Occurrence of vinyl chloride and other halogenated C_1- and C_2-hydrocarbons in German surface water

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Summary. In recent time a high sensitive analytical method for the determination of vinyl chloride (VC) in water with a detection limit of 0.4 ng/l has been developed. In this study during October 1989 to April 1990 more than 250 surface water samples of the Western German rivers Rhine (78 samples), Main (22), Lippe (54), Ruhr (60), Wupper (36) and from the river Saale (4) on the territory of the German Democratic Republic were taken. The sampling locations were spread over the course of the rivers to get longitudinal profiles. All samples were analysed for VC and furthermore for other halogenated C_1- and C_2-hydrocarbons, such as dichloromethane, 1,1-dichloroethene, cis- and trans-1,2-dichloroethene, 1,2-dichloroethane, trichloromethane, trichloroethene, 1,1,1- and 1,1,2-trichloroethane, tetrachloromethane, tetrachloroethene, bromodichloromethane, dibromochloromethane, tribromomethane, 1,1,1,2- and 1,1,2,2,-tetrachloroethane.
Thereby the contents of vinyl chloride varied between lower 0.4 ng/l to 400 ng/l in the Western German rivers, while the higher levels found in the river Lippe were caused by wastewater influents from VC/PVC-production plants. Tri- and tetrachloroethene were detected in more than 90 % of the Western German surface water samples, while levels in the lower or sub–µg/l-range were found. Trichloromethane was found in some samples in the µg/l-range. The other substances were either not detectable or only found as traces in some samples. Illustrating longitudinal profiles of the river Lippe are given for the substances vinyl chloride, tri- and tetrachloroethene.
On the other hand VC was determined in the river Saale up to 69 µg/l. Concentrations for other halocarbons reached to 54 µg/l (trichloroethene), 16 µg/l (tetrachloroethene), 31 µg/l (1,1,2-trichloroethane) or 10 µg/l (1,1,2,2-tetrachloroethane).

Introduction. Halogenated hydrocarbons are released into the environment and reach humans by several pathways. They are considered to be one of the criticalst substance-classes the water economy, especially the drinkingwater supply, are confronted with [5, 6, 16, 27, 28].
Vinyl chloride, which is known to be a potent human carcinogen, is a synthetic chemical with no natural sources. Since several years, the estimated yearly production of vinyl chloride has been more than 10 million t worldwide and approximately 1 million t in the Federal Republic of Germany [14]. Most of the vinyl chloride is polymerized. Because of limited release to areas where vinyl chloride is produced and used and rapid degradation in the atmosphere it does not occur widely in the environment. In relation to other C_1- and C_2-halocarbons it is a relatively rare contaminant in ground and surface waters, with higher levels found in ground water. Here it occurs as a metabolist of tetra- and trichloroethene during the anaerobic biodegradation of these contaminants. Vinyl chloride released to surface waters migrates to the atmosphere in a few hours or days, where it undergoes photochemical degradation [2, 26].
The multiple halogenated volatile hydrocarbons can be determined very sensitively by gas chromatography with an electron capture detector. The monochlorinated vinyl chloride shows less sensitivity using this analytical technique. So information about the occurence of vinyl chloride in the

1990

aquatic environment was limited to higher concentrations in the µg/l- to mg/l-range found at industrial releases, workplace studies or in problem landfills.
Using a recently developed highly sensitive method the studies could be extended to trace analysis of VC with a detection limit of 0.4 ng/l [29].

Experimental

During October 1989 to April 1990 more than 250 water samples of the rivers Rhine (78 samples), Main (22), Lippe (54), Ruhr (60), Wupper (36) and Saale (4) were taken and analysed. The study of each river took almost about two to three weeks. During this time water samples were taken over the whole course of the rivers at points from spring downstream and of some confluents. Areas showing higher contaminations or sudden increases were analysed intensively by a follow-up examination.

