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ORIGINAL PAPER

Chloroform in runoff water—a two-year study in a small catchment in Southeast Sweden

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Abstract Chloroform concentrations were observed and input and output fluxes estimated over a 2-yr period in a small coniferous catchment (0.22 km^2) in southeast Sweden. Water discharge was measured daily, and runoff water was sampled bi-weekly for chloroform analysis. An approximate chloroform budget was calculated, which indicated that the annual output of 6 $\mu g\ m^{-2}\ yr^{-1}$ was approximately six times higher than the input, inferring an internal source of chloroform in the catchment. To the best of our knowledge, neither flux estimates nor mass balances have previously been made for chloroform on a catchment scale, nor have data regarding natural runoff variation with time been gathered. Concentrations of chloroform in runoff were found to be generally high during wet periods, such as spring, but also peaked during summer rain events. The observed pattern suggests that chloroform is formed in surface soil layers and transported to the outlet under high-flow conditions and during dry-period rain events; it is lost through degradation or evaporation during drier periods due to longer soil water residence times. The data suggest that the variation among replicates increases with concentration; this emphasizes the need to know what the degree of on-site variation is, so one can collect a sufficient number of replicates to permit detection of spatial or temporal changes.

Keywords Biogeochemistry · Catchment · Chloroform · Water · VOCl

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Introduction

Chloroform has been detected in oceans, surface water, and groundwater as well as in snow, rain, soil, and air, which suggests that it is ubiquitous in the environment (Harper 1985; Laniewski 1998; Khalil 1999; Nikolaou et al. 1999; Squillace et al. 1999; Laturnus et al. 2000; Ballschmiter 2003; Cox et al. 2004). There is strong evidence that chloroform is naturally formed in soil and subsequently transported to air and groundwater (Hoekstra et al. 1998; Khalil and Rasmussen 2000; Haselmann et al. 2000a, b; Dimmer et al. 2001). The finding that chloroform is produced naturally has raised concern, since it is toxic and

natural sources seem to be as significant as anthropogenic sources (Boorman et al. 1999; Bove et al. 2002; Laturnus et al. 2002).

Even though there is indisputable evidence that chloroform is formed naturally, few field measurements have been made of chloroform in air, and even fewer of chloroform in water bodies in remote areas. Previous studies of naturally occurring chloroform in surface water, soil, and air have generally been based on single or only a few samples collected on each sampling occasion or at each site. Thus, previous conclusions regarding underlying natural formation processes and transport estimates have been derived from rather few field concentration measurements or by extrapolation from laboratory data.

It is well known that the chemical composition of soil and soil water varies greatly over time and in space. Hence, it is necessary to know the extent of the on-site variation in chloroform concentration before it is possible to reliably estimate (i) the magnitude of the natural production of chloroform in soil, (ii) the transport from soil to runoff water, and (iii) how the concentration in various environmental compartments varies over time and in space and why.

The aim of the present study is (i) to describe the on-site variation in chloroform concentration in precipitation and runoff from a small catchment, (ii) to estimate the magnitude of chloroform transport via wet deposition and runoff, and (iii) to discuss potential chloroform sources in light of observed patterns.

Material and methods

Catchment description

The studied catchment is situated in southeast Sweden (58°44′ N, 16°21′ E) (Fig. 1). The site is approximately 50 km from the Baltic Sea and the catchment is located in an area subject to no direct industrial impact. The catchment area is approximately 0.22 km^2 and is in the southern part of a larger catchment area previously described as the Stubbetorp catchment (Maxe 1995). The topography is broken and the bedrock contains little chloride (Maxe 1995). The catchment is forested and dominated by pine (*Pinus sylvestris* L.) and Norway spruce (*Pieca abies* L.). Water discharge has been measured in the Stubbetorp catchment for 10 yr and precipitation has been measured continuously since 1951 by the Swedish Meteorological and Hydrological Institute (SMHI) at Simonstorp Station, 5 km west of the catchment. The long-term actual mean precipitation for the 1951–1980 period is 696 mm yr^{-1}, compensating for measurement losses using SMHI's correction factors (Eriksson 1983). The precipitation in the catchment was measured from 1986 to 1990 and the actual precipitation was found to be 688 mm yr^{-1} (Maxe 1995). A more detailed description of the hydrochemistry of the Stubbetorp catchment can be found in Maxe (1995).

Sampling procedures

Runoff measurements

In 1987, a stainless steel V-notch weir was installed at the outlet of the catchment (hereafter denoted as "spring") to measure the water discharge from the catchment. The weir was installed 1 m downstream from a spring, so the runoff water had little contact with the air. The water level was continuously registered between January 2003 and December 2004 with the aid of a gauge (pegel, A. Ott, Kempten, Germany), except in June 2004 due to technical problems. The water level was interpolated for the flux measurement during this period. The water discharge was calculated using a discharge rating curve, and average daily discharge was calculated (Fig. 2) for the 2003–2004 period. Periods when there was no change in water level are considered to be "normal" as no obvious technical problem was observed and because the same pattern was observed in previous water discharge measurements made from 1987 to 1996 (Maxe 1995).

