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Dynamics of mercury fluxes and their controlling factors in large Hg-polluted floodplain areas

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\textquote{Capsul}\textquote{:}

Warmer environmental conditions result in higher Hg volatilization rates from floodplain soils.
Abstract

Environmental pollution by mercury (Hg) is a considerable environmental problem worldwide. Due to the occurrence of Hg volatilization from their soils, floodplains can function as an important source of volatile Hg. Soil temperature and soil water content related to flood dynamics are considered as important factors affecting seasonal dynamics of total gaseous mercury (TGM) fluxes. We quantified seasonal variations of TGM fluxes and conducted a laboratory microcosm experiment to assess the effect of temperature and moisture on TGM fluxes in heavily polluted floodplain soils. Observed TGM emissions ranged from 10 to 850 ng m\(^{-2}\) h\(^{-1}\) and extremely exceeded the emissions of non-polluted sites. TGM emissions increased exponentially with raised air and soil temperatures in both field (\(R^2: 0.49-0.70\)) and laboratory (\(R^2: 0.99\)) experiments. Wet soil material showed higher TGM fluxes, whereas the role of soil water content was affected by sampling time during the microcosm experiments.

Keywords: Hg soil-air exchange, TGM seasonality, wetland soils, Elbe River

1. Introduction

Environmental pollution by mercury is a world-wide problem (Munthe et al., 2001). Particularly floodplain ecosystems are frequently affected. One example is the Elbe River in Germany and its catchment areas; large amounts of heavy metals including Hg from a range of anthropogenic and geogenic sources have been accumulated in the soils of these floodplains (Kowalik et al., 2003; Overesch et al., 2007; Rinklebe et al., 2007; 2009). They serve as sink for Hg originating from the surface water of adjacent river. Until 1996, 1 500 ± 500 t of Hg were deposited in parts of the Elbe wetlands within a period of 60 years only (Wallschlager, 1996). Consequently, the wetland soils along the Elbe River contain 10 times more Hg compared to floodplain soils in the USA, as studied by Patrick et al. (2004) and Devai et al. (2005). Today, the vastly elevated Hg contents of the floodplain soils at the Elbe River often exceed even the action values of the German Soil Conservation Law (BBodSchG, 1998; BBodSchV, 1999). This is especially important as Hg polluted areas at the Elbe River achieve several hundreds square kilometers.
Thus, authorities are coerced by law to conduct an appropriate risk assessment and to implement practical actions to eliminate or reduce environmental problems. A reliable risk assessment particularly with view to organisms (vegetation as green fodder and hay production, grazing and wild animals) to avoid the transfer of Hg into the human food chain, requires an authentic determination of Hg fluxes and their dynamics since gaseous emissions from soil to atmosphere are probably the most important pathway of Hg.

The environmental chemistry of Hg has been reviewed extensively (e.g. Ebinghaus et al., 1999, Zhang et al., 2003). Special attention must be paid to the reduction of Hg(II) to Hg(I) or Hg(0), which is preferred under very low redox potentials in frequently or permanently flooded soils and sediments. Mercury may also exist in organometallic forms, of which monomethylmercury \((\text{CH}_3\text{Hg}^+)\) and dimethylmercury \([\text{(CH}_3\text{)}_2\text{Hg}]\) are the most important. Hg(0) and \((\text{CH}_3\text{)}_2\text{Hg}\) are volatile species. Therefore, gaseous emissions from soil to atmosphere are considered to be an important pathway (Du Laing et al., 2009), and Hg might be atmospherically distributed worldwide (Poissant and Casimir, 1998). The release of Hg into the atmosphere is caused by a diversity of natural and anthropogenic sources (e.g. Bash and Miller, 2007; Pacyna et al., 2005; Yan et al., 2003). The estimated gaseous Hg emission rate from anthropogenic sources in the year 2000 was comparable to estimates of Hg emissions from natural sources (Pacyna et al., 2006).

During the past twenty years different studies determined soil-air exchange rates of Hg at various sites to assess related risks (e.g. Schroeder et al., 1989; Schroeder and Munthe, 1998; Schlüter, 2000; Lindberg et al., 2002; Ravichandran, 2004). The release of Hg from soil to atmosphere was found to be influenced by many factors. Atmospheric Hg amounts above soil surfaces can be positively correlated to the Hg stocks in these soils, although other soil parameters and atmospheric conditions can affect the Hg emission and mask this relationship (Schlüter, 2000). Soil temperature and soil water content are described as the main factors controlling Hg emission from soils (Gillis and Miller, 2000; Johnson and Lindberg, 1995; Song and Heyst, 2005; Zhang et al., 2003). Rising soil water content can promote the reduction of Hg(II) to Hg(0) and subsequent Hg volatilization exponentially (Johnson and Lindberg, 1995,
Gillis and Miller, 2000, Song and Heyst, 2005). Consequently, precipitation has a positive influence on Hg volatilization from soils (Wallschläger et al., 2000, Song and Heyst, 2005), whereas in floodplain soils, soil water content and mercury volatilization are affected to a great extent by the variable water table levels. Increasing soil temperatures due to solar radiation are also correlated to TGM emissions (Zhang et al., 2003). The vapour pressure of volatile Hg species increases with rising soil temperatures, decreasing Hg sorption to the soil. Moreover, if soil air expands and air circulation increases, the reaction rates of Hg(II)-reduction and –methylation increase, additionally microbial activity is promoted (Schlüter, 2000). Significant, exponential relations between Hg emission rates and soil temperature were established for forest soils in North-American wetland areas (Lindberg et al., 1995; Poissant et al., 2004). However, reliable estimates of Hg fluxes from the highly polluted floodplain soils at the Elbe River and its tributaries, and its influencing factors are scarce.

The objectives of our study were i) to quantify seasonal variations of TGM fluxes for floodplain soils of the Elbe River and its tributary Saale in Germany, ii) to provide insights into physico-chemical processes regulating these TGM fluxes, and iii) to quantify the impacts of the controlling factors soil temperature and soil water content on Hg volatilization from a typical contaminated floodplain soil within soil microcosm experiments under various controlled temperature and moisture conditions.