Water samples for vinyl chloride analysis were taken in graduated 1-l-conical-shoulder-bottles with ground joints 29/32, samples for determination of other halogenated C_1- and C_2-hydrocarbons in graduated 50-ml-bottles with screw cap and a PTFE-coated silicone seal. Most of the samples were taken at the riverbank. Thereby sample bottles were dipped 5 to 10 cm into the running water and closed underwater so that no headspace remained in the bottles. Samples from the middle of a river were taken from bridges with a steel bucket and the sample bottles were filled in the same way from the bucket. All samples were transported under refrigeration and darkness and analysed on the same or next day. Furthermore the temperature of the water was recorded each time.
Vinyl chloride was enriched by stripping a 1-l-sample, adsorbed at activated charcoal, derivatizised to 1,2-dibromochloroethane and then determined by gaschromatography with an electron capture detector [29]. Other halogenated C_1- and C_2-hydrocarbons (detection limits in ng/l are given in parentheses), such as dichloromethane (500), 1,1-dichloroethene (500), cis- and trans-1,2-dichloroethene (6000, 4000), 1,2-dichloroethane (200), trichloromethane (40), trichloroethene (25), 1,1,1- and 1,1,2-trichloroethane (20, 40), tetrachloromethane (4.0), tetrachloroethene (10), bromodichloromethane (10), dibromochloromethane (15), tribromomethane (90), 1,1,1,2- and 1,1,2,2,-tetrachloroethane (20, 30), were extracted from a 40-ml-sample with 4.0 ml of pentane and also analysed by capillary-gaschromatography [12].

Results and discussion

Rhine. The river Rhine and his confluents are one of the most intensively studied surface waters, both by routine-analysis and separate studies [1, 3 a-d, 6, 9-11, 15, 17-24]. During this study the section between Karlsruhe (km 362) and Emmerich (km 857) was investigated at 78 sample locations at both river banks during March 1990. Vinyl chloride was determinated almost below 10 ng/l, but with higher levels of up to 31 ng/l at Nierstein. Furthermore increasing values for VC on the right bank of the Rhine were detected at Wesel caused by the river Lippe, flowing into the Rhine here. Tri-, tetrachloroethene and 1,1,1-Trichloroethane were found in all samples. The concentrations varied between 25 and 120 ng/l, 50 and 200 ng/l or 20 and 210 ng/l, respectively. However, priority contaminations were not observed like in the other rivers. The occurrence of trichloromethane (4.4 µg/l) was studied at the left bank at Worms. Increased values at the left bank were detectable more than 150 km downstream. Tetrachloromethane ranged almost below 20 ng/l, but higher values were found behind the mouth of the Main (see Tab. 1).

Main. The river Main, the most important confluent of the Rhine, can be described as high contaminated with volatile halogenated hydrocarbons [3, 9-11, 14, 17, 21]. In the course of this investigation 22 samples were taken at high water levels in February and March 1990. This involved in relation to normal water levels low concentrations for the volatile halocarbons. The concentrations were below 4 ng/l (vinyl chloride), 20 ng/l (trichloroethene) or 50 ng/l (tetrachloroethene), with higher values only found at Rüsselsheim (see Tab. 1).

Lippe. The river Lippe, a right confluent of the Rhine with a whole lenght of 226 km and passing the north of the Ruhr District, was studied during October and November 1989 with a total of 54 sampling places (Fig. 1). The longitudinal profile of the Lippe (Fig. 2 a-c) shows contaminations with tri-, tetrachloroethene and vinyl chloride at the industrial area around Marl, Dorsten and Wesel. The contaminations are caused by waste waters of the chemical industry producing or processing these solvents, VC and PVC in the region around Marl. The waste water from the synthesis of VC varied between 0.012 and 0.38 mg/l VC, the waste water from a PVC production plant between 0.97 and 13.8 mg/l VC. Furthermore, local concentration maxima were observed in the upper course of the Lippe caused by the tri- or tetrachloroethene pollutions of the confluents Pader (1.3 μg/l trichloroethane) and Thune (9.3 μg/l tetrachloroethene).
The obvious supposition is, that the river contamination takes place continuously. The higher concentrations of tri- and tetrachloroethene in the upper course of the Lippe are mainly reduced by the increasing dilution. The level of trichloroethene is reduced to less than 40 % from 740 ng/l (sample 3) to 280 ng/l (sample 5) over a flow distance of only 20 km and a further reduction to 120 ng/l (sample 7) after another 15 km. In sample 15 only 5 % of trichlorethene in relation to sample 3 were observed. The same process takes place with tetrachloroethene, which is reduced to less than 30 % from 970 ng/l (sample 4) to 290 ng/l (sample 7) over a flow distance of 25 km.
The levels of tri- and tetrachloroethene in the lower course, which is caused by the contamination at Marl, show a much lower reduction than in the upper course. The concentrations are reduced from 1100 ng/l trichloroethene or 890 ng/l tetrachloroethene (sample 33) to 520 ng/l or 440 ng/l (sample 41) over a flow distance of 40 km. The maximum VC-concentration of 400 ng/l (sample 31) is reduced to more than the half after a flow distance of 15 km; after another 15 km again (120 ng/l, sample 39). So in relation to tri- and tetrachloroethene, the VC-levels are reduced much faster - down to 30 % over the flow distance of 40 km.
Because the dilution process is much lower here, the evaporation into the atmosphere is mainly responsible for the reduction of the concentrations. The halflife periods $T_{1/2}$ in a watercourse were calculated by Scherb [26] to be 0.92 h (vinyl chloride), 3.14 h (trichloroethene) or 3.64 h (tetrachloroethene), whereas $T_{1/2}$ for high volatile halocarbons in water without atmospheric evaporation were calculated to be between some month up to some years [13, 30]. The partition coefficients water/air at 20 °C were measured to be 0.02 (vinyl chloride, 10 °C), 2.74 (trichloroethene) or 1.22 (tetrachloroethene) [30]. So the faster reduction of the VC-levels can be explained by its more rapid transfer into the atmosphere.
The levels of vinyl chloride were approximately one decade lower than that observed in 1977 by Bauer [6, 7] in the same river. Levels for tri- and tetrachloroethene were in the same range as found during routine analysis in 1987 [22].

