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

Anja During, Jörg Rinklebe, Mark Overesch, Gijs Du Laing, Rainer Wennrich, Hans-Joachim Stärk, Sibylle Mothes.

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

3

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25

26 **“Capsul”:**

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

28

29 **Abstract**

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

41

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

43

44 **1. Introduction**

45 Environmental pollution by mercury is a world-wide problem (Munthe et al., 2001). Particularly  
46 floodplain ecosystems are frequently affected. One example is the Elbe River in Germany and  
47 its catchment areas; large amounts of heavy metals including Hg from a range of anthropogenic  
48 and geogenic sources have been accumulated in the soils of these floodplains (Kowalik et al.,  
49 2003; Overesch et al., 2007; Rinklebe et al., 2007; 2009). They serve as sink for Hg originating  
50 from the surface water of adjacent river. Until 1996, 1 500 ± 500 t of Hg were deposited in parts  
51 of the Elbe wetlands within a period of 60 years only (Wallschläger, 1996). Consequently, the  
52 wetland soils along the Elbe River contain 10 times more Hg compared to floodplain soils in the  
53 USA, as studied by Patrick et al. (2004) and Devai et al. (2005). Today, the vastly elevated Hg  
54 contents of the floodplain soils at the Elbe River often exceed even the action values of the  
55 German Soil Conservation Law (BBodSchG, 1998; BBodSchV, 1999). This is especially  
56 important as Hg polluted areas at the Elbe River achieve several hundreds square kilometers.

57 Thus, authorities are coerced by law to conduct an appropriate risk assessment and to implement  
58 practical actions to eliminate or reduce environmental problems. A reliable risk assessment  
59 particularly with view to organisms (vegetation as green fodder and hay production, grazing and  
60 wild animals) to avoid the transfer of Hg into the human food chain, requires an authentic  
61 determination of Hg fluxes and their dynamics since gaseous emissions from soil to atmosphere  
62 are probably the most important pathway of Hg.

63 The environmental chemistry of Hg has been reviewed extensively (e.g. Ebinghaus et al., 1999,  
64 Zhang et al., 2003). Special attention must be paid to the reduction of Hg(II) to Hg(I) or Hg(0),  
65 which is preferred under very low redox potentials in frequently or permanently flooded soils  
66 and sediments. Mercury may also exist in organometallic forms, of which monomethylmercury  
67 ( $\text{CH}_3\text{Hg}^+$ ) and dimethylmercury  $[(\text{CH}_3)_2\text{Hg}]$  are the most important. Hg(0) and  $(\text{CH}_3)_2\text{Hg}$  are  
68 volatile species. Therefore, gaseous emissions from soil to atmosphere are considered to be an  
69 important pathway (Du Laing et al., 2009), and Hg might be atmospherically distributed world-  
70 wide (Poissant and Casimir, 1998). The release of Hg into the atmosphere is caused by a  
71 diversity of natural and anthropogenic sources (e.g. Bash and Miller, 2007; Pacyna et al., 2005;  
72 Yan et al., 2003). The estimated gaseous Hg emission rate from anthropogenic sources in the  
73 year 2000 was comparable to estimates of Hg emissions from natural sources (Pacyna et al.,  
74 2006).

75 During the past twenty years different studies determined soil-air exchange rates of Hg at  
76 various sites to assess related risks (e.g. Schroeder et al., 1989; Schroeder and Munthe, 1998;  
77 Schlüter, 2000; Lindberg et al., 2002; Ravichandran, 2004). The release of Hg from soil to  
78 atmosphere was found to be influenced by many factors. Atmospheric Hg amounts above soil  
79 surfaces can be positively correlated to the Hg stocks in these soils, although other soil  
80 parameters and atmospheric conditions can affect the Hg emission and mask this relationship  
81 (Schlüter, 2000). Soil temperature and soil water content are described as the main factors  
82 controlling Hg emission from soils (Gillis and Miller, 2000; Johnson and Lindberg, 1995; Song  
83 and Heyst, 2005; Zhang et al., 2003). Rising soil water content can promote the reduction of  
84 Hg(II) to Hg(0) and subsequent Hg volatilization exponentially (Johnson and Lindberg, 1995,

85 Gillis and Miller, 2000, Song and Heyst, 2005). Consequently, precipitation has a positive  
86 influence on Hg volatilization from soils (Wallschläger et al., 2000, Song and Heyst, 2005),  
87 whereas in floodplain soils, soil water content and mercury volatilization are affected to a great  
88 extent by the variable water table levels. Increasing soil temperatures due to solar radiation are  
89 also correlated to TGM emissions (Zhang et al., 2003). The vapour pressure of volatile Hg  
90 species increases with rising soil temperatures, decreasing Hg sorption to the soil. Moreover, if  
91 soil air expands and air circulation increases, the reaction rates of Hg(II)-reduction and –  
92 methylation increase, additionally microbial activity is promoted (Schlüter, 2000). Significant,  
93 exponential relations between Hg emission rates and soil temperature were established for forest  
94 soils in North-American wetland areas (Lindberg et al., 1995; Poissant et al., 2004). However,  
95 reliable estimates of Hg fluxes from the highly polluted floodplain soils at the Elbe River and its  
96 tributaries, and its influencing factors are scarce.

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

103

## 104 **2. Materials and Methods**

### 105 **2.1 Study Sites**

106 The study sites are situated in floodplains at the Central Elbe River in Germany (Fig. 1). The  
107 site Wörlitz is located at stream kilometer 242 (51°51'27''N, 12°23'06''E), the site  
108 Breitenhagen at stream kilometer 290 (51°57'15''N, 11°54'57''E), and the site Sandau at  
109 stream kilometer 417 (52°48'00''N, 12°02'15''E) (Fig. 1). The long-term annual precipitation  
110 ranges from 470 to 570 mm and the mean annual air temperature is around 8.0 °C (Rinklebe,  
111 2004). Air temperatures and amounts of precipitation at the study sites during the monitoring  
112 are given in Fig. 2. The study sites are periodically flooded by the Elbe River with amplitudes of

113 up to 8 m mainly depending on snowmelt (winter and spring) and heavy rainfalls (spring and  
114 summer). The site Breitenhagen is additionally influenced by its tributary Saale River.

115 **Insert Figure 1**

116 **Insert Figure 2**

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

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

128 **Insert Table 1**

## 129 **2.2 Sampling and analysis of bulk soil**

130 Soil samples were collected in soil profiles according to soil-genetic horizons. Sampling was  
131 performed in four replicates of about 1 kg which were pooled to one sample per horizon  
132 (Rinklebe, 2004). Air dried soil material was sieved to < 2 mm. Subsamples were ground in an  
133 agate disc mill. Soil properties were determined according to standard methods (Schlichting et  
134 al., 1995) as follows. Total C ( $C_t$ ) was measured using a C/N/S-Analyzer (Vario EL Heraeus,  
135 Analytik Jena). Inorganic C was quantified after treatment with phosphoric acid (15 %) and IR-  
136 Detection of the evolved  $CO_2$  with a C-MAT 550 (Strohlein). Soil organic C ( $C_{org}$ ) was  
137 calculated as the difference between  $C_t$  and inorganic C. Particle-size distribution was  
138 determined by wet sieving and sedimentation using the pipette sampling technique according to  
139 HBU (2000). Soil pH was measured in 0.01 M 2.5:1  $CaCl_2$ - soil suspension. Total Hg  
140 concentrations of soil samples were quantified after digestion using aqua regia - HCl (37 % v/v)

141 + HNO<sub>3</sub> & 5 % v/v), 3:1- ignoring that certain parts may remain in the residuum. Mercury in  
142 soil extracts was measured by cold vapor atomic absorption spectrometry (CV-AAS) (FIMS,  
143 Perkin Elmer). Blanks, triplicate measurements of Hg in extracts, and analysis of multi-element  
144 standards (Merck) were routinely included for quality control. The given results represent  
145 arithmetic means of duplicate samples (Table 1). Maximum allowable relative standard  
146 deviation between replicates was set to 10 %. Bulk densities ( $\rho_b$ ) represent arithmetic means of  
147 ten replicates per horizon using 250 cm<sup>3</sup> soil cores. Hg stocks in different soil layers were  
148 calculated from Hg<sub>tot</sub> and  $\rho_b$  of each soil horizon.

