ANALYSIS OF SHORT-CHAIN CHLORINATED PARAFFINS (C_{10}-C_{13}) IN GERMAN RIVER SUSPENDED PARTICULATE MATTER, SEWAGE SLUDGE AND INDUSTRIAL SLUDGE SAMPLES

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Introduction

Chloroparaffins are produced by chlorination of n-alkanes (C_{10}-C_{30}) and are used e.g. as high-pressure additives in lubricants in the metal-processing industry or as softeners in plastics such as polyvinyl chloride (PVC) [1]. Technical chloroparaffins consist of a mixture of straight-chain chloroparaffins of different chain length and degree of chlorination. Because of their physical and chemical features, chloroparaffins are hardly biologically degradable under environmental conditions. In examinations, the toxicity especially of short-chain chloroparaffins (C_{10}-C_{13}) in aquatic organisms as well as the carcinogenic features of this compound class in animal tests could be proved. Therefore, attempts are made on a national and international basis to ban the production and use of short-chain chloroparaffins.

Compared to other chloroorganic compounds only few data on chloroparaffin levels in the environment have been published up to now [2-3]. Because of the complex composition of chloroparaffins the quantification of these substances is very difficult. Thus, no recognised, validated method of analysis for the determination of chloroparaffins in environmental samples exists at the moment, which makes the published data difficult to compare. However, they admit to conclude that chloroparaffins are ubiquitously detectable.

A relatively simple and selective method of analysis for the determination of short-chain chloroparaffins in environmental samples (sludge, suspended particulate matter) has been developed and validated in case of which the quantification is done by GC/MS-NCI. With this method suspended particulate matter from different German rivers and creeks, sewage sludges from municipal sewage plants as well as sludges from industrial sewage plants have been examined for their content of short-chain chloroparaffins.

Methods and Materials

First of all the samples were freeze-dried and 5 g each of the dry sample material were Soxhlet extracted with toluene for 8 hours (which corresponds to about 120 extraction cycles). An aliquot of the resulting raw extract (approx. 2 g of the dry weighed portion) was cleaned from organic matrix contents and sulphur compounds after addition of cis-chlordane as internal standard by means of column chromatography via silica gel/silver nitrate (10 %) and benzenesulphonic acid/silica gel/H_2SO_4 (44 %). In a further cleaning step, the chloroparaffins could be separated by a fractionation with silica gel (1. fraction: n-hexane; 2. fraction: n-hexane/dichloromethane (1:1)) from interfering chloroorganic compounds such as PCBs. In the second fractionation no PCBs

