suspended solid matter from influents. Measured SCCPs and MCCPs concentrations measured by using ECNI-MS varied between n.d. and 4.6 µg/l.

**Introduction**
Chlorinated paraffins (CPs) are a compound class of chemicals containing 10–30 carbon atoms in a chain with a chlorine grade ranging between 30 and 72%. They are produced by unselective chlorination of *n*-alkane mixtures in the presence of UV-light or at high temperatures (1). They are categorised in short chain (SCCPs, C10–13), medium chain (MCCPs, C14–17), and long-chain chloroparaffins (LCCPs, C18–30). Chlorinated paraffins have been widely used since 1930`s mainly as metalworking fluids, plasticizers and flame retardants and are ubiquitous due to their persistence and wide use.

The acute toxicity of CPs is low (2). In rodent carcinogenicity studies, tested SCCPs produced toxicologically significant dose-related increases in the formation of several tumor types (3). Short chain chlorinated paraffins with an average carbon chain length of 12 and an average chlorination degree of 60% have been classified as "possibly carcinogenic to humans" by International Agency for Research on Cancer (IARC) in the USA (4). SCCPs have been put on the Toxic Release Inventory (TRI) list in USA. In many other countries SCCPs are included in monitoring programs.

As they are mixtures of probably several thousand single compounds showing very poor chromatographic resolution the analysis of them is very complicated. The situation gets much worse by the lack of suitable standards and by the lack of a reliable method that detects all chlorinated paraffins without any discrimination. Especially long chain chlorinated paraffins are either not detectable or very difficult to detect by gas-chromatographic methods due to their high vapour pressures. The mostly used method for analysing chlorinated paraffins is gas chromatography/electron capture negative ion mass spectrometry (HRGC/ECNI-MS). Available technical CP products have usually been used as standards for the quantification of CP residues regardless of their unsuitability as standards. Since CPs are produced having different chemical compositions for different purposes one should not expect that a CP product from any producer is suitable as standard for all chlorinated paraffins patterns in environmental samples. A better way for quantification is to use synthetically produced polychloro n-alkanes which posses the same or similar mass spectrometric peak pattern as in the sample. Since sensitivity in ECNI detection depends greatly e.g. on chlorination number, any CP analysis without considering the suitability of the standard creates high error levels in the results. A disadvantage of using a suitable polychloro alkane standard method is the requirement of numerous standards which are to be measured and compared for pattern matching. This circumstance is rather time consuming.

In the presenting study CPs were analyzed in river water, in treated and untreated wastewater samples.

**Materials and Methods**
Polychlorinated alkanes were synthesized from pure n-alkanes via photochlorination with a sun light lamp in tetrachloromethane at 0°C (5,6). The degree of chlorination was calculated from the increase in weight after the reaction. Cereclor 63L was kindly supplied by Imperial Chemicals (UK). All solvents used were of quality grade for residue analysis and obtained from Merck. Silica gel 60 (63-230 mesh, Merck) was activated at 200 °C for 24 h and deactivated by addition of 3% H2O.

GC/ECNI-MS analyses were conducted using a HP 5890II gas chromatograph with a quadrupole mass spectrometer 5989B using methane as reagent gas. Aliquots (2 µl) of the isooctane extracts were injected in splitless mode onto a split/splitless injector maintained at 280 ºC. An uncoated (Phenomenex) 1.5 m length × 0.25 mm ID quartz column was used. Helium was employed as carrier gas with a flow of 1.0 ml/min. The GC temperature was isothermal at 280 ºC. Mass spectra were obtained in electron capture negative chemical ionization mode with full scan monitoring.

As quantification standard for short chain CPs a mixture of C10-13 with a chlorination degree of 60% was used. Polychloro tetradecane (47% chlorine) (i.e. CP14*47), polychloro pentadecane (50% chlorine), and polychloro hexadecane (46% chlorine) were used as standards for determination of levels of middle chain CPs. The details of the dechlorination method will be published elsewhere.

**Samples**
Water samples were collected at different sites in a European country. In addition to 15 treated and 15 untreated wastewater treatment plant (WWTP) samples, 8 river water samples were collected and analyzed. Samples were preserved using sodium azide at 0.1 mg/l and stored in alumina bottles at 4 ºC before analysis. Suspended solid matter from influent samples were analyzed for CPs since other samples were almost free of suspended solid matter.