149

### 150 **2.3 TGM Measurements**

151 Mercury emissions were measured between November 2005 and November 2006. The dataset  
152 was collected during seven sampling campaigns, which contained all seasons (14<sup>th</sup> to 17<sup>th</sup> of  
153 November 2005, 13<sup>th</sup> to 14<sup>th</sup> of February 2006, 22<sup>nd</sup> to 24<sup>th</sup> of May 2006, 17<sup>th</sup> to 19<sup>th</sup> of July  
154 2006, 21<sup>st</sup> to 24<sup>th</sup> of August 2006, 11<sup>th</sup> to 13<sup>th</sup> of September 2006, and 06<sup>th</sup> to 08<sup>th</sup> of November  
155 2006). At each sampling site samples were taken around the same time of the day. Sampling at  
156 noon was elided to avoid incident solar radiation to affect the results.

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

169 analysis. Blank values were subtracted from measured samples.

170

#### 171 **2.4 Environmental conditions during TGM sampling**

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

#### 178 **Insert Table 2**

179

#### 180 **2.5 Laboratory experiments**

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

#### 184 **Insert Figure 3**

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

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

193 The experiments were set up in triplicates. Gas sampling was performed in each microcosm for  
194 one hour at intervals of 1, 3, 6, 24, and 48 hours and with a flow rate of 1 L min<sup>-1</sup>. Throughout  
195 the experiments, the microcosm pots were covered with aluminum foil to exclude solar  
196 radiation or algae cultivation. To ensure direct comparability between field and laboratory



197 experiments, exactly the same sampling and measurement technique was used in the laboratory  
198 experiments as described for the field setup (paragraph 2.3).

199

## 200 **2.6 Calculation of mercury fluxes**

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

$$203 \quad F = \frac{C_{abs}}{A} * Q ,$$

204 where F is the total flux of Hg in  $\text{ng m}^{-2} \text{h}^{-1}$ ,  $C_{abs}$  is the mean Hg concentration in  $\text{ng m}^{-3}$   
205 calculated from ng absolute at the outlet less blank value multiplied with  $1\,000 / v$  ( $v$  = volume  
206 in  $\text{L h}^{-1}$ ). A is the covered surface area of the chamber in  $\text{m}^2$  and Q is the flushing flow rate  
207 through the chamber in  $\text{m}^3 \text{h}^{-1}$ . In almost all measurements Hg bound in the second gold trap  
208 was very low or even below detection limit. Therefore, we can assume that Hg volatilizing from  
209 the soils is completely trapped in both gold traps and that the air returned into the chamber  
210 includes no measurable gaseous Hg compounds.

211

## 212 **3. Results**

### 213 **3.1 TGM emission and seasonal variations in the field**

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

#### 219 **Insert Figure 4**

220 All study sites (except site 6, Fig. 4/ F) reveal seasonal variations of measured Hg emission  
221 rates, soil temperature, and soil water content. Emissions of TGM at each study site tend to be  
222 higher during summer (Fig. 4/ A- E), although fairly high Hg fluxes were observed at study area  
223 ‘Sandau’ in November 2006 (Fig. 4/ D and E). A peak of TGM emission occurred at study site

224 1 in August 2006. At the same time, the maximum mean TGM emission rate of the replicates  
225 was quantified at this site as  $849 \text{ ng m}^{-2} \text{ h}^{-1}$  at a flow rate of 60 L (Fig. 4/ A). The lowest mean  
226 TGM emission of  $9.7 \text{ ng m}^{-2} \text{ h}^{-1}$  was found in February 2006 at site 2 (Fig. 4/ B). Mercury  
227 emission rates measured when using a pumped volume of 60 L reveal the same seasonal  
228 dynamics as those measured when using a pumped volume of 120 L, although differences can  
229 be occasionally observed.

230 In the summer months soil water content decreased while soil temperature and consequently the  
231 Hg volatilization increased. Fluctuating water levels of the Elbe River result in periodic  
232 flooding, which in turn have a strong impact on the moisture regime of the soils. In August 2006  
233 (e.g. Fig. 4/ A, B, C) and 11-2006 (e.g. D, F), gently increased soil water contents can be related  
234 to high TGM emission rates. However, the impact of soil water content on TGM emission  
235 seems to be of less importance compared to the role of soil temperature.

236 Indeed, emission rates are clearly related to soil temperatures: high emissions occur at high soil  
237 temperatures (Fig. 5). TGM emission rates increase exponentially with rising soil temperatures  
238 at all study sites with the exception of study site 1. This correlation was statistically significant,  
239 except for site 3 (120 L) and site 5, probably as a result of the small amount of samples. The  
240 impact of soil temperature on TGM emissions differs between study sites.

#### 241 **Insert Figure 5**

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

#### 246 **Insert Table 3**

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

252 between air pressure and TGM (Table 3).  
253 Mercury concentrations and stocks in top soil,  $C_{\text{org}}$  content, pH, and soil texture do not show  
254 significant correlations with TGM. Significant interrelations between soil characteristics were,  
255 however, found at the study sites No. 1 to 5. High  $C_{\text{org}}$  contents of the studied soils were  
256 interrelated with high  $\text{Hg}_{\text{tot}}$  and Hg stocks respectively (both:  $R^2 = 0.77$ ,  $p \leq 0.01$ ,  $n = 10$ ).  
257 Furthermore  $C_{\text{org}}$  content was positively correlated with soil temperature ( $R^2 = 0.64$ ,  $p \leq 0.01$ ,  $n$   
258  $= 10$ ). A significant positive relation between silt and  $\text{Hg}_{\text{tot}}$  was detected ( $R^2 = 0.50$ ,  $p \leq 0.05$ ,  $n$   
259  $= 8$ ).

260

### 261 **3.2 Laboratory experiments**

262 Figure 6 represents the time-dependent behavior of Hg volatilization from soil material of study  
263 site No. 3, as influenced by soil water contents (Fig. 6/ A) and soil temperatures (Fig. 6/ B). The  
264  $\text{Hg}_{\text{tot}}$  in soil averaged  $4.1 \text{ mg kg}^{-1}$ .

265 If measured Hg amounts trapped in the gold traps exceeded the linear zone of the calibration  
266 ( $0.3/ 0.5 - 14 \text{ ng}$ ), results were replaced by  $14 \text{ ng}$ . This was the case for four of 120 single  
267 values. One of the three replicates was not included in the dataset if the temporal trend of it  
268 diverged from the two other parallels. This was carried out in certain cases: soil water content  
269 experiment variant 'water holding capacity of 90 % (WC 90 %)' (parallel II, completely),  
270 variant 'air-dry' (parallel II, 3 h) and soil temperature test variant '40 °C' and '20 °C' (parallel I,  
271 completely).

272 The impact of soil water content on Hg emission is affected by sampling time after initiation of  
273 the experiment (Fig. 6/ A). After six hours, air-dried and submerged soil as well as soil with  
274 WC 90 % showed fairly small TGM emission rates (between  $58$  and  $203 \text{ ng m}^{-2} \text{ h}^{-1}$ ), while the  
275 soil with WC 60 % exposed the highest values ( $600 \text{ ng m}^{-2} \text{ h}^{-1}$ ). Afterwards, TGM emission at  
276 the variant 'WC 60 %' was relatively stable (around  $480 \text{ ng m}^{-2} \text{ h}^{-1}$ ), while it increased in the  
277 submerged soil. 'WC 90 %' reached the highest Hg emission rate ( $1120 \text{ ng m}^{-2} \text{ h}^{-1}$ ) after 24  
278 hours. However, after 48 hours, Hg emission of 'WC 90 %' decreased. TGM of air-dried soil  
279 was lowest (between  $19$  and  $203 \text{ ng m}^{-2} \text{ h}^{-1}$ ).

280 The effect of soil temperature on TGM emission from soil of study site No. 3 is shown in Fig. 5/  
281 B. Temperature levels of 10, 20, and 40 °C were chosen. These values exceed measured field  
282 soil temperatures at 10 cm depth (averaged 23 °C), but are more representative for soil  
283 temperatures found in the upper millimeters of soil, which are more important in relation to Hg  
284 volatilization. A positive effect of temperature on Hg emission can be observed. Highest mean  
285 Hg emission rates were 870 ng m<sup>-2</sup> h<sup>-1</sup> at 40 °C, 539 ng m<sup>-2</sup> h<sup>-1</sup> at 20 °C, and 366 ng m<sup>-2</sup> h<sup>-1</sup> at 10  
286 °C. At the end of the 48-hours sampling campaign, TGM emission rates of all temperature  
287 treatments decreased to 99-215 ng m<sup>-2</sup> h<sup>-1</sup> (Fig. 6).