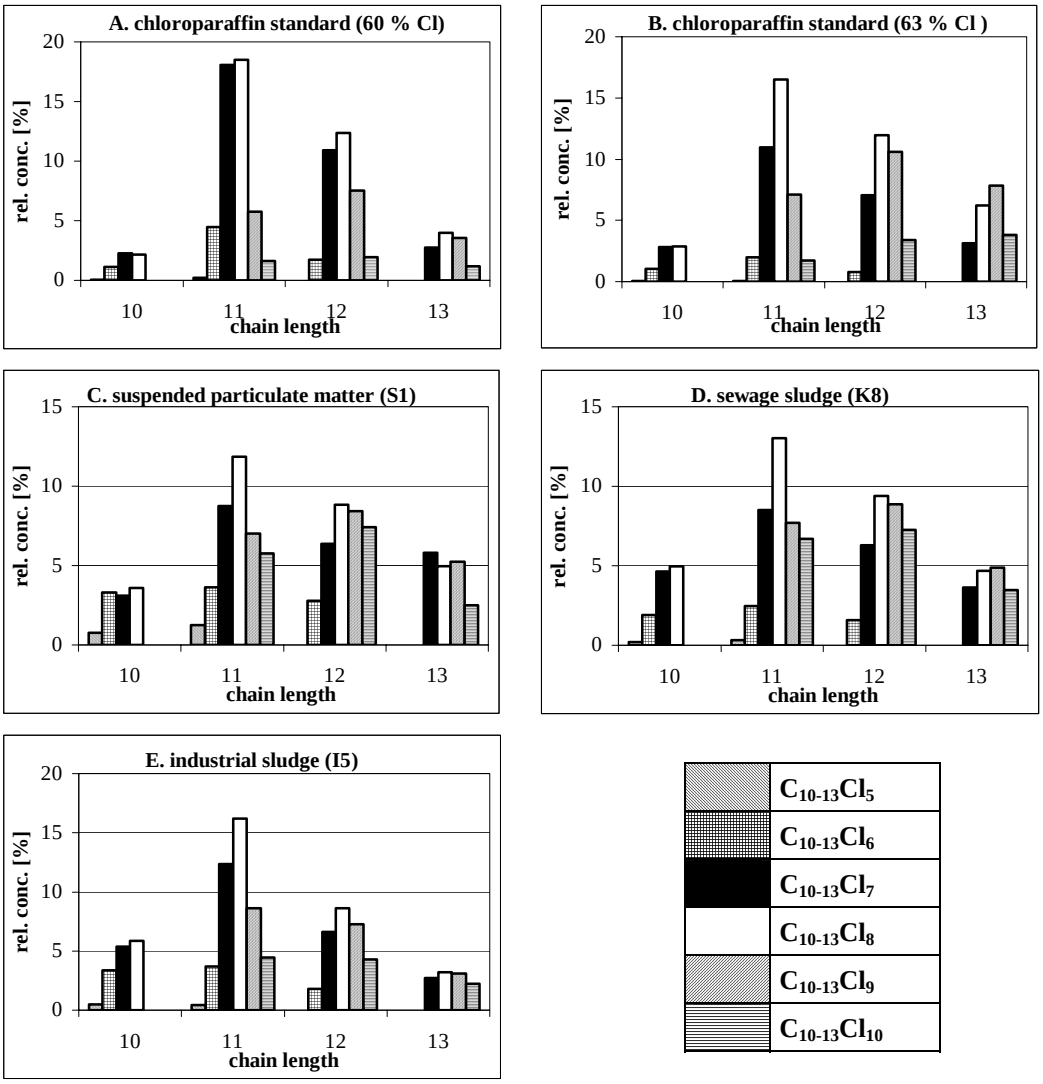
could be detected anymore, while the recovery rate of the chloroparaffins and the internal standard remained above 95 %.
The identification and quantification of short-chain chloroparaffins was done via GC/MS-NCI SIM mode following the Thomy et al. method [4]. The most intense signal of the $[M\text{-}Cl]^-$-fragment ion was used for quantification. For the identification of the individual short-chain chloroparaffin congeners the ratio of the signal intensities of the two most abundant masses (isotope ratio) of the $[M\text{-}Cl]^-$-fragment ion was taken.
The identified short-chain chloroparaffin congeners were quantified by means of the internal standard. The response factors of the individual chloroparaffins relative to the internal standard were determined by means of calibration mixtures. By use of individual calibration functions, the concentration of the short-chain chloroparaffins was determined. For the calibration, C_{10}-C_{13} chloroparaffins with different chlorine contents were available. However, the calibration was made with the standard mixture which was most similar to the chloroparaffin pattern in the analysed samples (compare Fig. 1). Because of the decreasing linearity in the response with increasing chain length and chlorine content, the quantification took place with a second degree calibration function.