Precipitation samples

Precipitation collectors ($n = 9$) were installed consistent with environmental monitoring standards in Sweden (Naturvårdsverket 2003). The collectors were placed at a height of 160 cm in an

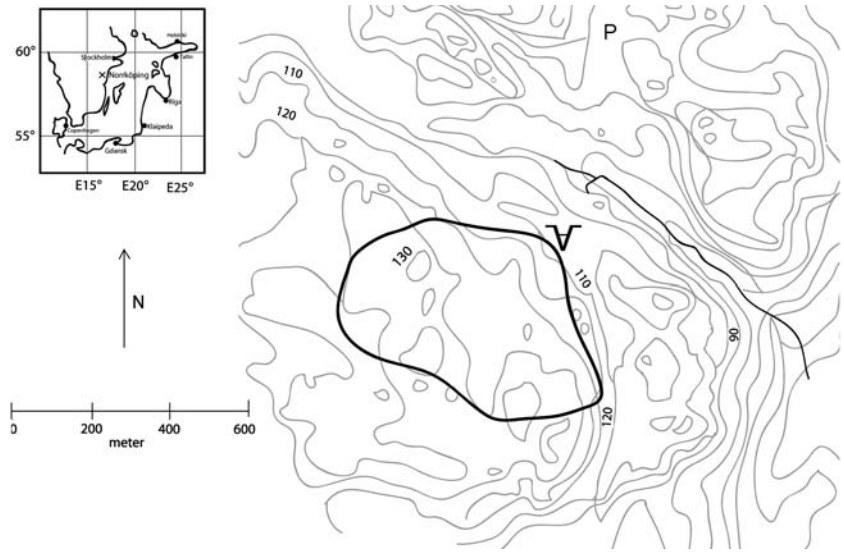

Fig. 1 The catchment area in southeast Sweden (58°44′ N, 16°21′ E) is approximately 0.22 km^2. Runoff water samples were collected at the weir marked with a V at the map. The precipitation collectors are located 300 m north of the catchment, marked with a P at the map

open field 300 m north of the catchment and spaced at least 3.5 m apart. To avoid the influence of surrounding trees, the collectors were situated so as to obtain an angle of at least 30° between the rain sampler and the tree tops. Precipitation samples were collected on six occasions from October 2004 to September 2005, with sampling periods of 9–19 days. Precipitation was collected

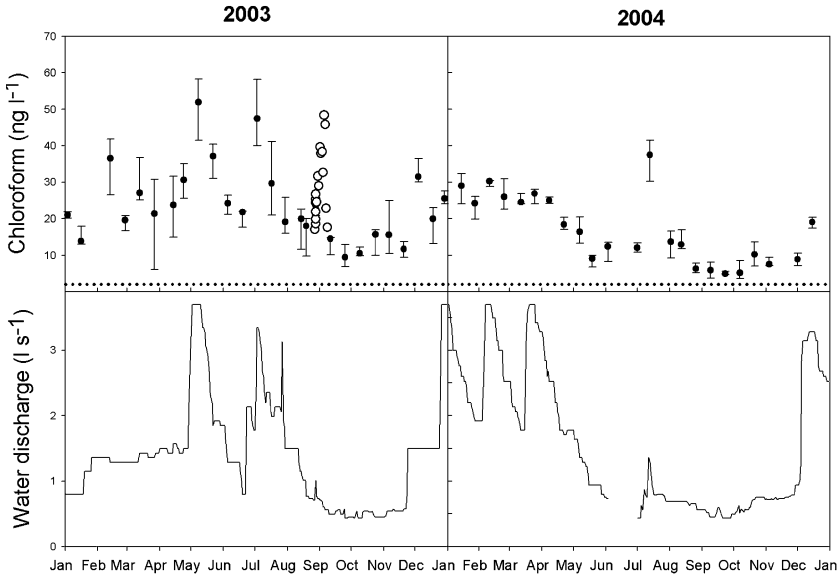

Fig. 2 Chloroform concentration (minimum, average, maximum, n = 5–6 on each sampling occasion) measured in the catchment runoff water and water discharge (daily values) in 2003 and 2004. Average runoff concentrations of chloroform were almost 15 times (range, 3–35 times) higher than the concentrations observed in precipitation (the dotted line). Open circles represent chloroform concentrations during a rain event in August 2003, when approximately 23 mm of rain fell within 2 days. A total of 17 water samples were collected on three occasions: (1) sample 1 was collected one week before the rain event, before the water level started to rise; (2) samples 2–16 were collected, one every 10 min, approximately 14 h after the rain had started and when the water level had risen 3 mm (corresponding to an increase of 0.05 l s^{-1}); and (3) sample 17 was collected a day after the rain had stopped, when the water had returned to its pre-rain event level

in glass funnels (each funnel collected rain from a surface of 0.31 m^2) and glass flasks (approximately 250 ml) that were pre-washed with Milli-Q water and thereafter rinsed with a hexane/acetone (1:1, p.a. Merck) mixture, five times. Samples from the nine collectors were analyzed on two occasions and samples from six and three collectors were analyzed on three and one additional occasions. The precipitation samples were transported and stored in a refrigerator at approximately 4°C and analyzed for chloroform within 6–24 h of sampling.