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

290

291 **Insert Figure 6**

292 **Insert Figure 7**

293 **Insert Table 4**

294 **Insert Table 5**

295

#### 296 **4. Discussion**

297 Table 4 presents data of TGM emission rates reported world-wide at different Hg contamination  
298 levels of bulk soil and measured with different methods. TGM fluxes of our study range  
299 between 10 and 849 ng m<sup>-2</sup> h<sup>-1</sup> or between 24 and 479 ng m<sup>-2</sup> h<sup>-1</sup>, for 60 and 120 L pumped gas  
300 volume, respectively. These fluxes are located above background fluxes from unpolluted soils,  
301 which rarely increase 10 ng m<sup>-2</sup> h<sup>-1</sup> (e.g. Carpi and Lindberg, 1998). They are comparable to  
302 values reported by Wallschläger (1996), who used different measurement systems at one site of  
303 the Elbe floodplain. However, we found slightly higher TGM values than those measured with a  
304 dynamic flux chamber at a soil temperature of 20 °C (42.7 ng m<sup>-2</sup> h<sup>-1</sup>, Wallschläger et al., 2002),  
305 while the studied soils contained nearly the same contamination level. Only site No. 5 showed  
306 an elevated Hg concentration (> 10 mg kg<sup>-1</sup>, e.g. Tab. 1) compared to those measured by  
307 Wallschläger et al. (2002). However, the larger flushing flow rate or the elevated frequency of

308 air exchange in the chamber of the modified sampling kit might affect the TGM values what  
309 Zhang et al. (2002) have also previously reported. Thus, the chosen flushing flow rate of our  
310 study was not too high to simulate Hg volatilization under natural conditions. Extremely high  
311 emissions, such as  $2\,000\text{ ng m}^{-2}\text{ h}^{-1}$ , determined in industrially or geogenic enriched areas  
312 (Nacht and Gustin, 2004; Wang et al., 2005), were not observed at the soils of the current study.  
313  
314 However, it should be noted that the use of various methods (Table 4) in the different studies  
315 might explain some divergence between results. Moreover, the measured Hg emission rates are  
316 mean values of three or four replicates in our study, whereas replicates can show a high standard  
317 deviation (e.g. Rinklebe et al., 2009).  
318 Mercury emission seems to increase during summer, when soil temperatures are high (Fig. 4/ A-  
319 E). A strong relationship can be observed between TGM and soil temperature, which can be  
320 considered as the main controlling factor (except site 1, Fig. 5). This relationship originates  
321 from the exponential increase of vapor pressure of  $\text{Hg}^0$  and  $(\text{CH}_3)_2\text{Hg}$  (Gustin et al., 1997;  
322 Schlüter, 2000), as well as the decreasing sorption to the solid soil phase with rising  
323 temperatures (Schlüter, 2000). An increase in temperature can be induced by solar radiation,  
324 whereas temperature effects can result in diurnal and seasonal variations of TGM emission.  
325 Stronger solar radiation in the daytime results in higher temperatures, which affect the Hg  
326 release (Frescholtz and Gustin, 2004). At night, Hg emission rates often decline (Poissant et al.,  
327 2004). Both diurnal and annual variations were observed in Swedish forests (Schroeder and  
328 Munthe, 1998). Gabriel et al. (2006) reported greater diurnal variances of TGM fluxes than  
329 seasonal flux variances for different soil surfaces. Sampling in our study was always conducted  
330 ante meridiem and if possible during the same timeframe, so that incident solar radiation was  
331 avoided and variations should be attributed to the sampling season.  
332 Relations between temperature and TGM emission are mainly exponential, which has been  
333 documented for other sampling sites as well (Kim et al., 1995; Lindberg et al., 1995; Carpi and  
334 Lindberg, 1998; Poissant et al., 2004). The temperature coefficients (except TGM emission on  
335 site 3 / 120 L) exceed the values  $e^{0.065 \pm 0.011 T(\text{soil})}$  given by Lindberg et al. (1995) or  $e^{0.044 \pm 0.005 T}$

336 (soil) cited by Gustin et al. (1997). Moreover, the relationship between temperature and TGM  
337 emission seems to be site-specific. E.g., a linear instead of exponential correlation between soil  
338 temperature and TGM emission rate occurred at site 1, which was also observed by Magarelli  
339 and Forstier (2005) in deforested floodplain soils. The fitting of exponential curves to the  
340 laboratory data is better, compared to when field data are used (Fig. 7). This should be attributed  
341 to the fact that other non-controllable factors also affect TGM emission under field conditions,  
342 e.g. flooding.

343 The water level of the Elbe River fluctuates extremely, which results in temporarily flooded  
344 areas. This in turn influences the water content of the soils, although TGM emissions are not as  
345 obviously influenced by this phenomenon as compared to the effect of soil temperature.

346 Poissant et al. (2004) also observed higher mercury volatilization under dry conditions ( $0.83 \text{ ng}$   
347  $\text{m}^{-2} \text{ h}^{-1}$ ) compared to flooded conditions ( $0.50 \text{ ng m}^{-2} \text{ h}^{-1}$ ) in floodplains of Québec (Canada). In  
348 contrast, Wallschläger et al. (2000) described a triplication of Hg fluxes from heavy metal  
349 enriched floodplain soils due to an increase of soil water content as a result of raining events  
350 (Wallschläger et al., 2000). Johnson and Lindberg (1995) assessed the  $\text{Hg}^0$  concentration in soil  
351 air at 10 cm soil depth as function of soil water content and  $\text{Hg}^0$  volatilization rate. Mercury  
352 emission rates grew with increasing  $\text{Hg}^0$  concentrations in soil air, which in turn exponentially  
353 increased with soil water content. This can be attributed to the mass transfer from the water  
354 phase to the gaseous phase being reduced due to a reduction of the volume of the gaseous phase  
355 when filling soil pores with water. Moreover, creation of anaerobic conditions, which might  
356 induced by increasing water contents, induces transformations between different Hg species  
357 towards more volatile species (Schlüter, 2000; Du Laing et al., 2009). A positive impact of soil  
358 water content on TGM emission can be confirmed by our laboratory experiments. For soils of  
359 sites 1, 2, and 3, which have almost equal total Hg contents, mean soil water contents and mean  
360 Hg volatilization rates increase in parallel ( $1 < 2 < 3$ ). In spite of highest total soil Hg stocks at site  
361 No. 5 (Table 5), we also observed a negative impact of soil water content on TGM emission.  
362 This could be attributed to a hampered diffusion of gaseous Hg to the atmosphere at high soil  
363 water contents (e.g. Johnson and Lindberg, 1995, Gillis and Miller, 2000, Schlüter, 2000).

364 Due to smaller precipitation and higher evapotranspiration during summer, soil water content  
365 was also negatively correlated to soil temperature in our study, which probably also partly  
366 explains the negative correlation between soil water content and Hg emission which mostly  
367 occur. Revealing the effect of soil water content is further complicated by the occurrence of  
368 interaction with other factors. Poissant et al. (2004) showed that during water saturation, Hg  
369 emissions are intensified by photo reduction of oxidized Hg complexes into volatile Hg species  
370 (especially elemental Hg) in presence of solar radiation. Moreover, an influence of soil water  
371 content on the temperature dependence of Hg emission cannot be excluded and requires further  
372 investigation.

373 TGM emissions might also be affected directly or indirectly by other soil parameters. High  $C_{org}$   
374 contents are often accompanied by elevated Hg contents (e.g. Rinklebe, 2004; Overesch et al.,  
375 2007) and positively correlated to soil temperature. The relation between temperature and  $C_{org}$   
376 contents can be a result of faster warming of humus enriched, dark colored top soils or the lower  
377 thermal conductivity of organic substances (Scheffer, 2002). Increasing soil temperatures in turn  
378 are related to increasing Hg emission rates, as stated above.

379 The vegetation cover was previously also found to affect Hg emission from soils. Lower Hg  
380 evaporation rates have been observed over grasslands compared to bare soils due to minor  
381 mixing of ground-level air films with air reclined above the herbage layer. Moreover, the  
382 shadow of vegetation on soil surface minimizes the temperatures next to the soil and thus Hg  
383 volatilization (Lindberg et al., 1979). In our study, the surface vegetation was removed at each  
384 study site, so only shadow effects of trees may have affected Hg emission and its seasonal  
385 variations. However, differences in soils temperatures between woody sites (study site 2, 3) and  
386 woodless sites (study site 1, 4-6) were hardly found. Volatile Hg can also be emitted from pools  
387 in the rhizosphere into the atmosphere by plenty of terrestrial and aquatic plants (Lindberg et al.,  
388 2002). Eckley and Branfireun (2008) generally agreed that soils consistently featured higher  
389 emissions than all other surfaces they studied, because soils revealed higher  $Hg_{tot}$  due to their  
390 capability to retain and accumulate deposited Hg over time (e.g. Aastrup et al., 1991).