2. Materials and Methods

2.1 Study Sites

The study sites are situated in floodplains at the Central Elbe River in Germany (Fig. 1). The site Wörlitz is located at stream kilometer 242 (51°51´27´´N, 12°23´06´´E), the site Breitenhagen at stream kilometer 290 (51°57´15´´N, 11°54´57´´E), and the site Sandau at stream kilometer 417 (52°48´00´´N, 12°02´15´´E) (Fig. 1). The long-term annual precipitation ranges from 470 to 570 mm and the mean annual air temperature is around 8.0 °C (Rinklebe, 2004). Air temperatures and amounts of precipitation at the study sites during the monitoring are given in Fig. 2. The study sites are periodically flooded by the Elbe River with amplitudes of
up to 8 m mainly depending on snowmelt (winter and spring) and heavy rainfalls (spring and summer). The site Breitenhagen is additionally influenced by its tributary Saale River.

Insert Figure 1

Insert Figure 2

The sites have been selected after large-scale conventional soil mapping and ten years of comprehensive field pedological research in the floodplains of the Elbe River (e.g. Langer and Rinklebe, 2009; Rinklebe and Langer, 2006; 2008; Rinklebe et al., 2000). Soils of the low-lying terraces expose largest concentrations of pollutants due to high contents of soil organic matter and fine mineral particles as a result of sedimentation through frequent or extended flooding periods with low flow-rates (Devai et al., 2005; Overesch et al., 2007, Rinklebe et al., 2007). These soils are common on lower-lying terraces (Rinklebe, 2004) and are classified as Mollic Fluvisols according to IUSS/ISRIC/FAO (2006).

Soils in flood channels (site No. 5 and 6) are classified as Eutric Gleysols. They reveal highest total Hg concentrations ($Hg_{tot}$) due to long flooding periods with a low flow velocity, and consequently the high content of fine mineral soil particles and soil organic carbon (Tab. 1).

2.2 Sampling and analysis of bulk soil

Soil samples were collected in soil profiles according to soil-genetic horizons. Sampling was performed in four replicates of about 1 kg which were pooled to one sample per horizon (Rinklebe, 2004). Air dried soil material was sieved to < 2 mm. Subsamples were ground in an agate disc mill. Soil properties were determined according to standard methods (Schlichting et al., 1995) as follows. Total C ($C_t$) was measured using a C/N/S-Analyzer (Vario EL Heraeus, Analytik Jena). Inorganic C was quantified after treatment with phosphoric acid (15 %) and IR-Detection of the evolved CO$_2$ with a C-MAT 550 (Stroehlein). Soil organic C ($C_{org}$) was calculated as the difference between $C_t$ and inorganic C. Particle-size distribution was determined by wet sieving and sedimentation using the pipette sampling technique according to HBU (2000). Soil pH was measured in 0.01 M 2.5:1 CaCl$_2$- soil suspension. Total Hg concentrations of soil samples were quantified after digestion using aqua regia - HCl (37 % v/v)
Mercury in soil extracts was measured by cold vapor atomic absorption spectrometry (CV-AAS) (FIMS, Perkin Elmer). Blanks, triplicate measurements of Hg in extracts, and analysis of multi-element standards (Merck) were routinely included for quality control. The given results represent arithmetic means of duplicate samples (Table 1). Maximum allowable relative standard deviation between replicates was set to 10%. Bulk densities ($\rho_b$) represent arithmetic means of ten replicates per horizon using 250 cm$^3$ soil cores. Hg stocks in different soil layers were calculated from Hg$_{tot}$ and $\rho_b$ of each soil horizon.

2.3 TGM Measurements

Mercury emissions were measured between November 2005 and November 2006. The dataset was collected during seven sampling campaigns, which contained all seasons (14$^{th}$ to 17$^{th}$ of November 2005, 13$^{th}$ to 14$^{th}$ of February 2006, 22$^{nd}$ to 24$^{th}$ of May 2006, 17$^{th}$ to 19$^{th}$ of July 2006, 21$^{st}$ to 24$^{th}$ of August 2006, 11$^{th}$ to 13$^{th}$ of September 2006, and 06$^{th}$ to 08$^{th}$ of November 2006). At each sampling site samples were taken around the same time of the day. Sampling at noon was elided to avoid incident solar radiation to affect the results.

To measure TGM emissions, the system described by Rinklebe et al. (2009), modified from Böhme et al. (2005), was used after removing surface vegetation carefully. Advantages of this system were described by During et al. (2009) and Rinklebe et al. (2009). Gas sampling was performed twice per sampling day: first with a sampling duration of one hour and secondly with a sampling duration of two hours, each with a flow rate of 1 L min$^{-1}$ in three or four replicates at each location. Blank values consisted of TGM background concentrations in the surrounding air, which were measured for 15 minutes. According to the guideline VDI 2267/ Blatt 8 (1999), total gaseous Hg amalgamated in the gold traps was determined by CV-AAS (FIMS, Perkin-Elmer) coupled with a prototype of amalgam analysis equipment from Analytik Jena. The detection limit was 0.3 ng for the measurements conducted in November 2005 and 0.5 ng during the following measurements. The calibration curve was linear up to 14 ng. Results below the detection limit were set at 1/5 of the detection limit for data interpretation and statistical
analysis. Blank values were subtracted from measured samples.

2.4 Environmental conditions during TGM sampling

Soil temperature at 10 cm depth was directly measured with a cut-in thermometer. Water content of soil samples collected from 0-10 cm soil depth was quantified in the laboratory using an electronic moisture analyzer (MA 30/Sartorius). Air temperature and air pressure at 10 to 20 cm above the soil surface (Table 2) were recorded by a sensor of the battery operated pump which was used during TGM measurements (Cap. 2.3). Additional climatic parameters are given in Fig. 2.

Insert Table 2

2.5 Laboratory experiments

Soil microcosm experiments under definite temperature and soil water conditions were carried out to study the impact of these main controlling factors on Hg emission from the soils. The sampling setup is shown in Fig. 3.