Ruhr. The river Ruhr, also a right confluent of the Rhine, with a length of 235 km passes the industrial region Ruhr District nowadays at the south and is primarily used for drinking water supply, but not for industrial wastewater disposal. The river, his (artifical) lakes and some confluents were studied by a total of 60 samples taken from spring downstream during February and March 1990. Except of three samples trichloroethene was determined in all samples, while the concentrations varied between 13 and 310 ng/l. Tetrachloroethene was found in all samples between 5 to 600 ng/l. The concentrations of vinyl chloride varied almost between lower 0.4 and 5.0 ng/l. Only in the Hengsteysee higher levels were found up to 60 ng/l. This value was proved by a follow-up examination. Higher levels of tri- and tetrachloroethene were found in the confluent Hönne (1100 ng/l each for tri- and tetrachloroethene) and in the surface water of the Ruhr near the bank at Fröndenberg (2200 ng/l tetrachloroethene). Here the contamination can be explained by a local subsoil passage from a nearby groundwater contamination. Higher levels of trichloromethane were found at Arnsberg (4.0 μg/l), and reduced to 0.15 μg/l at Schwerte.
Nevertheless the surface water of the Ruhr must be classified as only low contaminated with volatile halocarbons. The levels were in the same range as found during routine analysis [4].

Wupper. The river Wupper has a length of 114 km, passes the industrial region around Wuppertal and flows into the Rhine at Leverkusen. 36 samples of the river were taken in November and December 1989. In the upper course down to Oberbarmen the river shows only low contamination

with volatile halocarbons. At Barmen and Elberfeld the concentrations of tri- and tetrachloroethene reached levels of 2900 or 2000 ng/l, respectively. Vinyl chloride was found up to 69 ng/l. These increased concentrations were confirmed by a follow-up-examination, where similar levels of vinyl chloride and 3300 ng/l (trichloroethene) or 2500 ng/l (tetrachloroethene) were measured at the same locations. Behind Solingen the levels for both chemicals were reduced to lower 500 ng/l again. Most probably, the river contamination is a consequence of waste water influents from the chemical industries, which produce among other goods lacquers in this region. High values of trichloromethane of up to 36 µg/l and the occurence of other haloforms (see Tab. 1) were observed at Cronenberg behind the sewage plant of Ruthenbeck.
The levels found during this study were higher than those found during routine analysis from official laboratories [22]. The river Wupper in the region of Wuppertal is higher contaminated with volatile halocarbons (except vinyl chloride) than the other investigated Western German rivers during this study.

Saale. In comparison to the concentrations found in the rivers of the Federal Republic of Germany, some samples were taken from the river Saale, which passes an industrial area in the German Democratic Republic. The examination was limited to four samples taken on 30th March 1990 at Naumburg, Großkorbetha, Leuna and Korbetha. Between the third and fourth place one of the greatest chemical work plants of the German Democratic Republic is located at this river. While the concentrations found in the first three samples varied at levels equivalent to those found in some of the higher contaminated rivers described in this study like Lippe or Wupper, the levels in the fourth sample reached extreme values for some substances (see. Tab. 1).
These contaminations are caused by missing sewage treatment or technical deficiences in the plants.