Water samples in runoff

Runoff samples were collected in the spring, directly upstream from the weir, every second week from January 2003 to December 2004. On each sampling occasion, five to six samples were collected at 30-s intervals within a total sampling time of 3 min. The samples were collected in glass flasks of approximately 120 ml, which were pre-washed with Milli-Q water and a hexane/acetone (1:1) mixture, the latter procedure being repeated five times; the flasks were stored at 70°C until used for sampling. Immediately prior to sampling, the flasks were rinsed three times with the runoff water; then the flasks were filled with the water and capped without headspace using aluminum caps with a butyl PTFE (polytetrafluoroethylene) septum (VWR International, Stockholm) and transported to the laboratory within 1 h. The samples collected for VOCl analysis were stored in a refrigerator at approximately 4°C, in most cases for a maximum of 6 h but in a few cases for a maximum of 24 h before analysis.

To test for variation *between* samples collected one after another, 10 samples were collected at 1-min intervals in February 2004. To test for variation *within* a water sample, approximately a 5-l bulk sample was collected from the spring in March 2004 in a glass flask. The sample bottles and glass flasks were rinsed three times with the runoff water before the water was sampled. The water for testing the within-sample variation was gently stirred before it was divided between nine glass flasks (approximately 120 ml), which were first pre-washed with Milli-Q water and then with a hexane/acetone (1:1) mixture, five times. All sample bottles were sealed immediately using aluminum caps with a butyl PTFE septum (VWR International, Stockholm), and then directly transported to the lab. The samples were stored as described above until they were analyzed; the total duration of analysis was approximately 7 h. The samples were analyzed in the same order as they were divided into subsamples in the field.

In addition to the bi-weekly samplings, runoff samples were collected during a rain event in August 2003 when approximately 23 mm of rain fell in 2 days. Water samples were collected on three occasions. On the first occasion, one week before the water level had started to rise due to the rain event, one sample was collected. The second occasion was approximately 14 h after the rain started; at this point the water level had risen 3 mm, corresponding to an increase of 0.05 l s^{-1}, and one sample was collected every 10 min for a total of 17 samples. On the third sampling occasion, one day after the rain had stopped and the water level had returned to its pre-rain event level, one additional sample was collected.

Chemical analysis

Pretreatment

Two different sample treatments were used in the sampling period. Before May 2003, all samples were removed from the refrigerator at the same time and then stored at room temperature in darkness until they were analyzed, with approximately 7 h between analysis of the first and the last sample. After May 2003, the samples were kept in the refrigerator and were removed one by one and placed in a water bath (25°C) 5 min before being analyzed. The analysis of all samples was completed within 6 h.

VOCl analyses

The study focused on chloroform ($CHCl_3$), but the samples were also scanned for other volatile chlorinated organic compounds (VOCls) previously reported to be found in environmental samples, compounds such as tetrachloromethane (CCl_4), trichloroethene (C_2HCl_3), and tetrachloroethene (C_2Cl_4) (Hoekstra et al. 2001; Laturnus

2001; Laturnus et al. 2004). The instrument detection limit ranged from 0.001 to 0.035 pmol.

The concentration of detected VOCls was analyzed using a purge-and-trap unit, attached to a gas chromatograph with an electron capture detector (Hewlett Packard 5890). The water samples (100 ml) were purged with helium (purge flow, 60 ml min^{-1}) for 15 min and then trapped in a cold trap (filled with micro-glass spheres and deactivated glass wool) with liquid nitrogen (at approximately –196°C). A more detailed description of the method is given by Laturnus et al. (2000). The VOCls were then transferred to a capillary column by heating the cold trap with boiling water; in analyses conducted before December 2003, the SP-624 column (60 m, 0.25 mm i.d., 1.4-μm film) was used (Supelco, Bellefonte, USA), while for analyses conducted after December 2003 the CP-PoraBOND Q column (25 m, i.d. 0.32, 5-μm film) was used (ChromPack, Palo Alto, USA). Separation of the compounds was done using a temperature program of 40°C for 5 min, 5°C min^{-1}, 180°C for 5 min for the SP-624 column and 70°C for 1 min, 4°C min^{-1}, 200°C for 5 min for the CP-PoraBOND Q column.

To minimize the instrument blank, the water purge flask was cleaned by heating it under a continuous helium flow for 10 min. This cleaning procedure was tested with blank units and resulted in a blank below the detection limit for all screened chlorinated compounds. The cleaning procedure was repeated before the first purge and between each sample purge.

Water (pre-purged with helium for cleaning) was spiked with three concentration levels of a known standard solution of the four detected compounds: i.e., chloroform, tetrachloromethane, trichloroethene, and tetrachloroethene in methanol (all from VWR International) to produce calibration curves. The detections limits were calculated from calibration standards using a minimum detectable peak height corresponding to three times the base line noise. The detection limits of chloroform, tetrachloromethane, trichloroethene, and tetrachloroethene for the specified method were 0.4, 0.6, 0.2, and 0.1 ng l^{-1}, respectively. The variation in the method was analyzed by spiking pre-cleaned water with a known standard (approximately 5 ng l^{-1}), and repeating the procedure 10 times. Between each analysis, the water was cleaned by purging the water until blank levels were reached. The coefficient of variation (CV, calculated by dividing the standard deviation by its mean) of the method was calculated to be 11%.