Results and Discussion
The concentrations of short-chain chloroparaffins in 6 samples of river suspended particulate matter, 10 municipal and 7 industrial sewage sludge samples were determined by means of the forementioned method of analysis (compare Tab. 1). In case of this method of analysis, the recovery rate of the internal standard in the examined sample extract came up to 80-95 %, the limit of detection (LOD) for the individual chloroparaffin congeners was 1-3 µg/kg. The reproducibility of this method was proven by double and multiple determinations and addition of native chloroparaffins. In case of these examinations, the coefficient of variation ranged between < 1 and 17 % and the recovery rates in the spiked samples ranged between 80-130 %.
In the river suspended particulate matter, chloroparaffin concentrations (C_{10}-C_{13}-calibration standard with 63 % chlorine) of 75-859 µg/kg dry matter could be detected. Compared to published data of the C_{10}-C_{13} chloroparaffin concentrations in river suspended particulate matter or sediments, the concentrations determined here range in the same order of magnitude [2]. In case of the sewage sludge samples C_{10}-C_{13} chloroparaffin concentrations of 206-914 µg/kg dry matter (municipal sewage sludge) and 117-269 µg/kg dry matter (industrial sewage sludge) were measured. These data are significantly lower than data published before [3]. An explanation for this might of course be that the data published hitherto show the results of samples partly taken from the vicinity of chloroparaffin-producing plants. Since 1995 short-chain chloroparaffins have not been produced in Germany anymore, but they are still used. However, alternative products have been developed which might have led to decreasing chloroparaffin contents in environmental samples.
When comparing the determined concentrations in dependence of the used calibration standards, considerable deviations (30-90 %) could be found at slight differences in the chlorine content of the chloroparaffins. Thus, individual standards are needed for the analysis of chloroparaffins in order to increase the accuracy of the quantification.

Table 1. Concentrations of short-chain chlorinated paraffins (C_{10}-C_{13}) in river suspended particulate matter, sewage sludge and industrial sludge (LOD = limit of detection)