391

392 Different references (e.g. Schlüter, 2000; Nacht and Gustin, 2004) indicate that higher Hg  
393 emission rates are caused by increased Hg concentrations and stocks within soils. However,  
394 correlations and multiple regression analyses between Hg stocks and TGM emission rates did  
395 not reveal a significant relationship in our study.

396 Based on the determined mean annual Hg emission rate of 1.2 to 2.8 mg m<sup>-2</sup> y<sup>-1</sup>, a period  
397 between 59 (site 1, 60 L) and 648 years (site 5, 120 L) would be needed to bring Hg<sub>tot</sub> in soils  
398 lower than the required action value of the German Soil Conservation Law, when taking Hg  
399 output by leaching and Hg uptake by plants not into account. Nevertheless, an elevated Hg  
400 remobilization potential of those Hg enriched soils in form of volatile Hg exists and is affected  
401 by soil temperature and water content as well as the interaction of soil characteristic and  
402 environmental conditions.

403

## 404 **5. Conclusions**

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

419



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425 the gold traps with CV-AAS as well as Mr. H. Dittrich for his technical assistance and Mr. J. Steffen for  
426 analyzing total gaseous mercury.

427

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587

588 **Figures**

589 Fig. 1 Location of the study areas at the Elbe River in Germany (basic maps:

590 <http://de.wikipedia.org/wiki/Deutschland>)

591 Fig. 2 Air temperature and precipitation in the studied region

592 Fig. 3 Sampling set up of laboratory experiments (according to During et al., 2009 and Rinklebe

593 et al., 2009) with soil subjected to different temperature and soil water conditions: double-

594 walled microcosm container (1) glass chamber (2) with Teflon TM frame (3), four inputs (4),

595 silicone tubes (5), connecting piece (6), two gold traps (7), battery operated pump (8) with

596 integrated gas flow meter (9)

597 Fig. 4 Dynamics of TGM fluxes (field measurements using a pumped gas volume of 60 resp.

598 120 L), soil temperature and soil water content at 10 cm depth during sampling appointments at

599 site 1 (A), 2 (B), 3 (C), 4 (D), 5 (E), and site 6 (F)

600 Fig. 5 Correlation between soil temperature (10 cm depth) and TGM emission rate with a

601 pumped volume of 60 L (continuous line) and 120 L (broken line) during sampling at site 1 (A),

602 2 (B), 3 (C), 4 (D), 5 (E), and site 6 (F) (\*\*: statistically significant with  $p \leq 0.01$ , \*: statistically

603 significant with  $p \leq 0.05$ )

604 Fig. 6 Kinetics of Hg emission rates at different soil water contents (A) and different soil

605 temperatures (B) in a laboratory microcosm experiment (soil material: study site No. 3)

606 Fig. 7 Comparison of relations between soil temperatures and mean Hg emission rates for the

607 field study site Breitenhagen 3, both for the laboratory microcosm experiment test and field

608 measurements

609

610 **Tables**

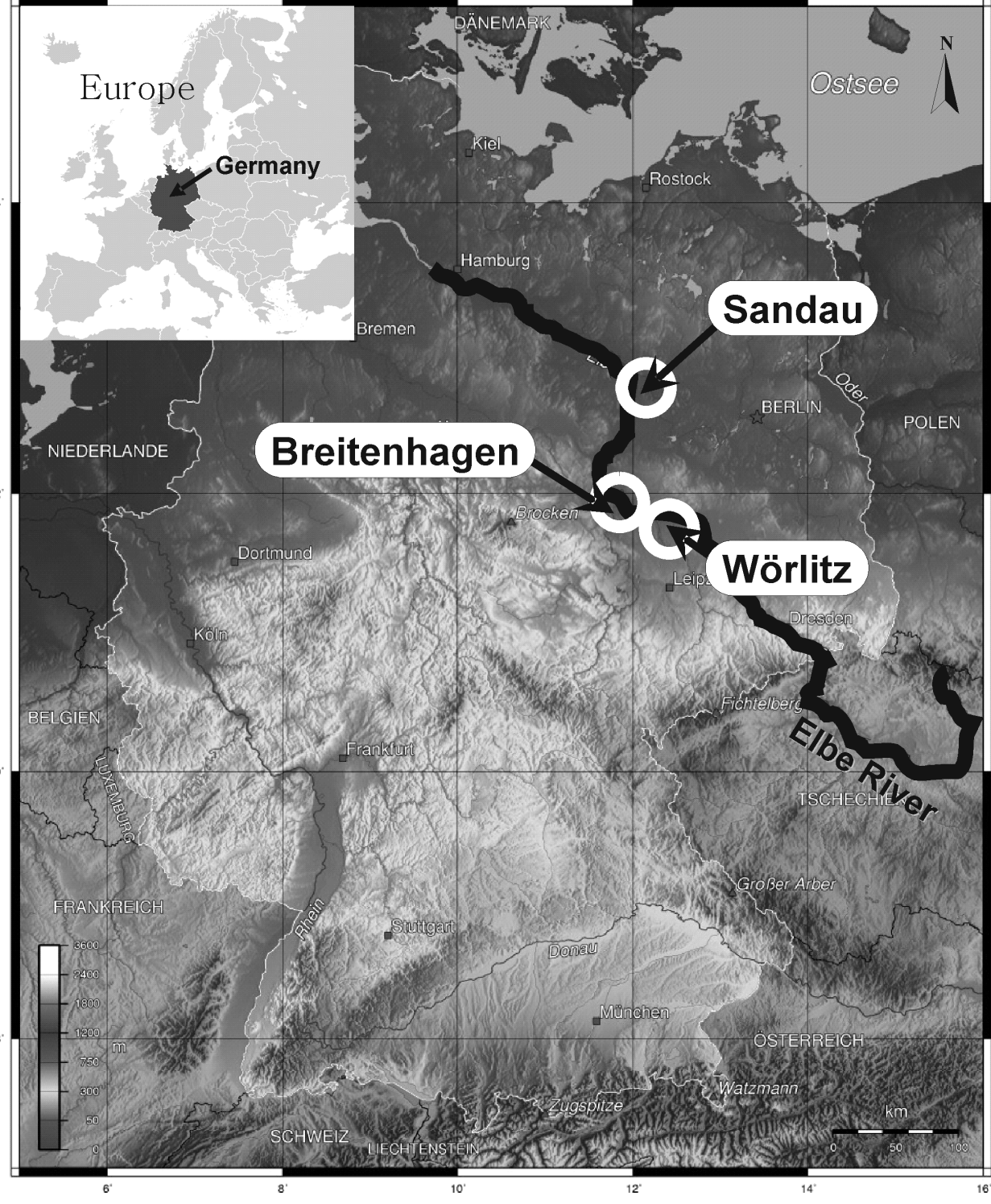
611 Tab.1 Selected soil properties and Hg concentration (aqua regia) (0-10 cm depth) for the six  
612 study sites

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

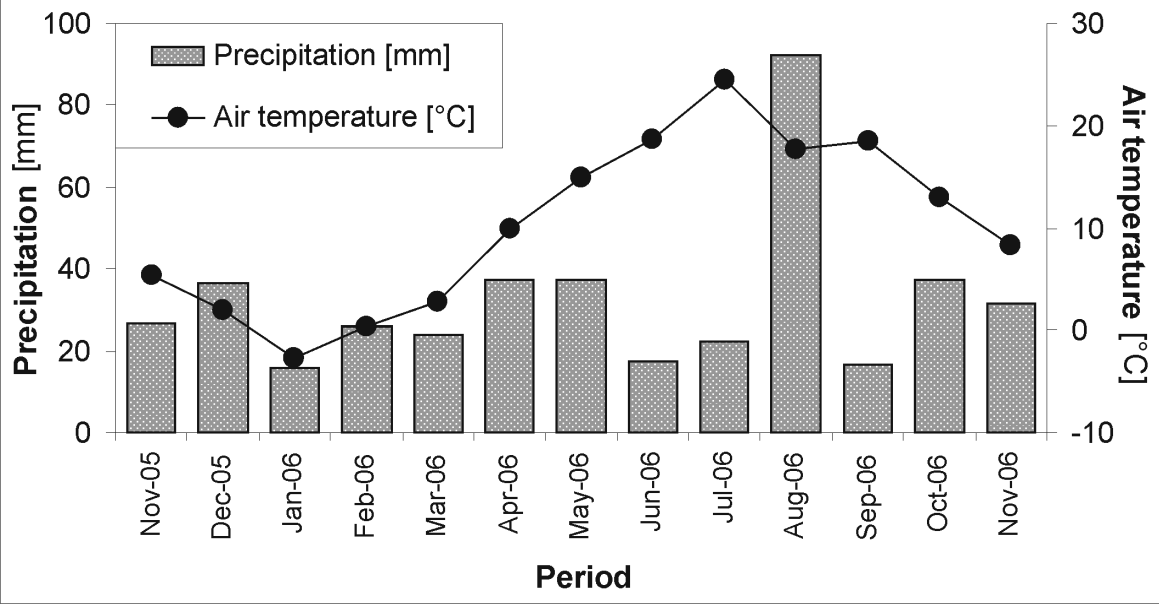
615 Tab. 3 Correlation coefficients (Pearson) for relations between TGM emission rates (seasonal  
616 measurements at six study sites with a pumped gas volume of 60 and 120 L), soil properties (10  
617 cm depth), and parameters of atmospheric conditions