Statistics

Correlation between the chloroform concentrations and runoff was tested using two-tailed Kendall's tau (95% significance level (P = 0.05)). The data displayed a monotonic relationship (non-linear), so Kendall's tau instead of Pearson's r was chosen to measure the strength of the correlation between the variables (Helsel and Hirsch 2002). Furthermore, Kendall's tau does not require a normal distribution among samples, is insensitive to extreme values, and does not presume a bivariate normal distribution. To separate the effects of the water discharge and other seasonal factors, a simple linear regression was made by using chloroform in runoff as the dependent variable and water discharge as the explanatory variable. The inter-annual variations in chloroform concentrations, which could not be explained by runoff, were regarded as seasonal effects. The residual variation over time that could not be explained by water discharge was used to determine the effect of other seasonal factors (Helsel and Hirsch 2002). A post hoc analysis was done to determine the statistical power of the analysis to detect differences of 5 ng l^{-1} and 10 ng l^{-1} between two sampling occasions when using two, three, and five replicates (Cohen 1988).

Results

Hydrology

The estimated annual precipitation levels for 2003 and 2004 were 762 mm and 697 mm, respectively, compensating for measurement losses using an SMHI correction model (Alexandersson 2003). Hence, the 2003 precipitation was higher than the 30-yr average (1951–1980) of 696 mm. The average runoff during the observation period was 1.4 l s^{-1}.

The total annual runoff of the subcatchment was approximately 200 mm in 2003 and 220 mm in 2004. In both years, water discharge was lowest in late summer and early autumn, but increased by a factor of three in late autumn. In spring 2003, water discharge increased slightly in January, followed by a three-fold increase in late spring; in 2004, however, water discharge increased at three occasions the same period. The spring did not dry out in the summer of either 2003 or 2004. The discharge data indicate that base-flow conditions, with discharge levels below 0.7 l s^{-1}, were observed in late summer and early fall in both 2003 and 2004.

Concentration of chloroform in precipitation

Chloroform, tetrachloromethane, and trichloroethene were detected in all precipitation samples, the median (minimum–maximum) precipitation concentrations found on the six sampling occasions taken together being 1.5 (0.8–2.3), 1.7 (0.5–16.2), and 0.3 (0.1–1.7) ng l^{-1} for the three compounds, respectively. The highest tetrachloromethane concentration was recorded in September 2005; on all five other occasions the concentration only reached 2.5 ng l^{-1} at the highest. Chloroform and the other compounds did not co-vary in terms of concentration, i.e., the highest average concentrations of all compounds did not occur at the same time.

Concentration of chloroform in runoff

Chloroform was detected in all collected runoff samples, whereas the other chlorinated organic compounds were either below the detection limit or could not be distinguished from the blanks i.e., most likely representing contamination from laboratory air. The concentration of chloroform in runoff during the observation period ranged between 5 ng l^{-1} and 52 ng l^{-1} (minimum and maximum), with a median value of 19 ng l^{-1} (Fig. 2). The volume-weighted average chloroform concentration was calculated to be 28 ng l^{-1} and 20 ng l^{-1}, based on data from 2003 and 2004, respectively, concerning water discharge and chloroform.

The concentration of chloroform in the runoff varied over time with what appear to be some random peaks; the changes observed in 2003 are more abrupt than those observed in 2004 and the patterns differ between the years (Fig. 2). The maximum level of 2004 was reached in January, and concentrations remained high until they decreased in April. The concentrations remained comparatively low in June, but there was a strong peak in July after which concentrations decreased still further in August. Levels remained low until December, when they increased again. High concentrations were found during high-flow periods and low concentrations at other times.

A simple linear regression analysis indicates that the chloroform concentration in the runoff is significantly positively correlated with water discharge (tau = 0.665, $P < 0.001$). The variables display a linear relationship when the variables are log transformed:

$$\text{Log } [CHCl_3] = 1.206 + 0.583 * \text{Log } Q,$$

where $CHCl_3$ is chloroform concentration (ng l^{-1}) and Q is water discharge. The adjusted r^2 is 0.521, hence the model explains approximately 50% of the variation in chloroform concentration in runoff from the Stubbetorp catchment ($P < 0.0001$). The residuals are randomly scattered around the mean, and there is no tendency towards heteroscedacity or other non-linear relationships. The residuals are quite normally distributed, although there is a tendency towards a positive skewness. When the residuals are plotted against time, no clear seasonal pattern in the distribution of the residuals is evident (Fig. 3).

To sum up, the concentration of chloroform in the runoff co-varied with the water discharge (tau = 0.334, $P < 0.001$), but the variability in water discharge could not explain all the variation in chloroform concentration. There were peaks in the water flux that were not accompanied by peaks in chloroform concentration, and vice versa.