Insert Figure 3

Soil material (air-dried, < 2mm, mixed sample) from 0 to 30 cm soil depth of study site No. 3 was filled into a double-walled glass microcosm pot. In a first part of the experiment defined temperature levels (10°C, 20°C, and 40°C) were adjusted. The temperatures were regulated by inducing water circulation between glass walls of the microcosm pots. The temperature of this water was regulated with a thermostat.

In a second part of the experiment, soil water content was adjusted. Therefore, soil samples were left air-dried or attuned to a water content of 60 and 90 % of the maximum water holding capacity by flooding the soil carefully with distilled water.

The experiments were set up in triplicates. Gas sampling was performed in each microcosm for one hour at intervals of 1, 3, 6, 24, and 48 hours and with a flow rate of 1 L min\(^{-1}\). Throughout the experiments, the microcosm pots were covered with aluminum foil to exclude solar radiation or algae cultivation. To ensure direct comparability between field and laboratory
experiments, exactly the same sampling and measurement technique was used in the laboratory experiments as described for the field setup (paragraph 2.3).

2.6 Calculation of mercury fluxes

The Hg amounts amalgamated in the gold traps during field measurements and laboratory experiments were converted into Hg emission fluxes according to the equation:

\[ F = \frac{C_{abs}}{A} \times Q, \]

where \( F \) is the total flux of Hg in ng m\(^{-2}\) h\(^{-1}\), \( C_{abs} \) is the mean Hg concentration in ng m\(^{-3}\) calculated from ng absolute at the outlet less blank value multiplied with \( 1000 / v \) (\( v = \) volume in L h\(^{-1}\)). \( A \) is the covered surface area of the chamber in m\(^2\) and \( Q \) is the flushing flow rate through the chamber in m\(^3\) h\(^{-1}\). In almost all measurements Hg bound in the second gold trap was very low or even below detection limit. Therefore, we can assume that Hg volatilizing from the soils is completely trapped in both gold traps and that the air returned into the chamber includes no measurable gaseous Hg compounds.

3. Results

3.1 TGM emission and seasonal variations in the field

Mercury emission rates, mean soil temperatures and soil water contents are plotted as a function of sampling time in Fig. 4. Please note, field measurements could not be carried out when the study sites were flooded (e.g. particularly site 6, Fig. 4/ F). Standard deviations of the three or four replicates (per measurement) range between 110 and 276 ng m\(^{-2}\) h\(^{-1}\) (with a pumped volume of 60 L) and 63 to 162 ng m\(^{-2}\) h\(^{-1}\) (with a pumped volume of 120 L).

Insert Figure 4

All study sites (except site 6, Fig. 4/ F) reveal seasonal variations of measured Hg emission rates, soil temperature, and soil water content. Emissions of TGM at each study site tend to be higher during summer (Fig. 4/ A- E), although fairly high Hg fluxes were observed at study area ‘Sandau’ in November 2006 (Fig. 4/ D and E). A peak of TGM emission occurred at study site
In August 2006. At the same time, the maximum mean TGM emission rate of the replicates was quantified at this site as 849 ng m$^{-2}$ h$^{-1}$ at a flow rate of 60 L (Fig. 4/ A). The lowest mean TGM emission of 9.7 ng m$^{-2}$ h$^{-1}$ was found in February 2006 at site 2 (Fig. 4/ B). Mercury emission rates measured when using a pumped volume of 60 L reveal the same seasonal dynamics as those measured when using a pumped volume of 120 L, although differences can be occasionally observed.

In the summer months soil water content decreased while soil temperature and consequently the Hg volatilization increased. Fluctuating water levels of the Elbe River result in periodic flooding, which in turn have a strong impact on the moisture regime of the soils. In August 2006 (e.g. Fig. 4/ A, B, C) and 11-2006 (e.g. D, F), gently increased soil water contents can be related to high TGM emission rates. However, the impact of soil water content on TGM emission seems to be of less importance compared to the role of soil temperature. Indeed, emission rates are clearly related to soil temperatures: high emissions occur at high soil temperatures (Fig. 5). TGM emission rates increase exponentially with rising soil temperatures at all study sites with the exception of study site 1. This correlation was statistically significant, except for site 3 (120 L) and site 5, probably as a result of the small amount of samples. The impact of soil temperature on TGM emissions differs between study sites.

Insert Figure 5

Correlations between TGM emission rate measured with 60 and 120 L pumped volume on the one hand, and soil parameters and atmospheric conditions on the other hand are given in Table 3. Because of the exponential relation between soil temperature and Hg emission, ln-transformed TGM measurements were also included in the statistical analyses.

Insert Table 3

Significant positive correlations were found between air temperature and soil temperature on the one hand and TGM emission rate on the other hand, especially for the ln-transformed TGM-data. Both, soil and air temperature could be related to soil temperature directly below the soil surface. Soil water content is negatively correlated with TGM emission (Table 3) but positively to soil temperature ($r = 0.66$, $p \leq 0.05$, $n = 10$). A weak positive correlation can be observed...
between air pressure and TGM (Table 3).

Mercury concentrations and stocks in top soil, $C_{\text{org}}$ content, pH, and soil texture do not show significant correlations with TGM. Significant interrelations between soil characteristics were, however, found at the study sites No. 1 to 5. High $C_{\text{org}}$ contents of the studied soils were interrelated with high $H_g_{\text{tot}}$ and Hg stocks respectively (both: $R^2 = 0.77$, $p \leq 0.01$, $n = 10$). Furthermore $C_{\text{org}}$ content was positively correlated with soil temperature ($R^2 = 0.64$, $p \leq 0.01$, $n = 10$). A significant positive relation between silt and $H_g_{\text{tot}}$ was detected ($R^2 = 0.50$, $p \leq 0.05$, $n = 8$).