Conclusion

Almost one measurement per cross-section is usually not sufficient for a representative diagram of the water quality of a river, because substances discharged at a river bank may be completely mixed across the whole cross-section at a distance of more than 100 km downstream [25]. Moreover the levels found during this study are still spot-checks and represent only an instantaneous value, concentration-variation over the time was not studied. Nevertheless, the levels found can be used to assess the situation of contamination of German surface water with volatile halogenated hydrocarbons.

Higher levels of vinyl chloride in German surface water were only detected as a result of direct waste water influents from industrial plants producing or processing with vinyl chloride or polyvinyl chloride. Values for other volatile halogenated hydrocarbons are in the same ranges as found in other studies [14].

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Tab. 1: Highest levels of some halogenated C_1- and C_2-hydrocarbons found in the rivers Rhine, Main, Lippe, Ruhr and Wupper [Federal Republic of Germany] and Saale [German Democratic Republic] during this study (confluents are not considered)

Substance [µg/l]	Rhine	Main *)	Lippe	Ruhr	Wupper	Saale **)
Vinyl chloride	0.031 (Nierstein)	0.008 (Rüsselsheim)	0.40 (Marl)	0.060 (Hengsteysee)	0.069 (Wuppertal)	69 (Korbetha)
Tetrachloroethane	0.20 (Dinslaken)	0.21 (Rüsselsheim)	0.97 (Paderborn)	0.51 (Langschede)	2.5 (Wuppertal)	16 (Korbetha)
Trichloroethene	0.12 (Worms)	0.10 (Rüsselsheim)	1.1 (Marl)	0.31 (Hengsteysee)	3.3 (Wuppertal)	54 (Korbetha)
Tetrachloromethane	0.063 (Wiesbaden)	<0.004	<0.004	0.080 (E.-Werden)	0.073 (Wuppertal)	0.029 (Korbetha)
1,1,1-Trichloroethane	0.21 (Lülsdorf)	<0.020	<0.020	0.62 (Arnsberg)	0.45 (Wuppertal)	<0.020 (Korbetha)
1,1,2-Trichloroethane	<0.040	<0.040	<0.040	<0.040	<0.040	31 (Korbetha)
1,1,1,2-Tetrachloroethane	<0.020	<0.020	<0.020	<0.020	<0.020	0.14 (Korbetha)
1,1,2,2-Tetrachloroethane	<0.030	<0.030	<0.030	<0.030	<0.030	10 (Korbetha)
Haloforms:						
Trichloromethane	4.4 (Worms)	<0.040	<0.040	4.0 (Arnsberg)	36 (Cronenberg)	1.3 (Korbetha)
Bromodichloromethane	0.030 (Mainz)	0.025 (Rüsselsheim)	<0.020	<0.020	0.066 (Cronenberg)	0.14 (Korbetha)
Dibromochloromethane	<0.015	<0.015	<0.015	<0.015	0.033 (Cronenberg)	0.34 (Korbetha)
Tribromomethane	<0.090	<0.090	<0.090	<0.090	0.28 (Cronenberg)	<0.090 (Korbetha)

*) The river Main was examined during a high water situation.

**) Only four samples of the river Saale were taken.

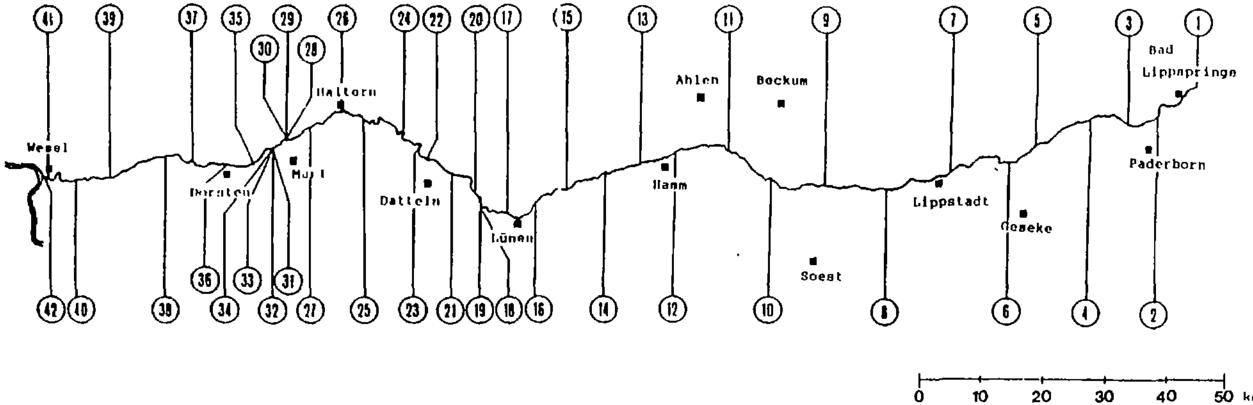

Fig. 1: Sampling profile of the river Lippe (FRG)