**Extraction and Clean up**
Water samples were filtered using a membrane glass fibre filter. Waste water influent samples were also analyzed for retained particles on filter. Filter material with retained particles were extracted using hexane/acetone (1:1, v) for 2 hours in an ultrasonic bath at 60 ºC. After extraction the extract was filtered and evaporated to dryness at rotary evaporator and redissolved in 300 µl of isooctane. Silica gel clean up was performed as described below. Water samples were extracted using phenomenex Strata-X solid phase extraction cartridges. Filtered samples were loaded onto the cartridges at a flow rate of approximately 6 mL/minute using a vacuum manifold. After extraction, cartridges were washed with 5 mL of 15% methanol in Milli-Q water and then dried with air before eluting CPs with 8 mL of tetrahydrofurane:dichloromethane (1:1, v:v) under gravity. The extracts were dried with a gentle nitrogen stream. The residue was dissolved in 300 µl of isooctane and cleaned up on a silica gel column. A pasteur pipette was filled from bottom to top with layers of 0.5 g silica gel (3% water), 0.4 g silica gel containing sodium hydroxide(10%), 0.1 g sodium sulphate and silica gel containing conc. sulphuric acid (40%) and. The extract was loaded quantitatively on the top of column and eluted first with 12 ml of hexane. The second fraction, that contained chlorinated paraffins, was eluted with 7 ml of hexane: dichloromethane (3+1, v). The fraction was blown down with nitrogen and redissolved in 50 µl of isooctane before GC/MS analysis.

**Results and Discussion**
CPs were detected in none of filtered water samples (LOD ≤ 0.10 µg/l). Except three, all suspended solid matter of filtered wastewater influent samples contained CPs at different levels according to ECNI-MS detection (Table 1). Though short chain CPs were detected in two of 15 samples, middle chain CPs were measured in 12 samples. The total ion chromatogram and mass spectrum of a suspended particular matter sample are displayed in Figure 1. Due to coelution of chromatographic separation, all gas chromatographical accessible compounds in sample are eluted as a peak. From the mass spectrum in Figure 1, it is clear that chlorinated paraffins are present in the studied sample, as a comparison of mass spectra of individual polychloro alkanes reveals. If subsequent polychloro alkane chains are contained in the sample, then a mass difference of 14 (methyl group) is observed as a compare of mass spectra of CP10 to CP16 shows. For instance, the ions m/z 312, 326, 340, 354, 368, 382, 396 are generated mainly from $C_nH_{2n-4}Cl_6$ by cleavage of an HCl group, where n rises successively from 10 for dodecane chain to16 for hexadecane chain.

The sum of MCCPs (CP14 to CP16) varied between n.d and 4500 ng/l and that of SCCP in two samples were 600 and 500 ng/l. Since SCCPs were quantified by using a SCCP mixture with a chlorination degree of 60% without considering of peak pattern matching, real levels might be greatly different than the measured concentra-

**Table 1. Concentrations of CPs in influents measured by two methods (µg/l, suspended solid matter)**

| WWTP No. | CP10-13# | CP14# | CP15# | CP16# | CP14-16# | CP10-13* | CP14-16* | CP17-28* |
|---|---|---|---|---|---|---|---|---|
| 1 | <0.1 | n.d. | n.d. | n.d. | n.d. | 0.11 | 0.36 | 0.52 |
| 2 | <0.1 | n.d. | n.d. | n.d. | n.d. | 0.07 | 0.34 | 0.61 |
| 3 | <0.1 | 0.30 | 0.40 | n.d. | 0.70 | 0.28 | 0.97 | 0.26 |
| 4 | <0.1 | 0.20 | 0.25 | n.d. | 0.45 | 0.10 | 0.94 | 0.77 |
| 5 | <0.1 | 0.10 | 0.10 | n.d. | 0.20 | 0.05 | 0.22 | n.d. |
| 6 | 0.60 | 0.70 | 0.65 | 0.30 | 1.65 | 0.28 | 0.89 | n.d. |
| 7 | 0.45 | 0.85 | 0.70 | 0.40 | 1.95 | 0.30 | 1.38 | 1.82 |
| 8 | <0.1 | 1.30 | 1.10 | 0.55 | 2.95 | 0.16 | 0.86 | 0.18 |
| 9 | <0.1 | 1.90 | 1.60 | 1.10 | 4.60 | 0.38 | 1.88 | 0.57 |
| 10 | <0.1 | 0.15 | 0.10 | n.d. | 0.25 | 0.09 | 0.90 | 0.18 |
| 11 | <0.1 | n.d. | n.d. | n.d. | n.d | 0.10 | 0.69 | 0.26 |
| 12 | <0.1 | 0.85 | 0.90 | 0.70 | 2.45 | 0.10 | 1.26 | 0.14 |
| 13 | <0.1 | 0.45 | 0.45 | 0.30 | 1.2 | n.a | n.a | n.a |
| 14 | <0.1 | 0.55 | 0.50 | 0.30 | 1.35 | 0.21 | 0.90 | 2.41 |
| 15 | <0.1 | 0.30 | 0.40 | n.d. | 0.7 | 0.04 | 0.19 | 0.08 |