Detecting temporal or spatial changes in chloroform concentrations in runoff: methodological considerations

No change with time in chloroform concentration could be observed in the nine samples collected one by one from a bulk water sample (5 l;

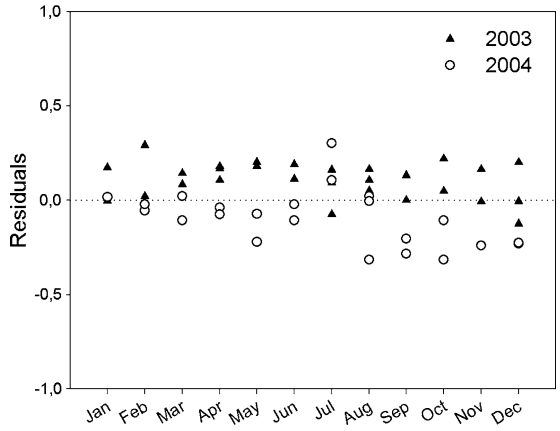

Fig. 3 The figure shows a scatterplot of the residuals from a simple linear regression, with chloroform in runoff as the dependent variable and water discharge as the explanatory variable. The residuals are plotted against month to separate the effects of water discharge from those of other seasonal factors. There are no obvious seasonal patterns in the residual data

collected on one occasion in March 2004) or in the 5–6 samples collected on each sampling occasion from the spring. The variation among the nine samples was equivalent to the variation among the samples collected biweekly. The standard deviation among the 10 samples collected within 10 min of each other was 2.4 ng l^{-1}; therefore, the variation was not primarily dependent on the short sampling duration used in the study, but was instead more dependent on variation over a larger time scale.

The average standard deviation of chloroform in runoff samples was 2.5 ng l^{-1} among the replicate samples collected biweekly in the two studied years and 0.1 ng l^{-1} among the precipitation samples. There was a positive correlation between the variation among replicates and concentration, with a maximum standard deviation of 7.4 ng l^{-1} (Fig. 4).

The altered pretreatment of the samples decreased the CV among replicates from 22% to 15%. There are no indications that the altered procedure had an impact on the concentration level.

Post hoc analysis indicates that when five replicates were used in analyzing the chloroform concentration in runoff water, the present study had a statistical power of 97% to detect a difference of 5 ng l^{-1} between the two sampling occasions, when alpha (significance level) was set to 0.05 and the standard deviation of chloroform was 1.8 ng l^{-1}. If the number of replicates is reduced to three or two, as often recommended in literature dealing with relevant methodology, the statistical power decreases to 72% and 35%, respectively (Table 1). If one only wishes to

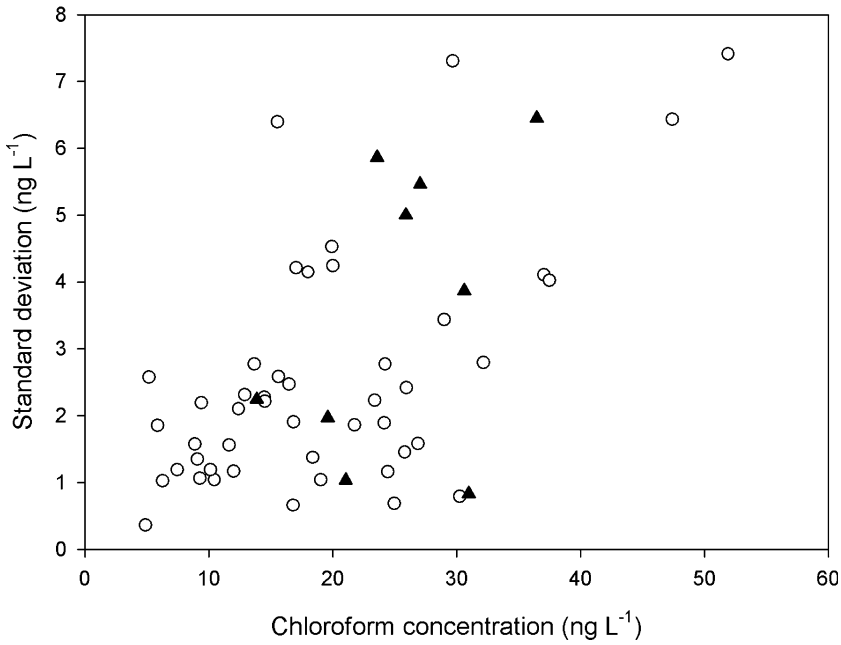

Fig. 4 Chloroform concentrations detected in runoff, 2003 and 2004, versus the estimated standard deviation for the replicates (n = 5–6). Filled triangles represent samples analyzed with the pretreatment used before May 2004 and open circles represent those analyzed after May. For more specific information regarding the different pretreatment methods, please see the section, ''Material and methods''

detect a difference of 10 ng l^{-1}, the statistical power increases to 99% with three replicates and 79% with two. In summation our study suggests that at least five replicates need to be made on each sampling occasion to detect changes in the chloroform concentration of 5 ng l^{-1} in runoff of the studied catchment, but that three samples are sufficient if one only wishes to detect a change of 10 ng l^{-1}.

Observations during a rain event

During the observed rain event in August 2003, the chloroform concentrations in runoff water increased from 17 ng l^{-1} to 48 ng l^{-1} as the water discharge increased (Fig. 2). One day after the event, water discharge had decreased to the level of the day before the rain started, and similarly, the chloroform concentration had decreased to 18 ng l^{-1}. These observations suggest that changes in water discharge rendered changes in chloroform concentration.