### 3.2 Laboratory experiments

Figure 6 represents the time-dependent behavior of Hg volatilization from soil material of study site No. 3, as influenced by soil water contents (Fig. 6/ A) and soil temperatures (Fig. 6/ B). The $H_g_{\text{tot}}$ in soil averaged 4.1 mg kg$^{-1}$. If measured Hg amounts trapped in the gold traps exceeded the linear zone of the calibration (0.3/ 0.5 – 14 ng), results were replaced by 14 ng. This was the case for four of 120 single values. One of the three replicates was not included in the dataset if the temporal trend of it diverged from the two other parallels. This was carried out in certain cases: soil water content experiment variant ‘water holding capacity of 90 % (WC 90 %)’ (parallel II, completely), variant ‘air-dry’ (parallel II, 3 h) and soil temperature test variant ’40 °C’ and ’20 °C’ (parallel I, completely).

The impact of soil water content on Hg emission is affected by sampling time after initiation of the experiment (Fig. 6/ A). After six hours, air-dried and submerged soil as well as soil with WC 90 % showed fairly small TGM emission rates (between 58 and 203 ng m$^{-2}$ h$^{-1}$), while the soil with WC 60 % exposed the highest values (600 ng m$^{-2}$ h$^{-1}$). Afterwards, TGM emission at the variant ‘WC 60 %’ was relatively stable (around 480 ng m$^{-2}$ h$^{-1}$), while it increased in the submerged soil. ‘WC 90 %’ reached the highest Hg emission rate (1120 ng m$^{-2}$ h$^{-1}$) after 24 hours. However, after 48 hours, Hg emission of ‘WC 90 %’ decreased. TGM of air-dried soil was lowest (between 19 and 203 ng m$^{-2}$ h$^{-1}$).
The effect of soil temperature on TGM emission from soil of study site No. 3 is shown in Fig. 5. Temperature levels of 10, 20, and 40 °C were chosen. These values exceed measured field soil temperatures at 10 cm depth (averaged 23 °C), but are more representative for soil temperatures found in the upper millimeters of soil, which are more important in relation to Hg volatilization. A positive effect of temperature on Hg emission can be observed. Highest mean Hg emission rates were 870 ng m\(^{-2}\) h\(^{-1}\) at 40 °C, 539 ng m\(^{-2}\) h\(^{-1}\) at 20 °C, and 366 ng m\(^{-2}\) h\(^{-1}\) at 10 °C. At the end of the 48-hours sampling campaign, TGM emission rates of all temperature treatments decreased to 99-215 ng m\(^{-2}\) h\(^{-1}\) (Fig. 6).

The interrelation between soil temperature and TGM emission of soil of study site No. 3 is represented in Fig. 7, for both the field measurements and the laboratory experiments.

4. Discussion

Table 4 presents data of TGM emission rates reported world-wide at different Hg contamination levels of bulk soil and measured with different methods. TGM fluxes of our study range between 10 and 849 ng m\(^{-2}\) h\(^{-1}\) or between 24 and 479 ng m\(^{-2}\) h\(^{-1}\), for 60 and 120 L pumped gas volume, respectively. These fluxes are located above background fluxes from unpolluted soils, which rarely increase 10 ng m\(^{-2}\) h\(^{-1}\) (e.g. Carpi and Lindberg, 1998). They are comparable to values reported by Wallschläger (1996), who used different measurement systems at one site of the Elbe floodplain. However, we found slightly higher TGM values than those measured with a dynamic flux chamber at a soil temperature of 20 °C (42.7 ng m\(^{-2}\) h\(^{-1}\), Wallschläger et al., 2002), while the studied soils contained nearly the same contamination level. Only site No. 5 showed an elevated Hg concentration (> 10 mg kg\(^{-1}\), e.g. Tab. 1) compared to those measured by Wallschläger et al. (2002). However, the larger flushing flow rate or the elevated frequency of
air exchange in the chamber of the modified sampling kit might affect the TGM values what
Zhang et al. (2002) have also previously reported. Thus, the chosen flushing flow rate of our
study was not too high to simulate Hg volatilization under natural conditions. Extremely high
emissions, such as 2 000 ng m$^{-2}$ h$^{-1}$, determined in industrially or geogenic enriched areas
(Nacht and Gustin, 2004; Wang et al., 2005), were not observed at the soils of the current study.

However, it should be noted that the use of various methods (Table 4) in the different studies
might explain some divergence between results. Moreover, the measured Hg emission rates are
mean values of three or four replicates in our study, whereas replicates can show a high standard
deviation (e.g. Rinklebe et al., 2009).

Mercury emission seems to increase during summer, when soil temperatures are high (Fig. 4/ A-E). A strong relationship can be observed between TGM and soil temperature, which can be
considered as the main controlling factor (except site 1, Fig. 5). This relationship originates
from the exponential increase of vapor pressure of Hg$^0$ and (CH$_3$)$_2$Hg (Gustin et al., 1997;
Schlüter, 2000), as well as the decreasing sorption to the solid soil phase with rising
temperatures (Schlüter, 2000). An increase in temperature can be induced by solar radiation,
whereas temperature effects can result in diurnal and seasonal variations of TGM emission.
Stronger solar radiation in the daytime results in higher temperatures, which affect the Hg
release (Frescholtz and Gustin, 2004). At night, Hg emission rates often decline (Poissant et al.,
2004). Both diurnal and annual variations were observed in Swedish forests (Schroeder and
Munthe, 1998). Gabriel et al. (2006) reported greater diurnal variances of TGM fluxes than
seasonal flux variances for different soil surfaces. Sampling in our study was always conducted
ante meridiem and if possible during the same timeframe, so that incident solar radiation was
avoided and variations should be attributed to the sampling season.

Relations between temperature and TGM emission are mainly exponential, which has been
documented for other sampling sites as well (Kim et al., 1995; Lindberg et al., 1995; Carpi and
Lindberg, 1998; Poissant et al., 2004). The temperature coefficients (except TGM emission on
site 3 / 120 L) exceed the values e$^{0.065 \pm 0.011}$ T (soil) given by Lindberg et al. (1995) or e$^{0.044 \pm 0.005}$ T
(soil) cited by Gustin et al. (1997). Moreover, the relationship between temperature and TGM emission seems to be site-specific. E.g., a linear instead of exponential correlation between soil temperature and TGM emission rate occurred at site 1, which was also observed by Magarelli and Forstier (2005) in deforested floodplain soils. The fitting of exponential curves to the laboratory data is better, compared to when field data are used (Fig. 7). This should be attributed to the fact that other non-controllable factors also affect TGM emission under field conditions, e.g. flooding.