# ECNI-MS Detection, *EI-MS detection after dechlorination, n.a. not analyzed, n.d. not detected

tions as responses of polychloroalkanes change significantly depending among other things on the chlorination degree, chain length, and ion source temperature. To give an example; if a sample contained polychlorodecanes with a chlorination degree of 69.8% in an amount of say 100 ng the measured value would be (32.1:3.7) * 100= 867 ng if a polychlorodecane with a chlorination degree of 50.2 would be used at an ion source temperature of 150 ℃. If the ion source temperature is 250 ℃, then the value would be even as high as 1380 ng indicating the great importance of the right choice of standard (Table 2).

**Table 2. Relative response factors of chlorinated paraffins in dependence on ion source temperature**

| CP | $N^*_{Cl}$ | mol weight | RF at 150 °C | RF at 250 °C | 150 °C/250 °C |
|---|---|---|---|---|---|
| CP10*50.2 | 3.9 | 275.4 | 3.7 | 1 | 3.7 |
| CP10*60.0 | 5.8 | 342.7 | 14.8 | 4.4 | 3.6 |
| CP10*69.8 | 8.7 | 441.9 | 32.1 | 13.8 | 2.3 |
| CP11*50.2 | 4.3 | 304.1 | 6.3 | 2.6 | 2.4 |
| CP11*60.5 | 6.5 | 379.3 | 14.4 | 5.7 | 2.5 |
| CP11*70.5 | 9.8 | 493.6 | 29.4 | 17.6 | 1.7 |
| CP12*50.2 | 4.7 | 331.9 | 6.4 | 2.3 | 2.8 |
| CP12*59.8 | 6.9 | 406.5 | 13.6 | 6.6 | 2.1 |
| CP12*70.0 | 10.5 | 531.7 | 21.4 | 18.4 | 1.7 |
| CP13*50.2 | 5.1 | 359.7 | 4.7 | 3.6 | 1.3 |
| CP13*60.0 | 7.5 | 442.4 | 7.8 | 9.1 | 0.9 |
| CP13*70.0 | 11.4 | 576.7 | 12.7 | 32.1 | 0.4 |
| CP14*47 | 4.8 | 364.3 | 3.1 | 4.2 | 0.7 |
| CP15*50 | 5.8 | 413.5 | 3.9 | 5.1 | 0.8 |
| CP16*46 | 5.3 | 409.4 | 1.4 | 4.4 | 0.3 |