Transport via precipitation and runoff

By combining the average chloroform, tetrachloromethane, and trichloromethane concentrations in the precipitation samples with the average estimated annual precipitation of 730 mm for 2003 and 2004, the annual input via wet deposition of the studied VOCls was estimated to be 1.0, 1.2, and 0.3 μg m^{-2} yr^{-1}, respectively.

The chloroform flux in runoff was calculated using the daily water discharge values and bi-weekly concentration values interpolated to daily values. The lowest monthly fluxes were observed from August to November both years, while the highest monthly fluxes were observed in May and July in 2003 and from January to April and in December in 2004 (Fig. 5). The annual output of chloroform via runoff from the catchment was estimated to be 6 μg m^{-2} yr^{-1} and 5 μg m^{-2} yr^{-1} in 2003 and 2004, respectively.

Table 1 Post hoc analysis to determine the statistical power of the present study to detect differences of 5 ng l^{-1} and 10 ng l^{-1} between two sampling occasions when using two, three, and five replicates (Cohen 1988). The standard deviation is 1.8 ng l^{-1}

Replicates	Effect size (ng l^{-1})	
	5	10
	Power (%)	
2	35	79
3	72	99
5	97	100

Discussion

A chloroform budget on a catchment scale suggesting an internal source

The chloroform budget of the studied catchment provides evidence of a net-source of chloroform in the catchment since the annual output of 6 μg m^{-2} yr^{-1} is approximately six times higher than the input via wet-deposition.

To the best of our knowledge, this is the first flux estimate and mass balance estimate for chloroform on a catchment scale. It is also the first report regarding the variation of the background concentrations of chloroform in runoff with time in a remote, seemingly unpolluted area. The estimated input should be taken with some caution since it is based on only six sampling occasions of chloroform concentration in precipitation. However, the concentration data is combined with precipitation data of the region with a known coefficient of variation of the annual deposition of 10% (Alexandersson 2003). The input estimate is consequently less reliable than the output estimate but as the variation among the six sampling occasions was comparably small and no seasonal pattern is discernable the data is sufficient to conclude that the input via wet deposition is smaller than the output via runoff.

The results of the present study suggests an internal chloroform source in the catchment, which is in line with previous studies that show that chloroform may be formed in soil (Laturnus et al. 2002). Furthermore, previous studies have provided evidence of net-fluxes of chloroform to the atmosphere from forested terrestrial ecosystems, which also suggests that chloroform is formed in soil (Khalil and Rasmussen 2000; Haselmann et al. 2000b; Dimmer et al. 2001; Hoekstra et al. 2001). The reported fluxes from soil to air range from

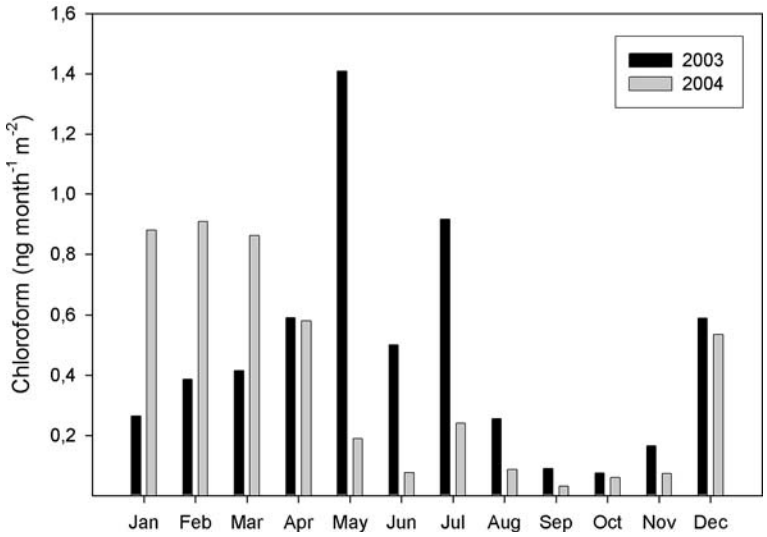

Fig. 5 Monthly output fluxes of chloroform from the catchment, based on bi-weekly sampling and daily water discharge measurements, 2003–2004

approximately 3 μg m^{-2} yr^{-1} to 150,000 μg m^{-2} yr^{-1}. The largest chloroform fluxes were reported for an evergreen forested bog (Dimmer et al. 2001) and the lowest from a Douglas fir forest (Hoekstra et al. 2001). The transport to groundwater in the present study is 6 μg m^{-2} yr^{-1}, which is of the same order of magnitude as some previously observed fluxes to the atmosphere from a Douglas fir forest but considerably smaller than the fluxes to the atmosphere found, for example, in an evergreen forested bog.