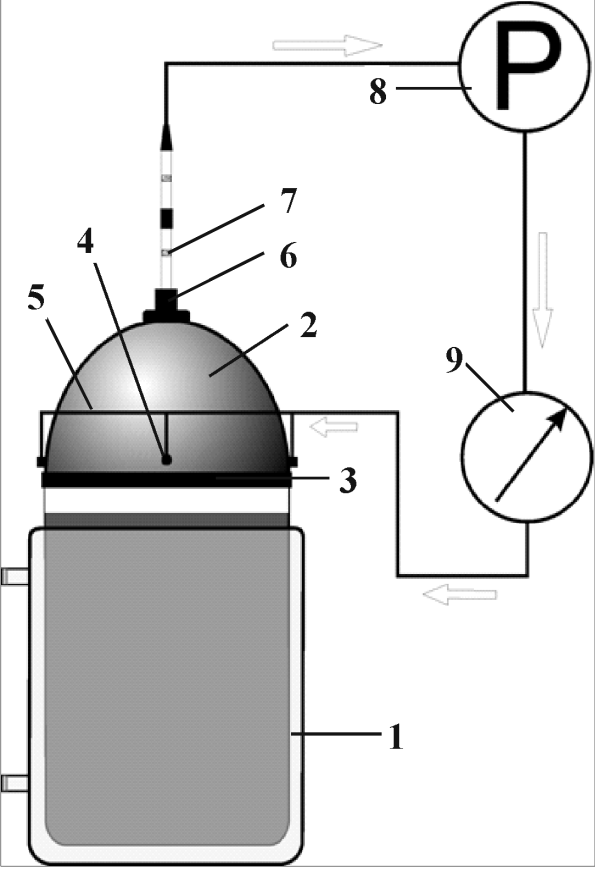
618 Tab. 4 TGM emission rates at different Hg contamination levels in soils world-wide

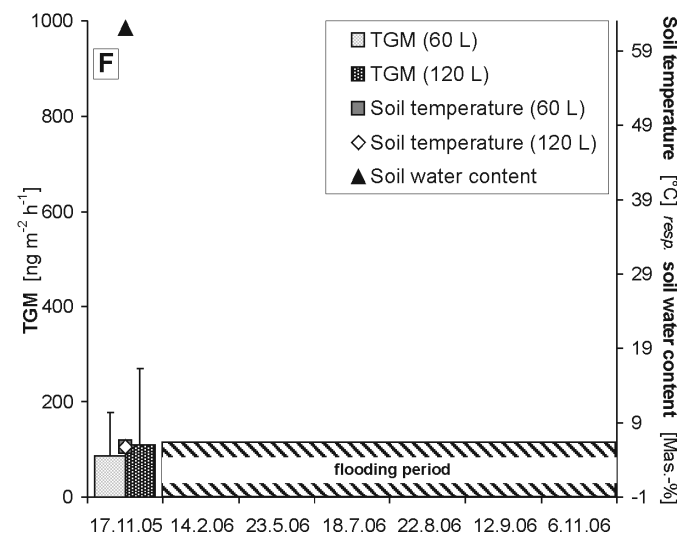
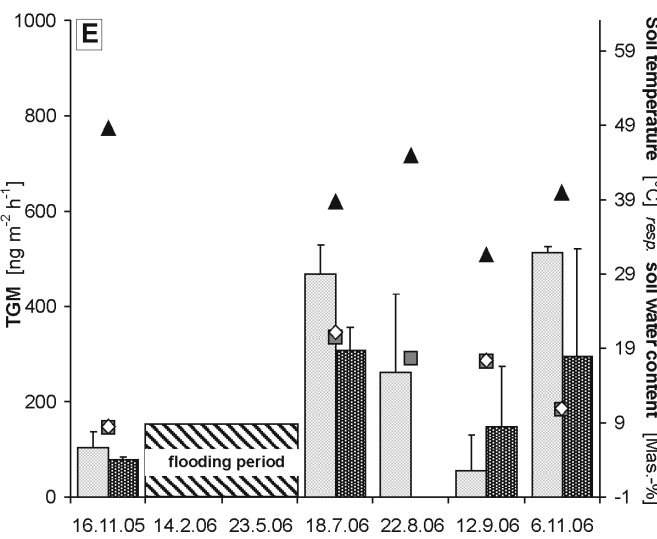
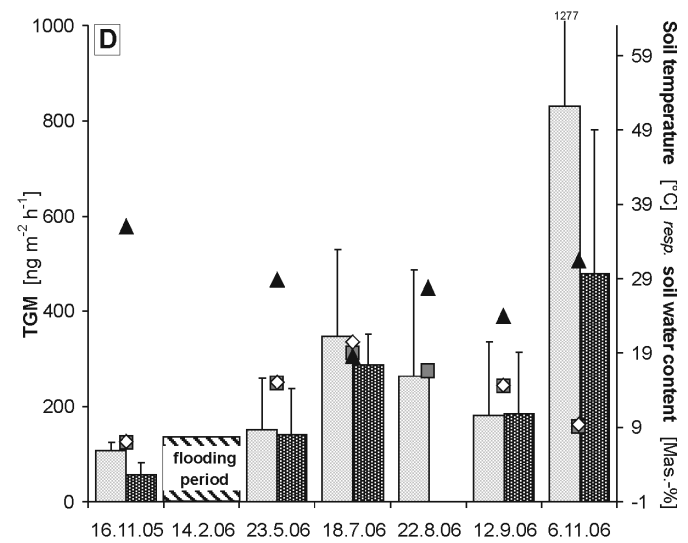
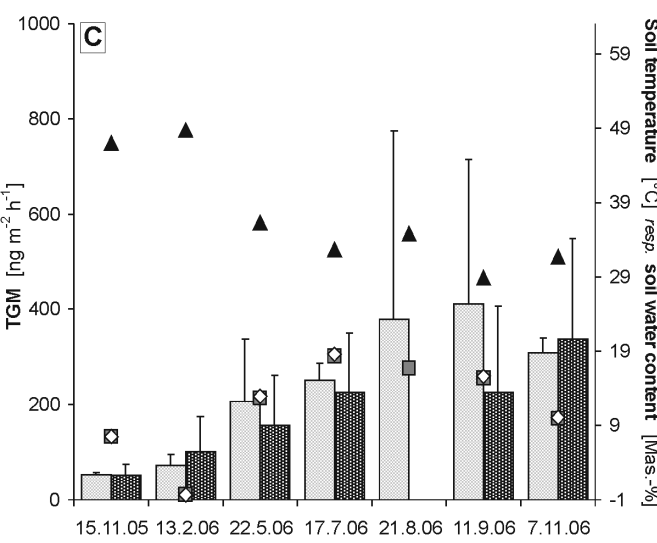
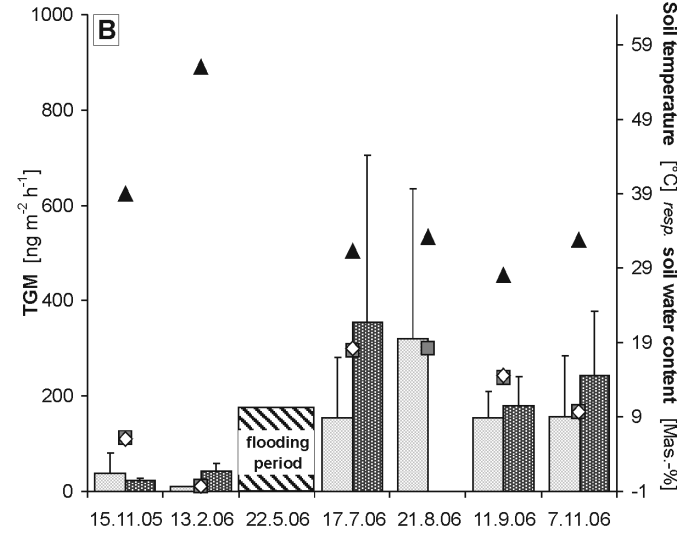
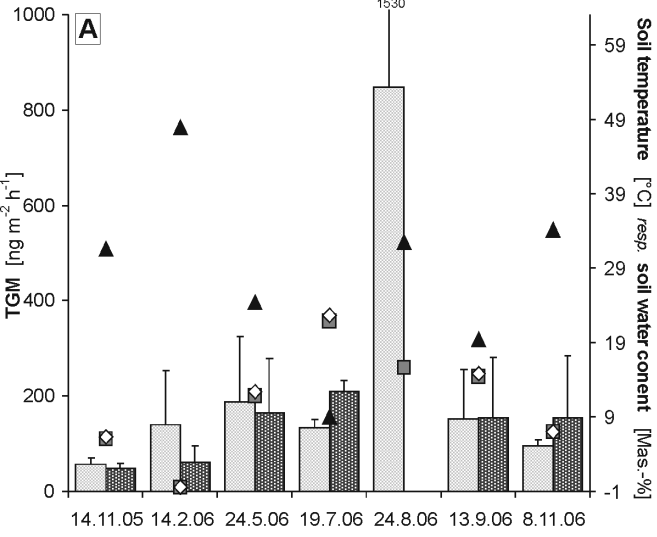
619 Tab. 5 Mercury stocks in soils (10 cm depth), Hg stocks required within the action value (2 mg  
620 kg<sup>-1</sup>) of the German Soil Conservation Law (BBodSchG, 1998), mean Hg emission rates and  
621 figured period needed to achieve the action value when Hg is considered to be only exported  
622 through gaseous emissions.