RF: response factor; Responce of CP10 (50.2% chlorine) at 250 °C was set 1.0, *aver. number of chlorines
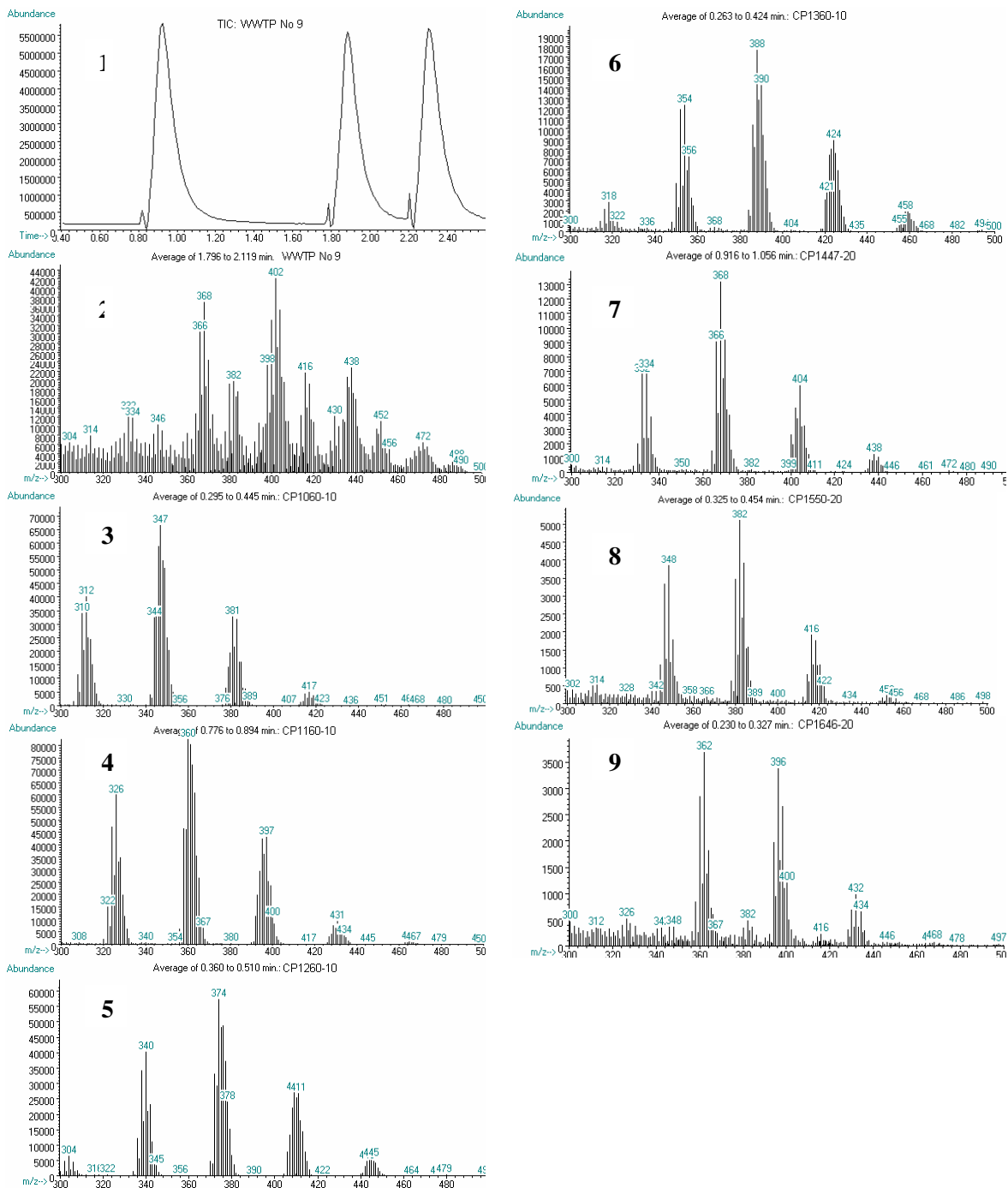
Figure 1: Total ion chromatogram (1) and mass spectrum of WWTP sample 9 (2), mass spectra of CP10*60 (3), CP11*60 (4), CP12*60 (5), CP13*60 (6), CP14*47 (7), CP15*50 (8), and CP16*46 (9)

After completing ECNI-MS measurements all samples were analyzed further by employing a dechlorination method. Detection was performed using GC/MS in EI mode. By this method, detection as well as quantification

was greatly simplified as each alkane chain was recognized without any interference. For giving the results on basis of concentration of a CP the values have to be multiplied by a suitable factor. This factor is the ratio of a defined amount of a CP to the amount of alkane formed after dechlorination. As an example, 100 ng of a CP with 50% chlorination degree would give after dechlorination $[(100-50) + 50/35.453] = 51.4$ ng alkane, so the factor is F= $100/51.41=1.945$ for this case. The appropriate factor depends on the degree of chlorination of the alkane. For SCCPs we decided on a factor of 2.265 that resulted as average value from the factors of a low chlorinated alkane (45% Cl) F= 1.777 and a highly chlorinated alkane F = 3.127 (70% Cl). The value of 2.265 is around in the middle of both low and high ends and corresponds to a CP with a chlorine content of 57.5 %. The factor for MCCPs and LCCPs was set as 1.94 assuming an average chlorine content of 50% for the chlorinated paraffins group in the studied samples.

CPs levels obtained by dechlorination method were markedly lower than using ECNI-MS method. The reason might be using of standards without considering of chlorination degrees.

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