The water level of the Elbe River fluctuates extremely, which results in temporarily flooded areas. This in turn influences the water content of the soils, although TGM emissions are not as obviously influenced by this phenomenon as compared to the effect of soil temperature. Poissant et al. (2004) also observed higher mercury volatilization under dry conditions (0.83 ng m\(^{-2}\) h\(^{-1}\)) compared to flooded conditions (0.50 ng m\(^{-2}\) h\(^{-1}\)) in floodplains of Quebec (Canada). In contrast, Wallschläger et al. (2000) described a triplication of Hg fluxes from heavy metal enriched floodplain soils due to an increase of soil water content as a result of raining events (Wallschläger et al., 2000). Johnson and Lindberg (1995) assessed the Hg\(^0\) concentration in soil air at 10 cm soil depth as function of soil water content and Hg\(^0\) volatilization rate. Mercury emission rates grew with increasing Hg\(^0\) concentrations in soil air, which in turn exponentially increased with soil water content. This can be attributed to the mass transfer from the water phase to the gaseous phase being reduced due to a reduction of the volume of the gaseous phase when filling soil pores with water. Moreover, creation of anaerobic conditions, which might induced by increasing water contents, induces transformations between different Hg species towards more volatile species (Schlüter, 2000; Du Laing et al., 2009). A positive impact of soil water content on TGM emission can be confirmed by our laboratory experiments. For soils of sites 1, 2, and 3, which have almost equal total Hg contents, mean soil water contents and mean Hg volatilization rates increase in parallel (1<2<3). In spite of highest total soil Hg stocks at site No. 5 (Table 5), we also observed a negative impact of soil water content on TGM emission. This could be attributed to a hampered diffusion of gaseous Hg to the atmosphere at high soil water contents (e.g. Johnson and Lindberg, 1995, Gillis and Miller, 2000, Schlüter, 2000).
Due to smaller precipitation and higher evapotranspiration during summer, soil water content was also negatively correlated to soil temperature in our study, which probably also partly explains the negative correlation between soil water content and Hg emission which mostly occur. Revealing the effect of soil water content is further complicated by the occurrence of interaction with other factors. Poissant et al. (2004) showed that during water saturation, Hg emissions are intensified by photo reduction of oxidized Hg complexes into volatile Hg species (especially elemental Hg) in presence of solar radiation. Moreover, an influence of soil water content on the temperature dependence of Hg emission cannot be excluded and requires further investigation.

TGM emissions might also be affected directly or indirectly by other soil parameters. High $C_{org}$ contents are often accompanied by elevated Hg contents (e.g. Rinklebe, 2004; Overesch et al., 2007) and positively correlated to soil temperature. The relation between temperature and $C_{org}$ contents can be a result of faster warming of humus enriched, dark colored top soils or the lower thermal conductivity of organic substances (Scheffer, 2002). Increasing soil temperatures in turn are related to increasing Hg emission rates, as stated above.

The vegetation cover was previously also found to affect Hg emission from soils. Lower Hg evaporation rates have been observed over grasslands compared to bare soils due to minor mixing of ground-level air films with air reclined above the herbage layer. Moreover, the shadow of vegetation on soil surface minimizes the temperatures next to the soil and thus Hg volatilization (Lindberg et al., 1979). In our study, the surface vegetation was removed at each study site, so only shadow effects of threes may have affected Hg emission and its seasonal variations. However, differences in soils temperatures between woody sites (study site 2, 3) and woodless sites (study site 1, 4-6) were hardly found. Volatile Hg can also be emitted from pools in the rhizosphere into the atmosphere by plenty of terrestrial and aquatic plants (Lindberg et al., 2002). Eckley and Branfireun (2008) generally agreed that soils consistently featured higher emissions than all other surfaces they studied, because soils revealed higher $Hg_{tot}$ due to their capability to retain and accumulate deposited Hg over time (e.g. Aastrup et al., 1991).
Different references (e.g. Schlüter, 2000; Nacht and Gustin, 2004) indicate that higher Hg emission rates are caused by increased Hg concentrations and stocks within soils. However, correlations and multiple regression analyses between Hg stocks and TGM emission rates did not reveal a significant relationship in our study. Based on the determined mean annual Hg emission rate of 1.2 to 2.8 mg m$^{-2}$ y$^{-1}$, a period between 59 (site 1, 60 L) and 648 years (site 5, 120 L) would be needed to bring Hg$_{\text{tot}}$ in soils lower than the required action value of the German Soil Conservation Law, when taking Hg output by leaching and Hg uptake by plants not into account. Nevertheless, an elevated Hg remobilization potential of those Hg enriched soils in form of volatile Hg exists and is affected by soil temperature and water content as well as the interaction of soil characteristic and environmental conditions.

5. Conclusions

Soil temperature, soil water content and flood dynamics are considered as important factors of seasonal dynamics of the total gaseous mercury (TGM) fluxes in floodplains. In contrast, mercury concentrations and stocks in top soil, C$_{\text{org}}$ content, pH, and soil texture, however, did not show significant correlations with TGM. Rather, we have detected seasonal variations of TGM fluxes due to large fluctuations of soil temperature, soil water content and flood dynamics. Hg emission rates increased exponentially with raised air and soil temperatures in both field and laboratory experiments. The effect of soil water content was interfered by the effect of soil temperature during field measurements. Wet soil material showed higher TGM fluxes compared to dry soil, whereas the role of soil water content was also affected by sampling time during microcosm experiments. Our study provides insight into TGM emissions from highly Hg-polluted floodplain soils. Moreover, it will contribute to a better understanding of seasonal dynamics of Hg fluxes and its controlling factors. The presented data should be of large interest for a wide international audience, such as environmental scientists and managers, applied ecologists, environmental and technical engineers, and authorities.
Acknowledgements

This study was supported by a research grant of the European Fund for Regional Development (EFRE), of the Ministry of Agriculture and Environment, and advised of the Department of Environmental Protection (LAU) of the Federal German state Saxony-Anhalt, which also provided climate data (FKZ: 76213/01/05). We thank Analytik Jena AG for supplying the device used to establish the connection of the gold traps with CV-AAS as well as Mr. H. Dittrich for his technical assistance and Mr. J. Steffen for analyzing total gaseous mercury.