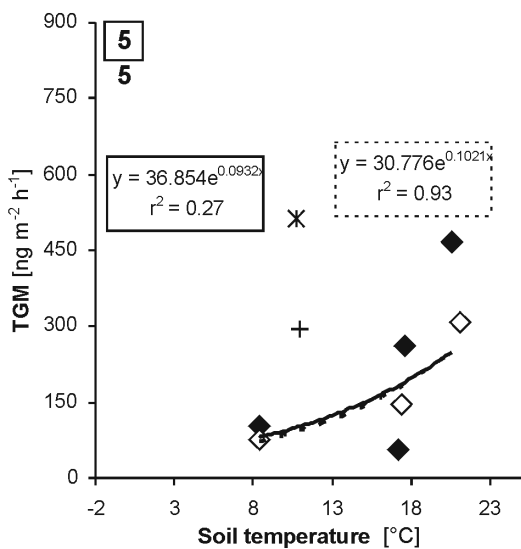
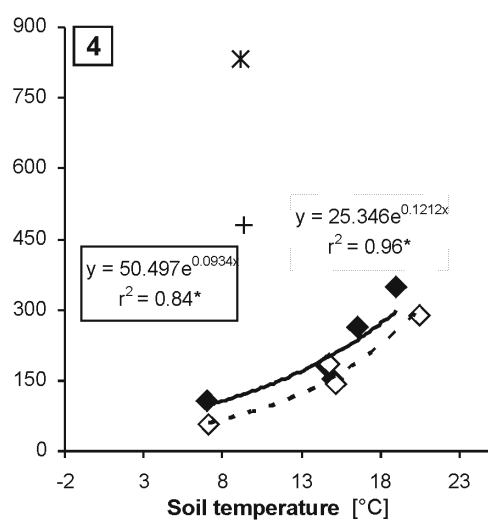
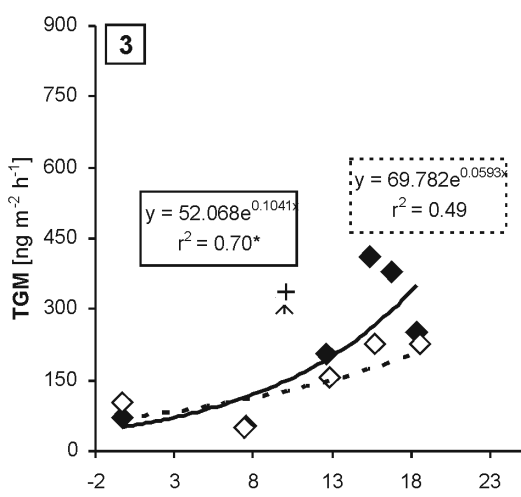
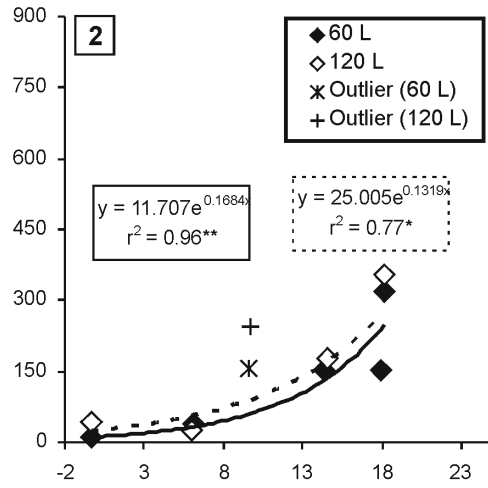
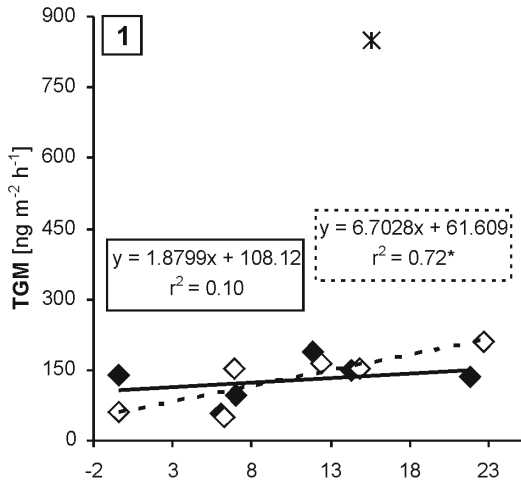