Earlier measurements of chloroform in rain have been made in industrial or highly populated areas (Class and Ballschmiter 1986; Schleyer et al. 1991; McCulloch 2003; Polkowska 2004). Class and Ballschmiter report concentrations of chloroform of 3–25 ng l^{-1} and Schleyer reports concentrations of 11–17 ng l^{-1}, both monitored in Germany (Class and Ballschmiter 1986; Schleyer et al. 1991). The concentration at sites in densely populated areas can reach 100 ng l^{-1} and even occasionally 1,010 ng l^{-1}, as reported in the case of Tricity in Poland (Polkowska 2004). The concentrations in precipitation observed in the present study are in the lower range of the previously reported results. This indicates that the concentration in air is also low, and that the transport to the atmosphere also ought to be in the lower range relative other studied areas. It can be assumed that the concentration detected in rain mirrors that in air. Based on that assumption, the concentration in air of the studied catchment can be estimated to 0.2 (0.1–0.4) ng l^{-1} by using the dimensionless Henry's law constant for chloroform in combination with the chloroform concentrations observed in precipitation. The estimated values are within the range of previously reported values for chloroform in air of semi-remote sites, even though compilations of air concentrations of chloroform suggest that elevated air concentrations can be found in both industrial and forested areas, for example, in Germany (McCulloch 2003). This suggests that natural chloroform formation varies among sites and that the concentration in air is a combined effect of natural and industrial sources. The studies of chloroform transport from soil to atmosphere suggest that air concentrations in remote areas reflect the formation at the actual ecosystem. The present study suggests that the concentration of chloroform in ground water, and perhaps also rain, also may reflect the formation at the actual ecosystem.

Origin and transport patterns

Based on previous understanding of hydrological patterns, some general conclusions can be drawn regarding the origin of compounds brought to the outlet in time periods when runoff is dominated by water with a long water residence time (base flow) as compared to periods with a strong influence of water from recent precipitation or

snow melt (high flow) (Brutsaert 2005). In the present study, discharge data indicate base-flow conditions at discharge levels below 0.7 l s^{-1}, which occurred in late summer and early fall in both 2003 and 2004 (Fig. 2). During base-flow conditions, even a small rain event has a clear impact on the chloroform concentrations whereas rain events during high-flow conditions have a small or negligible influence on the chloroform concentrations. The amount of water present in soil during wetter periods is considerably larger than during drier periods. Dilution will consequently cause the water brought to the soil during a wet-period rain event to have a small to negligible influence on the water residence time and soil water chemistry; this stands in marked contrast to the effect of water brought to the soil during rain events occurring in drier periods. The data support this line of reasoning, as rain events during high-flow periods did not induce clear peaks in chloroform concentration.

Indications of chloroform formation in surface soil

The increasing chloroform concentrations caused by rain events taking place at times of base-flow conditions suggest that chloroform in soil originates from the top layer, for the following three reasons.

First, under base-flow conditions the elements brought to the outlet originate from deeper soil levels, but as the water rises, elements from layers closer to the surface will also be included. Hence, increasing concentrations of chloroform following a rain event at times of base-flow conditions infers that the concentrations of chloroform increase with decreasing depth. Second, a parallel study conducted in the same catchment and during the same time-period as the present study report concentrations of TOC during rain-events under base-flow conditions (Svensson et al., accepted). It is well known that TOC originates mainly from the topsoil, i.e., increased concentrations of TOC are obtained when the water table reaches the surface soil water in organic rich soil layers that are hydrologically connected to stream water (Bishop et al. 1993, 2004). A closer analysis of the data reveals that the increasing concentrations of chloroform occurred simultaneously with increasing TOC concentrations. This suggests a common origin and gives further support of the hypothesis that the water brought to the outlet during the rain event, and thus the chloroform originates from surficial soil layers. Third, the above-mentioned study provides evidence that the steep increase in chloroform concentration from 17 ng l^{-1} to 48 ng l^{-1} that was observed during a rain event coincides with a pronounced decrease in the chlorine-to-carbon ratios of the organic matter (11 mg to 5 mg Cl_{org} g^{-1} C_{org}; Svensson et al., accepted). Previous studies show that the chlorine-to-carbon ratio in organic matter of coniferous soils in the temperate region increases steadily with soil depth, from less than 1 mg Cl_{org} g^{-1} C in the organic layer to 2–6 in the A-horizon to 10 mg Cl_{org} g^{-1} C or even more in deeper layers (Öberg and Grön 1998). The decrease in the chlorine-to-carbon ratio provides further evidence that the water brought to the outlet during the rain-event originates from surficial soil layers and thus that chloroform concentrations increase with decreasing depth.

In conclusion, the results of the present study suggest the concentration of chloroform decreases with depth, which suggests that chloroform in runoff either originates from deposition or is formed in surficial soil layers. The fact that the concentration of chloroform in precipitation is considerably lower than in runoff, infers that chloroform in runoff originates only to a minor extent from precipitation and mainly from formation in surficial soil.