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Rinklebe, J. 2004. Differenzierung von Auenböden der Mittleren Elbe und Quantifizierung des Einflusses von deren Bodenkennwerten auf die mikrobielle Biomasse und die Bodenenzymaktivitäten von β-


Figures

Fig. 1 Location of the study areas at the Elbe River in Germany (basic maps: http://de.wikipedia.org/wiki/Deutschland)

Fig. 2 Air temperature and precipitation in the studied region

Fig. 3 Sampling set up of laboratory experiments (according to During et al., 2009 and Rinklebe et al., 2009) with soil subjected to different temperature and soil water conditions: double-walled microcosm container (1) glass chamber (2) with Teflon TM frame (3), four inputs (4), silicone tubes (5), connecting piece (6), two gold traps (7), battery operated pump (8) with integrated gas flow meter (9)

Fig. 4 Dynamics of TGM fluxes (field measurements using a pumped gas volume of 60 resp. 120 L), soil temperature and soil water content at 10 cm depth during sampling appointments at site 1 (A), 2 (B), 3 (C), 4 (D), 5 (E), and site 6 (F)

Fig. 5 Correlation between soil temperature (10 cm depth) and TGM emission rate with a pumped volume of 60 L (continuous line) and 120 L (broken line) during sampling at site 1 (A), 2 (B), 3 (C), 4 (D), 5 (E), and site 6 (F) (**: statistically significant with p ≤ 0.01, *: statistically significant with p ≤ 0.05)

Fig. 6 Kinetics of Hg emission rates at different soil water contents (A) and different soil temperatures (B) in a laboratory microcosm experiment (soil material: study site No. 3)

Fig. 7 Comparison of relations between soil temperatures and mean Hg emission rates for the field study site Breitenhagen 3, both for the laboratory microcosm experiment test and field measurements
Tables

Tab. 1 Selected soil properties and Hg concentration (aqua regia) (0-10 cm depth) for the six study sites

Tab. 2 Air temperatures and air pressures at the study sites during sampling, including mean values, standard deviation (SD) and numbers of samples (n)

Tab. 3 Correlation coefficients (Pearson) for relations between TGM emission rates (seasonal measurements at six study sites with a pumped gas volume of 60 and 120 L), soil properties (10 cm depth), and parameters of atmospheric conditions

Tab. 4 TGM emission rates at different Hg contamination levels in soils world-wide

Tab. 5 Mercury stocks in soils (10 cm depth), Hg stocks required within the action value (2 mg kg$^{-1}$) of the German Soil Conservation Law (BBodSchG, 1998), mean Hg emission rates and figured period needed to achieve the action value when Hg is considered to be only exported through gaseous emissions.
Table 1
Selected soil properties and Hg concentration (aqua regia) (0-10 cm depth) for the six study sites

<table>
<thead>
<tr>
<th>Site-No.</th>
<th>Study area</th>
<th>Soil classification</th>
<th>Land form</th>
<th>Land use</th>
<th>Texture [%]</th>
<th>pH (CaCl$_2$)</th>
<th>C$_{org}$ [%]</th>
<th>$\rho_b$ [g cm$^{-3}$]</th>
<th>Hg$_{tot}$ [mg kg$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Wörlitz 20</td>
<td>Mollific Fluvisol</td>
<td>low stream terrace</td>
<td>extensive grassland</td>
<td>17 40 43</td>
<td>5.8</td>
<td>4.99</td>
<td>0.82</td>
<td>3.45</td>
</tr>
<tr>
<td>2</td>
<td>Breitenhagen 2</td>
<td>Mollific Fluvisol</td>
<td>bank of back water (River Saale)</td>
<td>riparian bank/ riverside woodland</td>
<td>15$^b$ 55$^b$ 30$^b$</td>
<td>6.9</td>
<td>4.02</td>
<td>0.80</td>
<td>3.89</td>
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<tr>
<td>3</td>
<td>Breitenhagen 3</td>
<td>Mollific Fluvisol</td>
<td>floodplain with scouring channel</td>
<td>riverside woodland</td>
<td>35 51 14</td>
<td>5.9</td>
<td>6.26</td>
<td>0.78</td>
<td>4.08</td>
</tr>
<tr>
<td>4</td>
<td>Sandau 32</td>
<td>Mollific Fluvisol</td>
<td>low stream terrace</td>
<td>pasture</td>
<td>26 43 31</td>
<td>6.7</td>
<td>8.08</td>
<td>0.81</td>
<td>9.49</td>
</tr>
<tr>
<td>5</td>
<td>Sandau 31</td>
<td>Eutric Gleysoil</td>
<td>flood channel (periphery)</td>
<td>pasture</td>
<td>30 58 12</td>
<td>6.2</td>
<td>8.93</td>
<td>0.80</td>
<td>16.70</td>
</tr>
<tr>
<td>6</td>
<td>Sandau 30</td>
<td>Eutric Gleysoil</td>
<td>flood channel (center)</td>
<td>extensive grassland</td>
<td>41 50 9</td>
<td>5.1</td>
<td>8.33</td>
<td>0.80</td>
<td>15.4</td>
</tr>
</tbody>
</table>

$^a$according to IUSS/ISRIC/FAO (2006), $^b$ determined by “finger test” AG Boden (2005), $\rho_b$ bulk density
Table 2
Air temperature and air pressure at the study sites during sampling including mean values, standard deviation (SD) and numbers of samples (n)