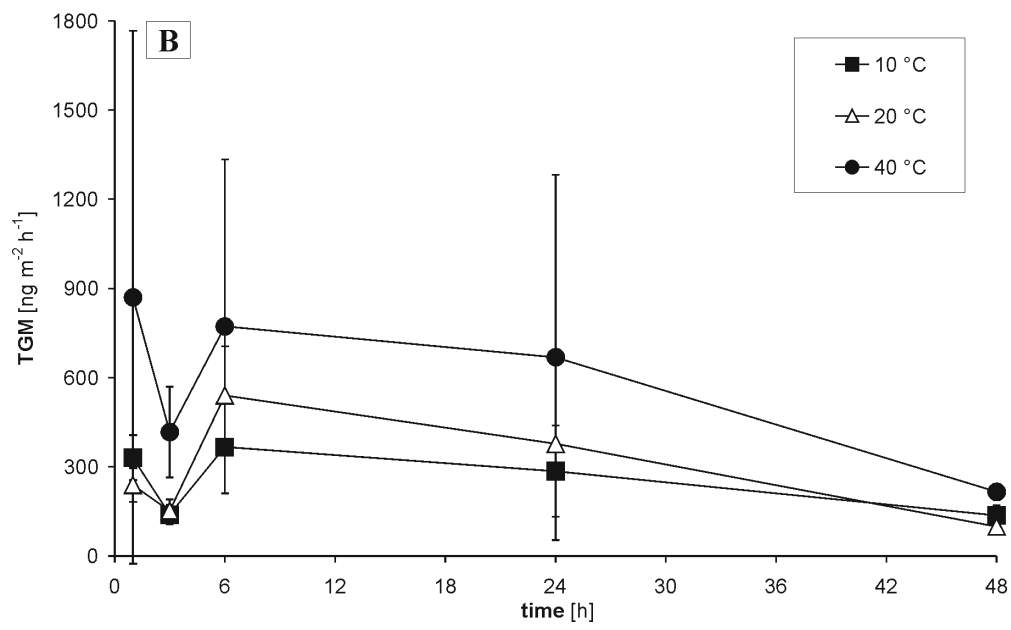
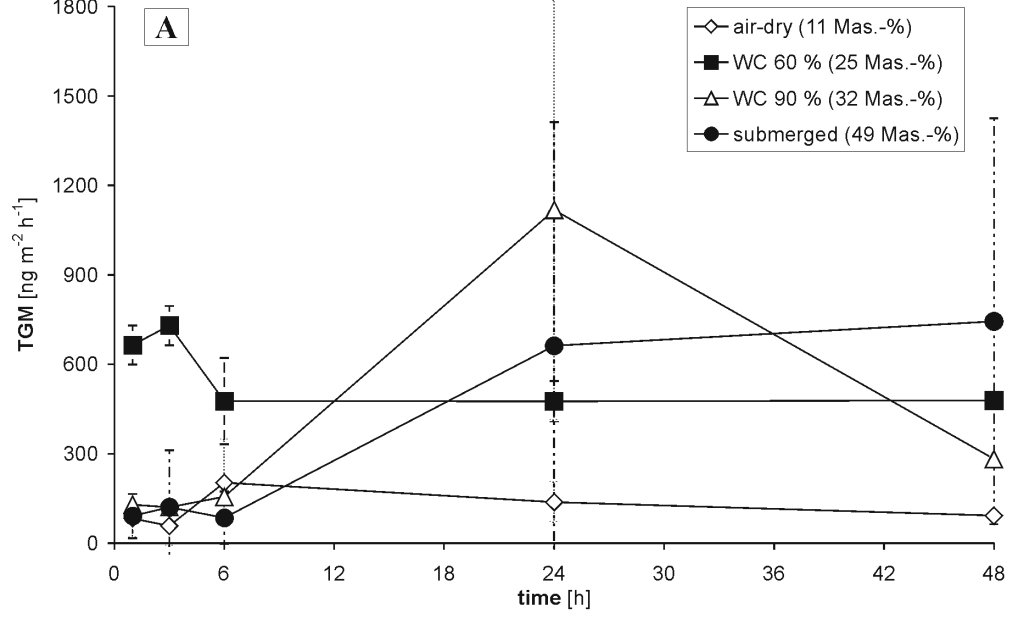












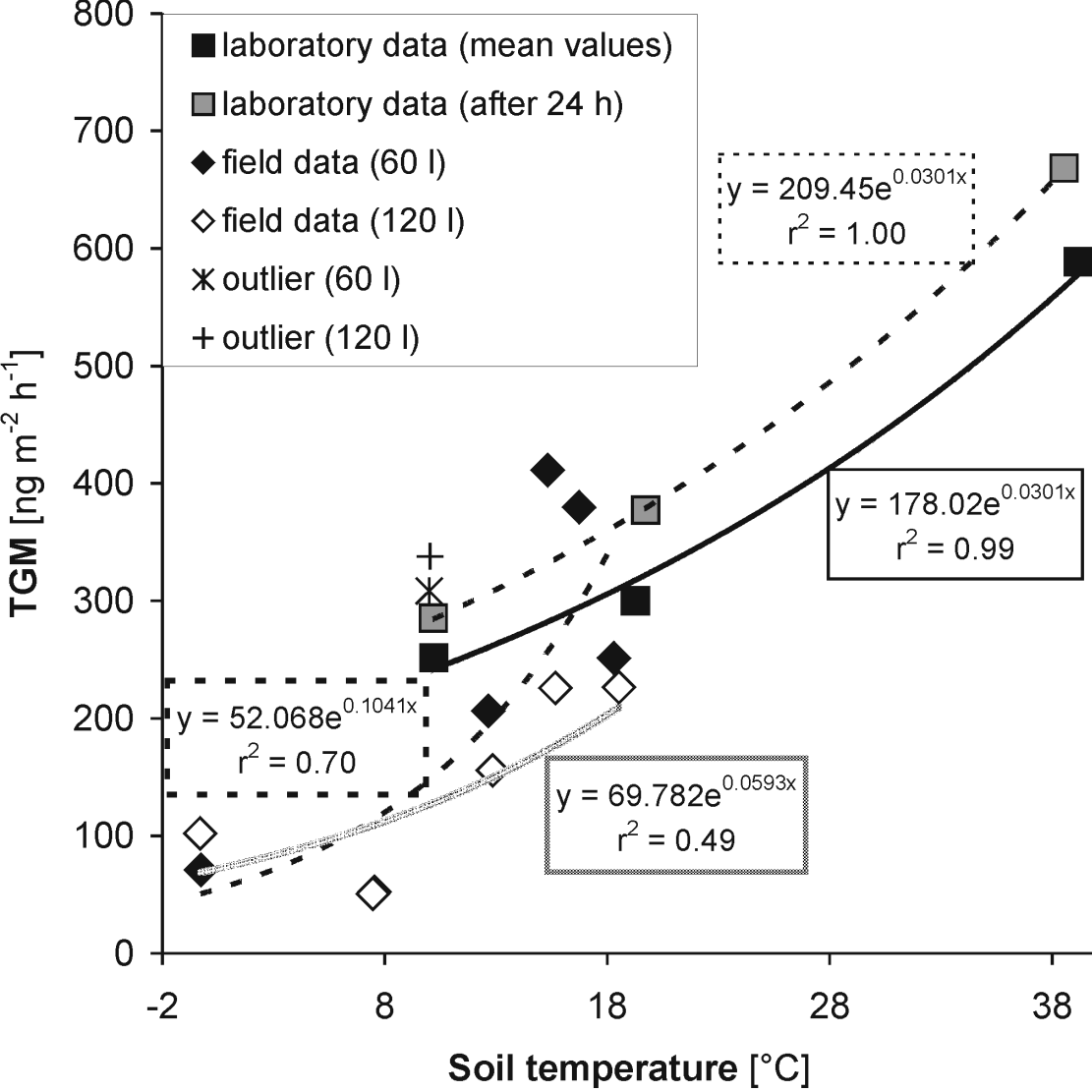


Table 1

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

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

<sup>a</sup>according to IUSS/ISRIC/FAO (2006), <sup>b</sup>determined by “finger test” AG Boden (2005), <sup>c</sup> $\rho_b^c$  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)