Indications of chloroform loss through volatilization, degradation, and run-off

It is well documented that chloroform can be subjected to degradation in deeper soil layers and in groundwater (Borch et al. 2003), which, given sufficient time, will decrease the chloroform output in runoff. Runoff water during base-flow conditions generally consists of deeper groundwater that has spent a relatively long time in the catchment as compared to high-flow conditions (Brutsaert 2005). During base-flow conditions,

there is consequently considerable time for processes such as degradation and evaporation to take place. In periods of high flow, the residence time of the runoff water is shorter than it is during base-flow conditions and consequently less time for evaporation or degradation processes to take place. Hence, the lower chloroform concentrations observed during base-flow conditions as compared to high-flow conditions is most likely due to a combined effect of larger losses via volatilization and degradation. The peaks observed during base-flow condition rain events would then be due to that the portion of the chloroform formed in topsoil during dry periods that is not evaporated is flushed out with the rainwater, quickly reaching the outlet as it spends too short time in the soil to be subject to degradation processes.

Previous studies show that forest soil emits chloroform to air (Haselmann et al. 2000a; Dimmer et al. 2001; Hoekstra et al. 2001), we suggest that the observed pattern with high chloroform concentrations during wet periods is due to that a larger portion of the chloroform formed in soil is subjected to soil water during wet periods, and thus dissolved and transported to the outlet rather than emitted to air. The fact that larger amounts of chloroform are transported during high-flow conditions as compared to base-flow conditions provides supports of the hypothesis. In addition, the finding that relatively small amounts of chloroform are transported during base-flow condition rain events, despite the elevated concentrations, provides further support (Fig. 2).

Detection of temporal and spatial changes in runoff—methodological considerations

Many standard methods recommend using duplicate samples when analyzing chloroform, or other VOCls in environmental samples. Such recommendations are generally aimed at keeping track of the method variation and are rarely meant to deal with the number of samples needed to enable accurate and reliable statistical estimates of changes in the field under conditions of natural variation. Since the natural variation usually varies both *within* a compartment and *between* different environments, assessing the number of replicates needed to be able to detect change with any certainty demands knowledge of the field variation. To the best of our knowledge, field data concerning natural variation in concentrations of chloroform or other VOCls in precipitation and runoff have not previously been gathered. We therefore wanted to study how the sampling design affects the evaluation of the on-site variation of chloroform in runoff water. The results of the present study are thus valuable for those who wish to study or monitor temporal or spatial changes of VOCls.

The variation among replicates collected on the same occasion and site depends on the natural variation in combination with the method variation; the method variation may be reduced (preferably to zero) whereas the natural variation is unavoidable as it reflects the heterogeneity in the field. A remarkable number of studies appear to confuse method variation with natural, on-site variation, which may be devastating when, for example, it comes to the evaluation of environmental trends and their implications. Hence, a few words on this issue. If the degree of natural variation is known, power analysis can reveal how many replicates are needed to be able to determine with, for example, a 95% probability whether or not a change has taken place (Cohen 1988).

The concentration in runoff water of chloroform found in the present study ranged from 5 ng l^{-1} to 50 ng l^{-1}. We did a post hoc analysis to determine the statistical power when detecting a difference of 5 ng l^{-1} between two sampling occasions while using two, three, and five replicates (Cohen 1988). The analysis shows that when five replicates are used, the present study has a power of 97% to detect a difference of 5 ng l^{-1} between two sampling occasions (significance level, 0.05; standard deviation, 1.8 ng l^{-1}). If the number of replicates is reduced to three or two, as is often recommended in methodology literature, the power decrease to 72% and 35%, respectively (Table 1). Hence, our study suggests that at least five replicates are needed on each sampling occasion if the goal is to detect changes in chloroform concentration in runoff from the studied catchment of 5 ng l^{-1} or more.

The chloroform concentrations we found in runoff are in the lower range detected in river waters, but similar to those in non-industrial rivers (Zok et al. 1998). Concentration in water samples can often exceed 50 ng l^{-1}, and chloroform concentrations in industrial rivers have been found to be as high as 10,000 ng l^{-1} in the Ruhr area (Zok et al. 1998). In less-industrialized areas the concentrations in rivers and estuaries are generally lower than 500 ng l^{-1} and often below 100 ng l^{-1} (Zok et al. 1998; Christof et al. 2002; Huybrechts et al. 2004). The results of the present study indicate that the variation among samples increases with increasing concentration (Fig. 4). We cannot make any conclusive statements concerning the relationship at intervals above 50 ng l^{-1}, but it appears likely that the standard deviation continues to increase with increased concentration. If one assumes a linear relationship, and demands a statistical power of at least 95%, one would need five replicates to detect a difference of 500 ng in water with concentrations varying from 500 ng l^{-1} mg to 5,000 ng l^{-1} mg. This conclusion is of course rather speculative, but hints at the importance of knowing the degree of variation in the field when studying and discussing changes over time or in space.

A slight change in procedure let us reduce the method variation, while a power analysis (using the free program, G-power, available at http://www.psycho.uni-duesseldorf.de/aap/projects/gpower/) let us show that with a statistical power of 95%, the number of replicates needed to detect a change of 5 ng l^{-1} was reduced from 14 to 5.

The method used in the present study follows the procedure of an EPA method frequently used for the determination of VOCl concentrations in water (EPA 1995). According to the instructions, the samples may either be analyzed directly or preserved by adjusting the pH to <2 at the time of collection to avoid microbial influence. Our results show that storage of unpreserved water samples at room temperature even for a few hours influences the variation among the samples. Hence, our results strongly suggest that samples should be refrigerated until analyzed in order to minimize the method variation.

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