<table>
<thead>
<tr>
<th>Site-No.</th>
<th>Date</th>
<th>Temperature [°C]</th>
<th>Pressure [hPa]</th>
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<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
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<td>8.18</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>14.02.06</td>
<td>2.03</td>
<td>0.19</td>
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<tr>
<td></td>
<td>24.05.06</td>
<td>18.74</td>
<td>1.61</td>
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<tr>
<td></td>
<td>19.07.06</td>
<td>32.91</td>
<td>3.53</td>
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<tr>
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<td>24.08.06</td>
<td>18.93</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>13.09.06</td>
<td>24.44</td>
<td>3.85</td>
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<td>08.11.06</td>
<td>8.10</td>
<td>1.86</td>
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<td>15.11.05</td>
<td>5.87</td>
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<tr>
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<td>26.46</td>
<td>4.41</td>
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<td>21.08.06</td>
<td>21.83</td>
<td>0.45</td>
</tr>
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<td></td>
<td>11.09.06</td>
<td>22.59</td>
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<td>07.11.06</td>
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<td>1.14</td>
</tr>
<tr>
<td>3</td>
<td>15.11.05</td>
<td>5.98</td>
<td>0.54</td>
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<td>17.07.06</td>
<td>27.13</td>
<td>0.62</td>
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<td>21.08.06</td>
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<td>11.09.06</td>
<td>24.24</td>
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<td>07.11.06</td>
<td>12.46</td>
<td>0.79</td>
</tr>
<tr>
<td>4</td>
<td>16.11.05</td>
<td>5.92</td>
<td>0.41</td>
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<td>23.05.06</td>
<td>16.13</td>
<td>0.39</td>
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<td>18.07.06</td>
<td>27.54</td>
<td>1.38</td>
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<td>12.09.06</td>
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<td>3.55</td>
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<td>06.11.06</td>
<td>12.35</td>
<td>0.52</td>
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<td>16.11.05</td>
<td>6.00</td>
<td>0.80</td>
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<td>23.05.06</td>
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<td>n.d.</td>
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<td>34.68</td>
<td>1.76</td>
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<td>24.60</td>
<td>1.34</td>
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<td>06.11.06</td>
<td>12.70</td>
<td>0.40</td>
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<td>6</td>
<td>17.11.05</td>
<td>1.85</td>
<td>1.10</td>
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<td>23.05.06</td>
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<td>n.d.</td>
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<td>22.08.06</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td></td>
<td>06.11.06</td>
<td>n.d.</td>
<td>n.d.</td>
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</table>

n.d.: not determined due to flooding
Table 3
Correlation coefficients (Pearson) for relations between TGM emission rates (seasonal measurements at six study sites with a pumped gas volume of 60 and 120 L), soil properties (10 cm depth), and parameters of atmospheric conditions

<table>
<thead>
<tr>
<th></th>
<th>TGM&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ln TGM&lt;sup&gt;a&lt;/sup&gt;</th>
<th>TGM&lt;sup&gt;b&lt;/sup&gt;</th>
<th>ln TGM&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil temperature</td>
<td>0.35&lt;sup&gt;*&lt;/sup&gt;</td>
<td>0.57&lt;sup&gt;**&lt;/sup&gt;</td>
<td>0.54&lt;sup&gt;**&lt;/sup&gt;</td>
<td>0.65&lt;sup&gt;**&lt;/sup&gt;</td>
</tr>
<tr>
<td>Air temperature</td>
<td>0.37&lt;sup&gt;*&lt;/sup&gt;</td>
<td>0.55&lt;sup&gt;**&lt;/sup&gt;</td>
<td>0.51&lt;sup&gt;**&lt;/sup&gt;</td>
<td>0.63&lt;sup&gt;**&lt;/sup&gt;</td>
</tr>
<tr>
<td>Soil water content</td>
<td>n.s.</td>
<td>-0.40&lt;sup&gt;*&lt;/sup&gt;</td>
<td>-0.41&lt;sup&gt;*&lt;/sup&gt;</td>
<td>-0.49&lt;sup&gt;**&lt;/sup&gt;</td>
</tr>
<tr>
<td>Air pressure</td>
<td>n.s.</td>
<td>n.s.</td>
<td>0.49&lt;sup&gt;**&lt;/sup&gt;</td>
<td>0.49&lt;sup&gt;**&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> TGM emission rate at a pumped volume of 60 L (n=32), <sup>b</sup> TGM emission rate at a pumped volume of 120 L (n=27), * p ≤ 0.05, ** p ≤ 0.01
Table 4
TGM emission rates at different Hg contamination levels in soils world-wide