| Site-No. | Date     | Air parameter (10 – 20 cm above soil surface) |      |      |                |      |      |
|----------|----------|---|------|------|----------------|------|------|
|          |          | Temperature [°C]                              |      |      | Pressure [hPa] |      |      |
|          |          | Mean  | SD   | n    | Mean           | SD   | n    |
| 1        | 14.11.05 | 8.18  | 1.44 | 6    | 1016           | 2.17 | 6    |
|          | 14.02.06 | 2.03  | 0.19 | 6    | 1013           | 2.43 | 6    |
|          | 24.05.06 | 18.74   | 1.61 | 8    | 1011           | 1.60 | 8    |
|          | 19.07.06 | 32.91   | 3.53 | 8    | 1011           | 0.89 | 8    |
|          | 24.08.06 | 18.93   | 0.22 | 4    | 1002           | 1.29 | 4    |
|          | 13.09.06 | 24.44   | 3.85 | 8    | 1008           | 0.71 | 8    |
|          | 08.11.06 | 8.10  | 1.86 | 8    | 1009           | 2.07 | 8    |
|          | 2        | 15.11.05                                      | 5.87 | 0.71 | 6              | 999  | 2.16 |
| 13.02.06 |          | 2.63  | 1.30 | 6    | 1017           | 2.73 | 6    |
| 22.05.06 |          | n.d.  | n.d. | n.d. | n.d.           | n.d. | n.d. |
| 17.07.06 |          | 26.46   | 4.41 | 8    | 1018           | 1.16 | 8    |
| 21.08.06 |          | 21.83   | 0.45 | 4    | 1006           | 0.50 | 4    |
| 11.09.06 |          | 22.59   | 3.80 | 8    | 1015           | 0.92 | 8    |
| 07.11.06 |          | 11.63   | 1.14 | 8    | 1015           | 1.19 | 8    |
| 3        |          | 15.11.05                                      | 5.98 | 0.54 | 6              | 996  | 2.31 |
|          | 13.02.06 | 5.77  | 0.32 | 6    | 1015           | 1.75 | 6    |
|          | 22.05.06 | 19.20   | 1.13 | 8    | 993            | 1.58 | 8    |
|          | 17.07.06 | 27.13   | 0.62 | 8    | 1016           | 1.00 | 8    |
|          | 21.08.06 | 18.18   | 0.22 | 4    | 1007           | 1.00 | 4    |
|          | 11.09.06 | 24.24   | 0.48 | 8    | 1014           | 1.04 | 8    |
|          | 07.11.06 | 12.46   | 0.79 | 8    | 1012           | 1.13 | 8    |
|          | 4        | 16.11.05                                      | 5.92 | 0.41 | 6              | 991  | 2.42 |
| 14.02.06 |          | n.d.  | n.d. | n.d. | n.d.           | n.d. | n.d. |
| 23.05.06 |          | 16.13   | 0.39 | 8    | 1004           | 1.46 | 8    |
| 18.07.06 |          | 27.54   | 1.38 | 8    | 1015           | 0.64 | 8    |
| 22.08.06 |          | 16.33   | 0.50 | 4    | 1007           | 1.00 | 4    |
| 12.09.06 |          | 21.20   | 3.55 | 8    | 1015           | 0.71 | 8    |
| 06.11.06 |          | 12.35   | 0.52 | 8    | 1014           | 1.20 | 8    |
| 5        |          | 16.11.05                                      | 6.00 | 0.80 | 6              | 989  | 2.37 |
|          | 14.02.06 | n.d.  | n.d. | n.d. | n.d.           | n.d. | n.d. |
|          | 23.05.06 | n.d.  | n.d. | n.d. | n.d.           | n.d. | n.d. |
|          | 18.07.06 | 34.68   | 1.76 | 8    | 1014           | 0.92 | 8    |
|          | 22.08.06 | 17.93   | 0.22 | 4    | 1006           | 0.58 | 4    |
|          | 12.09.06 | 24.60   | 1.34 | 8    | 1014           | 1.07 | 8    |
|          | 06.11.06 | 12.70   | 0.40 | 8    | 1015           | 1.92 | 8    |
|          | 6        | 17.11.05                                      | 1.85 | 1.10 | 6              | 1000 | 3.00 |
| 14.02.06 |          | n.d.  | n.d. | n.d. | n.d.           | n.d. | n.d. |
| 23.05.06 |          | n.d.  | n.d. | n.d. | n.d.           | n.d. | n.d. |
| 18.07.06 |          | n.d.  | n.d. | n.d. | n.d.           | n.d. | n.d. |
| 22.08.06 |          | n.d.  | n.d. | n.d. | n.d.           | n.d. | n.d. |
| 12.09.06 |          | n.d.  | n.d. | n.d. | n.d.           | n.d. | n.d. |
| 06.11.06 |          | n.d.  | n.d. | n.d. | n.d.           | n.d. | n.d. |

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

|                    | TGM <sup>a</sup> | ln TGM <sup>a</sup> | TGM <sup>b</sup> | ln TGM <sup>b</sup> |
|--------------------|------------------|---------------------|------------------|---------------------|
| Soil temperature   | <b>0.35*</b>     | <b>0.57**</b>       | <b>0.54**</b>    | <b>0.65**</b>       |
| Air temperature    | <b>0.37*</b>     | <b>0.55**</b>       | <b>0.51**</b>    | <b>0.63**</b>       |
| Soil water content | n.s.             | <b>-0.40*</b>       | <b>-0.41*</b>    | <b>-0.49**</b>      |
| Air pressure       | n.s.             | n.s.                | <b>0.49**</b>    | <b>0.49**</b>       |

<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

| Region, Country             | Site/ Soil   | Method  | Hg content (topsoil)<br>[mg kg <sup>-1</sup> ]  | TGM emission rate<br>[ng m <sup>-2</sup> h <sup>-1</sup> ] | Reference  |
|-----------------------------|--|---|---|--|--|
| Global                      | natural Hg emission / natural enriched areas                               | estimated   | not specified   | ~0.7 to ~1.1   | Lindqvist et al., 1991;<br>Mason et al., 1994;<br>Schroeder & Munthe, 1998 |
| Sweden                      | forest soils, background level   | dynamic flux chamber  | not specified   | -2.0 to +2.5   | Xiao et al., 1991  |
| USA                         | max. minor contaminated soils  | dynamic flux chamber  | < 0.01 bis 0.06   | -0.1 to 2.7  | Ericksen et al., 2006  |
| Rio Negro, Brasilia         | alluvial soil, deforested plain (day)<br>(night)                           | dynamic flux chamber  | not specified   | 2.6 ± 2.0 <sup>a</sup>                                     | Magarelli & Fostier, 2005  |
| France                      | unpolluted wetlands (dry)<br>(flooded)                                     | dynamic flux chamber  | not specified   | 1.6 ± 0.2 <sup>a</sup>                                     | Poissant et al., 2004  |
| Tennessee, USA              | forest soils, background levels<br>field soils, background levels          | dynamic flux chamber  | 0.47 ± 0.08 resp. 0.68 ± 0.14 <sup>a, b</sup><br>0.06 ± 0.02 resp. 0.11 ± 0.01 <sup>a</sup> | 2 to 7<br>12 to 45   | Carpj & Lindberg, 1998   |
| Northern Germany            | contaminated wetlands of the Elbe River                                    | dynamic flux chamber<br>calculation about soil<br>diffusion   | approx. 10  | 43 ± 5 <sup>a</sup><br>53 ± 17 <sup>a</sup>                | Wallschläger et al., 2002  |
| Tennessee, USA              | unpolluted wetlands, environmental impact by<br>factory of nuclear weapons | micrometeorological   | ≥ 50  | 10 to 200  | Lindberg et al., 1995  |
| Northern Germany            | contaminated wetland at the Elbe River                                     | different methods   | approx. 10  | 20 to 500  | Wallschläger, 1996   |
| Lanmuchang, China           | soils at Hg-Tl mining areas  | dynamic flux chamber  | 170.0 to 614.0  | 242 to 2283  | Wang et al., 2005  |
| Nevada, USA                 | substrate with background levels<br>substrate with geogen enriched content | dynamic flux chamber  | < 0.005 to 0.1<br>0.01 to 44.7  | -3.7 to 9.3<br>-15.4 to 3344                               | Nacht & Gustin, 2004   |
| Toronto, Ontario, Canada    | Toronto soils  | dynamic flux chamber  | 60.7 ng g <sup>-1</sup> (median)  | 6.2 (range 0.7 to 35)                                      | Eckley & Branfireun, 2008  |
| Tuscaloosa, Alabama,<br>USA | bare soil (sandy clay)<br>turf grass<br>pavement (asphalt-aggregate mix)   | polycarbonate flux chamber  | 0.025 to 0.047<br>0.034 to 0.035<br>2.70 µg m <sup>-2</sup>                                 | 5.69 ± 5.79<br>0.53 ± 1.25<br>0.26 ± 0.41                  | Gabriel & Williamson,<br>2008  |
| Eastern Seaboard, USA       | terrestrial background surfaces (forest soils)                             | dynamic flux chamber  | 0.013 to 0.219  | 0.2 ± 0.9  | Kuiken et al., 2008  |
| Central Germany             | contaminated floodplain soils at the Elbe River                            | new sampling setup (modi-<br>fied flux chamber), 60 L<br>new sampling setup (modi-<br>fied flux chamber), 120 L | 3.5 bis 16.7  | 10 to 849<br>24 to 479                                     | This study   |

<sup>a</sup> mean value ± standard deviation, <sup>b</sup> organic layer

Table 5

Mercury stocks in soils (10 cm depth), Hg stocks required within the action value ( $2 \text{ mg kg}^{-1}$ ) 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

| Site-No. | Current Hg stocks<br>in soil<br>(0-10 cm depth) | Critical value of Hg stocks<br>in soils ( 0-10 cm depth)<br>based on action value | Mean Hg<br>emission rate<br>[ $\text{mg m}^{-2} \text{ a}^{-1}$ ] |                    | Years until Hg emission<br>can achieve action value |                    |
|----------|---|---|---|--------------------|---|--------------------|
|          | [ $\text{mg m}^{-2}$ ]                          | [ $\text{mg m}^{-2}$ ]  | 60 L <sup>a</sup>   | 120 L <sup>a</sup> | 60 L <sup>a</sup>                                   | 120 L <sup>a</sup> |
| 1        | 282   | 164   | 2.0   | 1.2                | 59  | 103                |
| 2        | 311   | 160   | 1.2   | 1.5                | 125   | 103                |
| 3        | 319   | 157   | 2.1   | 1.6                | 77  | 102                |
| 4        | 769   | 162   | 2.8   | 2.0                | 221   | 301                |
| 5        | 1336  | 160   | 2.5   | 1.8                | 480   | 648                |

<sup>a</sup>pumped gas volume during sampling