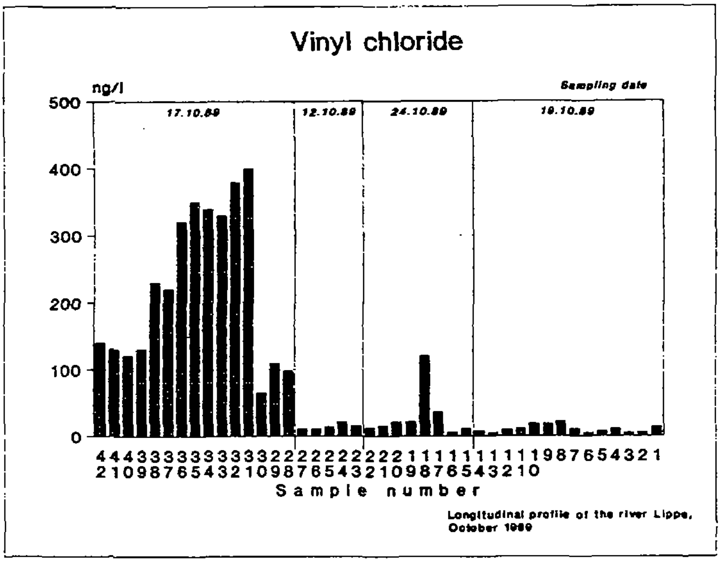

Fig. 2 a: Occurence of vinyl chloride in the surface water of the river Lippe

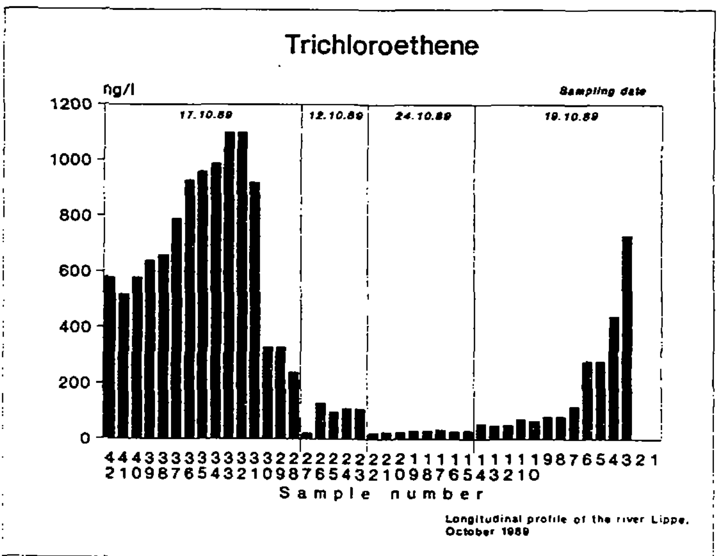

Fig. 2 b: Occurence of trichloroethene in the surface water of the river Lippe

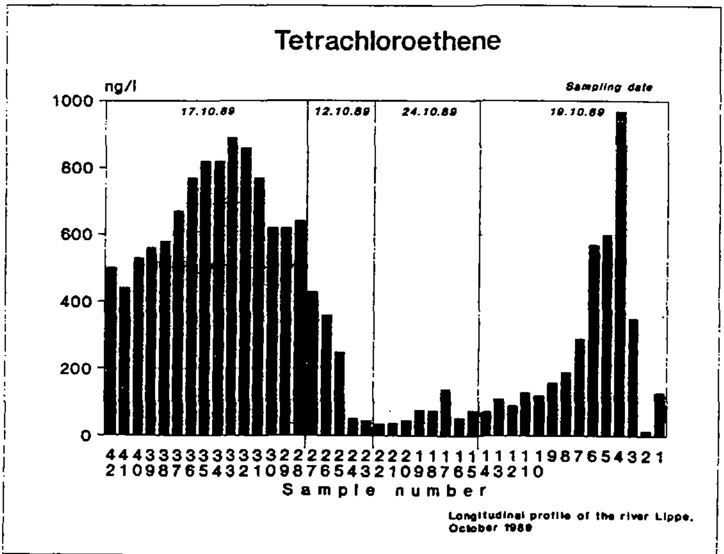

Fig. 2 c: Occurence of tetrachloroethene in the surface water of the river Lippe