C_{10}-C_{13} chloroparaffins	concentration [µg/kg $_{dry\ matter}$]																						
	suspended particulate matter						sewage sludge										industrial sludge						
	S1	S2	S3	S4	S5	S6	K1	K2	K3	K4	K5	K6	K7	K8	K9	K10	I1	I2	I3	I4	I5	I6	I7
$C_{10}H_{17}Cl_5$	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 3	< 1	< 1	< 1
$C_{10}H_{16}Cl_6$	< 4	< 5	< 5	8	< 4	< 6	18	7	8	11	6	6	7	10	16	19	6	< 5	< 4	<12	7	< 5	4
$C_{10}H_{15}Cl_7$	4	4	3	20	2	3	37	12	14	18	7	7	9	27	24	35	5	6	5	9	13	6	5
$C_{10}H_{14}Cl_8$	5	7	4	29	3	4	35	12	20	18	6	6	7	30	20	35	4	10	7	13	14	6	7
Σ C_{10} excl. LOD	**9**	**11**	**7**	**57**	**5**	**7**	**90**	**31**	**42**	**47**	**19**	**19**	**23**	**67**	**60**	**89**	**15**	**16**	**12**	**22**	**34**	**12**	**16**
Σ C_{10} incl. LOD	**14**	**17**	**13**	**58**	**10**	**14**	**91**	**32**	**43**	**48**	**20**	**20**	**24**	**68**	**61**	**90**	**16**	**22**	**17**	**37**	**35**	**18**	**17**
$C_{11}H_{19}Cl_5$	< 1	< 1	< 1	< 1	< 1	< 1	2	1	1	2	1	2	1	1	2	3	1	< 1	< 1	< 3	1	2	1
$C_{11}H_{18}Cl_6$	4	3	3	14	2	3	28	11	10	13	9	10	11	14	20	26	4	6	5	7	8	6	4
$C_{11}H_{17}Cl_7$	9	11	12	70	5	8	95	31	38	37	23	26	29	48	65	86	11	18	14	15	31	14	13
$C_{11}H_{16}Cl_8$	17	20	20	126	9	14	134	52	71	56	25	29	36	89	79	121	17	37	21	26	44	18	21
$C_{11}H_{15}Cl_9$	11	13	11	80	6	10	75	39	58	38	11	13	16	52	35	70	10	25	17	18	24	10	17
$C_{11}H_{14}Cl_{10}$	9	11	9	52	6	9	51	35	49	32	7	9	11	32	19	49	7	16	15	12	11	6	16
Σ C_{11} excl. LOD	**50**	**58**	**55**	**342**	**28**	**44**	**385**	**169**	**227**	**178**	**76**	**89**	**104**	**236**	**220**	**355**	**50**	**102**	**72**	**78**	**119**	**56**	**72**
Σ C_{11} incl. LOD	**51**	**59**	**56**	**343**	**29**	**45**	**385**	**169**	**227**	**178**	**76**	**89**	**104**	**236**	**220**	**355**	**50**	**103**	**73**	**81**	**119**	**56**	**72**
$C_{12}H_{20}Cl_6$	3	2	2	10	1	2	16	7	7	7	5	7	6	9	11	16	2	4	3	< 3	4	3	3
$C_{12}H_{19}Cl_7$	9	9	9	51	4	6	68	21	30	27	19	25	23	43	42	61	8	16	10	28	17	10	10
$C_{12}H_{18}Cl_8$	14	14	14	85	6	9	90	33	48	34	22	28	27	67	52	79	10	26	13	23	24	11	12
$C_{12}H_{17}Cl_9$	14	14	14	90	6	10	77	34	49	31	16	20	19	62	39	66	9	24	12	14	21	9	12
$C_{12}H_{16}Cl_{10}$	12	12	12	63	7	10	52	39	54	29	10	12	12	41	25	49	5	14	12	12	12	6	13
Σ C_{12} excl. LOD	**52**	**51**	**51**	**299**	**24**	**37**	**303**	**134**	**188**	**128**	**72**	**92**	**87**	**222**	**169**	**271**	**34**	**84**	**50**	**77**	**78**	**39**	**50**
Σ C_{12} incl. LOD	**52**	**51**	**51**	**299**	**24**	**37**	**303**	**134**	**188**	**128**	**72**	**92**	**87**	**222**	**169**	**271**	**34**	**84**	**50**	**80**	**78**	**39**	**50**
$C_{13}H_{21}Cl_7$	8	5	9	30	3	4	35	12	22	13	12	15	14	24	25	34	5	11	6	17	7	4	7
$C_{13}H_{20}Cl_8$	8	6	8	42	3	5	37	12	22	12	11	14	13	33	27	34	5	15	5	15	9	5	6
$C_{13}H_{19}Cl_9$	9	7	9	50	3	5	38	13	22	13	9	11	10	35	22	34	4	17	7	10	9	4	7
$C_{13}H_{18}Cl_{10}$	5	6	6	37	3	5	25	15	20	11	6	7	6	24	14	23	3	17	6	7	6	3	6
Σ C_{13} excl. LOD	**30**	**24**	**32**	**159**	**12**	**19**	**135**	**52**	**86**	**49**	**38**	**47**	**43**	**116**	**88**	**125**	**17**	**60**	**24**	**49**	**31**	**16**	**26**
Σ C_{13} incl. LOD	**30**	**24**	**32**	**159**	**12**	**19**	**135**	**52**	**86**	**49**	**38**	**47**	**43**	**116**	**88**	**125**	**17**	**60**	**24**	**49**	**31**	**16**	**26**
Σ $C_{10\text{-}13}$ excl. LOD	**141**	**144**	**145**	**857**	**69**	**107**	**913**	**386**	**543**	**402**	**205**	**247**	**257**	**641**	**537**	**840**	**116**	**262**	**158**	**226**	**262**	**123**	**164**
Σ $C_{10\text{-}13}$ incl. LOD	**147**	**151**	**152**	**859**	**75**	**115**	**914**	**387**	**544**	**403**	**206**	**248**	**258**	**642**	**538**	**841**	**117**	**269**	**164**	**247**	**263**	**129**	**165**

Figure 1: Relative concentrations [%] of the groups of C_{10}-C_{13}-chloroparaffins with 5-10 chlorine atoms in 2 standard mixtures (A. and B.) and 3 samples (C., D. and E.)



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