<table>
<thead>
<tr>
<th>Region, Country</th>
<th>Site/ Soil</th>
<th>Method</th>
<th>Hg content (topsoil) [mg kg⁻¹]</th>
<th>TGM emission rate [ng m⁻² h⁻¹]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global</td>
<td>natural Hg emission / natural enriched areas</td>
<td>estimated</td>
<td>not specified</td>
<td>~ 0.7 to ~ 1.1</td>
<td>Lindqvist et al., 1991; Mason et al., 1994; Schroeder &amp; Munthe, 1998</td>
</tr>
<tr>
<td>Sweden</td>
<td>forest soils, background level</td>
<td>dynamic flux chamber</td>
<td>not specified</td>
<td>-2.0 to + 2.5</td>
<td>Xiao et al., 1991</td>
</tr>
<tr>
<td>USA</td>
<td>max. minor contaminated soils</td>
<td>dynamic flux chamber</td>
<td>&lt; 0.01 bis 0.06</td>
<td>-0.1 to 2.7</td>
<td>Ericksen et al., 2006</td>
</tr>
<tr>
<td>Rio Negro, Brasilia</td>
<td>alluvial soil, deforested plain (day)</td>
<td>dynamic flux chamber</td>
<td>not specified</td>
<td>2.6 ± 2.0²</td>
<td>Magarelli &amp; Fostier, 2005</td>
</tr>
<tr>
<td>(night)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>France</td>
<td>unpolluted wetlands (dry)</td>
<td>dynamic flux chamber</td>
<td>0.06</td>
<td>-1.5 to 2.4</td>
<td>Poissant et al., 2004</td>
</tr>
<tr>
<td>(flooded)</td>
<td></td>
<td></td>
<td></td>
<td>-0.5 to 7.1</td>
<td></td>
</tr>
<tr>
<td>Tennessee, USA</td>
<td>forest soils, background levels</td>
<td>dynamic flux chamber</td>
<td>0.47 ± 0.08 resp. 0.68 ± 0.14⁴⁰</td>
<td>2 to 7</td>
<td>Carpi &amp; Lindberg, 1998</td>
</tr>
<tr>
<td>(field soils, background levels)</td>
<td></td>
<td></td>
<td>0.06 ± 0.02 resp. 0.11 ± 0.01⁴⁰</td>
<td>12 to 45</td>
<td></td>
</tr>
<tr>
<td>Northern Germany</td>
<td>contaminated wetlands of the Elbe River</td>
<td>calculation about soil diffusion</td>
<td>approx. 10</td>
<td>43 ± 5⁶</td>
<td>Wallschlager et al., 2002</td>
</tr>
<tr>
<td>Tennessee, USA</td>
<td>unpolluted wetlands, environmental impact by factory of nuclear weapons</td>
<td>micrometeorological</td>
<td>≥ 50</td>
<td>10 to 200</td>
<td>Lindberg et al., 1995</td>
</tr>
<tr>
<td>Northern Germany</td>
<td>contaminated wetland at the Elbe River</td>
<td>different methods</td>
<td>approx. 10</td>
<td>20 to 500</td>
<td>Wallschlager, 1996</td>
</tr>
<tr>
<td>Lanmuchang, China</td>
<td>soils at Hg-Tl mining areas</td>
<td>dynamic flux chamber</td>
<td>170.0 to 614.0</td>
<td>242 to 2283</td>
<td>Wang et al., 2005</td>
</tr>
<tr>
<td>Nevada, USA</td>
<td>substrate with background levels</td>
<td>dynamic flux chamber</td>
<td>&lt; 0.005 to 0.1</td>
<td>-3.7 to 9.3</td>
<td>Nacht &amp; Gustin, 2004</td>
</tr>
<tr>
<td>(substrate with geogen enriched content)</td>
<td></td>
<td></td>
<td>0.01 to 44.7</td>
<td>-15.4 to 3344</td>
<td></td>
</tr>
<tr>
<td>Toronto, Ontario, Canada</td>
<td>Toronto soils</td>
<td>dynamic flux chamber</td>
<td>60.7 ng g⁻¹ (median)</td>
<td>6.2 (range 0.7 to 35)</td>
<td>Eckley &amp; Branfireun, 2008</td>
</tr>
<tr>
<td>Tuscaloosa, Alabama, USA</td>
<td>bare soil (sandy clay)</td>
<td>polycarbonate flux chamber</td>
<td>0.025 to 0.047</td>
<td>5.69 ± 5.79</td>
<td>Gabriel &amp; Williamson, 2008</td>
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<tr>
<td>USA</td>
<td>turf grass</td>
<td></td>
<td>0.034 to 0.035</td>
<td>0.53 ± 1.25</td>
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</tr>
<tr>
<td>Eastern Seaboard, USA</td>
<td>pavement (asphalt-aggregate mix)</td>
<td></td>
<td>2.70 µg m⁻²</td>
<td>0.26 ± 0.41</td>
<td></td>
</tr>
<tr>
<td>Central Germany</td>
<td>terrestrial background surfaces (forest soils)</td>
<td>dynamic flux chamber</td>
<td>0.013 to 0.219</td>
<td>0.2 ± 0.9</td>
<td>Kuijken et al., 2008</td>
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<tr>
<td>(contaminated floodplain soils at the Elbe River)</td>
<td>new sampling setup (modified flux chamber), 60 L</td>
<td></td>
<td>3.5 bis 16.7</td>
<td>10 to 849</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>new sampling setup (modified flux chamber), 120 L</td>
<td></td>
<td></td>
<td>24 to 479</td>
<td></td>
</tr>
</tbody>
</table>

 commentator: mean value ± standard deviation, ²organic layer

References:
- Lindqvist et al., 1991
- Mason et al., 1994
- Schroeder & Munthe, 1998
- Xiao et al., 1991
- Ericksen et al., 2006
- Magarelli & Fostier, 2005
- Poissant et al., 2004
- Carpi & Lindberg, 1998
- Wallschlager et al., 2002
- Lindberg et al., 1995
- Wallschlager, 1996
- Wang et al., 2005
- Nacht & Gustin, 2004
- Eckley & Branfireun, 2008
- Gabriel & Williamson, 2008
- Kuijken et al., 2008
- This study

Note: The emission rates and Hg content values are given in various units, including ng m⁻² h⁻¹, mg kg⁻¹, and µg m⁻².
Table 5
Mercury stocks in soils (10 cm depth), Hg stocks required within the action value (2 mg kg\(^{-1}\)) of the German Soil Conservation Law (BBodSchG, 1998), mean Hg emission rates and figured period needed to achieve the action value when Hg is considered to be only exported through gaseous emissions

<table>
<thead>
<tr>
<th>Site-No.</th>
<th>Current Hg stocks in soil (0-10 cm depth) [mg m(^{-2})]</th>
<th>Critical value of Hg stocks in soils (0-10 cm depth) based on action value [mg m(^{-2})]</th>
<th>Mean Hg emission rate [mg m(^{2}) a(^{-1})]</th>
<th>Years until Hg emission can achieve action value</th>
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<tr>
<td></td>
<td></td>
<td>60 L(^a)</td>
<td>120 L(^a)</td>
<td>60 L(^a)</td>
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<tr>
<td>1</td>
<td>282</td>
<td>164</td>
<td>2.0</td>
<td>1.2</td>
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<tr>
<td>2</td>
<td>311</td>
<td>160</td>
<td>1.2</td>
<td>1.5</td>
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<td>319</td>
<td>157</td>
<td>2.1</td>
<td>1.6</td>
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<td>4</td>
<td>769</td>
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<td>1336</td>
<td>160</td>
<td>2.5</td>
<td>1.8</td>
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\(^a\) pumped gas volume during sampling