Total mercury accumulation in aboveground parts of maize plants (Zea mays) throughout a growing season

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ABSTRACT
We investigated Hg accumulation in maize (Zea mays) plants grown in non-contaminated conditions on a farm in Switzerland throughout a growing season. Concentrations of Hg in leaves and husk followed the same temporal pattern as the mass growth of these parts. In contrast, silk and tassel accumulated Hg almost linearly over time until harvest. At the end of the growing season Hg concentration was highest in tassel (10.4 ng g\(^{-1}\)), followed by leaves (7.3 ng g\(^{-1}\)) and silk (5.7 ng g\(^{-1}\)). Silk and tassel had accumulated 5–10 times more Hg per unit dry mass than all aboveground parts of the plant on average. Cob and kernels contained only very small amounts of Hg. Greater exposure of a plant part to the atmosphere was clearly associated with higher rates of Hg accumulation.

Introduction
Since the beginning of the industrialization, combustion of coal and other anthropogenic activities has increased atmospheric mercury (Hg) concentrations by a factor of three to five (Pacyna et al. 2001; Schuster et al. 2002; Driscoll et al. 2013). Natural sources of Hg are volcanoes and the volatilization of Hg\(_0\) from ocean and soil surfaces. Hg occurs in the atmosphere of the Northern Hemisphere at concentrations typically between 1 and 2 ng m\(^{-3}\) (Sprovieri et al. 2016). The atmosphere loses Hg through deposition to Earth surfaces (Schuster et al. 2002; Rutter et al. 2011), including Hg uptake by plants and its transfer to soil with depositing foli- age (Schuster et al. 2002; Horowitz et al. 2017; Zhou et al. 2021). On contaminated soils with elevated Hg levels, plants may take up a considerable fraction of their Hg content through the roots (Yin et al. 2013; Zhou et al. 2021). In particular methylmercury is taken up by the roots of rice plants (Oryza sativa) growing in paddy soil (Zhang et al. 2010). However, even in paddy rice plants, the majority of total Hg in aboveground parts originates from the atmosphere (Zhang et al. 2010). Much evidence for an atmospheric source of Hg in plants comes from studies on tree leaves (Ericksen et al. 2003; Rutter et al. 2011; Laacouri et al. 2013; Richardson and Friedland 2015; Teixeira et al. 2018). In concurrence to tree leaf studies, Niu et al. (2014) found Hg concentrations in maize leaves to be affected by Hg levels in air while soil Hg content did not impact Hg leaf concentrations. The main pathway of Hg into leaves is probably stomatal uptake and subsequent absorption to mesophyll tissues (Rutter et al. 2011; Laacouri et al. 2013). Nonstomatal Hg uptake has been observed under conditions of reduced stomatal conductance (Stamenkovic and Gustin 2009). Methyl- ation of Hg on leaf surfaces is a pathway mechanism by which Hg can be adsorbed from the atmosphere to leaf surfaces (Sun et al. 2020).

Material and methods
We sampled on 10 days between 4th June and 17th of September 2019 duplicate maize plants from a commercial farm in Basel, Switzerland. The crop was planted for producing silage, at a density of eight plants per square meter. Average air temperature and total precipitation during the growing period were 20.1°C and 300 mm. The loam soil contained around 80 ng Hg g\(^{-1}\), which is similar to other natural background soils in Switzerland (Osterwalder et al. 2020). The entire sampled maize plants were separated into their aboveground parts: leaves, stalk, and upon appearance of the respective parts into tassel, husks, cob, kernels, and silk. On the first three sampling days plants were very small. Therefore, we combined for analysis the material from duplicate plants into one leaf sample, and one stalk sample. For later sampling days, the material was analyzed separately for each individual plant.

Fresh material was stored in zip-lock bags at −20°C, then cut into smaller pieces and dried for 24 h at 60°C. Based on a
previous test we exclude any potential Hg loss associated with drying plant material at 60°C (Wohlgemuth et al. 2020). Ground to a powder fine enough for Hg analysis, 0.2 g of each sample was analyzed on a Direct Mercury Analyzer (model DMA-80, MWS Gmbh, Heerbrugg, Switzerland). Repeated SRM measurements of BFW spruce needle B were 29.1 ± 0.8 ng g$^{-1}$ (mean ± 1 SD, n = 11) and NIST-1515 Apple leaves were 45.0 ± 1.1 ng g$^{-1}$ (mean ± 1SD, n = 4) and agreed with certified values of 28.27 ± 6.4 ng g$^{-1}$ and 43.2 ± 2.3 ng g$^{-1}$, respectively. Each part of each plant was analyzed for dry mass and for Hg concentration. The individual values for each plant are shown in the supplementary material (Tables S1 and S2). Figures in the next section show the averages of the duplicate plants.

**Results and discussion**

Different parts of the maize plant grew in mass as expected for this species (Figure 1, Table S1). The first sample, collected on the 4th of June, only consisted of cotyledons. In the subsequent samples, from the middle of June to the middle of July, leaves and stalk had grown at a similar rate, whereby leaves constituted approximately 50% of the total aboveground dry mass. The reproductive parts, tassel, and silk, were large enough for Hg analysis from the 26th of July onwards. By the 26th of July the plants had accumulated 16% of their maximum dry mass as observed on the 17th of September. All parts of the plant had approached their maximum dry mass by the middle of August, except the kernels, which continued to add mass until the final sampling occasion. At the end of the cropping period, the kernels made up roughly 50% of the total plant mass.

Between the 26th of July and 17th of September, the concentration of Hg in leaves and husks increased in a similar manner as their dry mass, whereby both Hg concentration and dry mass changed little during the last three weeks. The comparable evolution of leaves and husks is to be expected as husks are a specialized type of leaves with similar tissue structure and physiology. In contrast, Hg concentrations in tassel and silk continued to increase almost linearly until harvest (Figure 2, Table S2), with the tassel accumulating Hg at twice the rate (0.2 ng g$^{-1}$ d$^{-1}$) as the silk (0.1 ng g$^{-1}$ d$^{-1}$), as derived from the slope of regression lines fitted to Hg concentrations over time (Figure 2). This finding is unexpected because tassel and silk are reproductive parts and as such, they are physiologically active only for a short time. Silk is completely senesced within 14 days after its appearance (Bassetti and Westgate 1993) which corresponds to early to mid-August in case of the here sampled maize plants. The pattern of increase in Hg concentration suggests that leaves and husks incorporate Hg primarily in their inner tissue. To be absorbed to these tissues, Hg has to pass through the stomata. When stomata deform with age and become closed with wax (Kolodziejek et al. 2006), the inner surfaces of leaves and husks are cut off from the atmosphere, which could explain why Hg uptake by leaves and husks ceased about three weeks before harvest. In contrast, tassel and silk seem to adsorb Hg on their outer surface, even when senesced. However, passive adsorption on the outside of these parts would have to be very efficient for this interpretation to be correct. The final concentration of Hg was highest in tassel (10.4 ng g$^{-1}$) and final Hg concentration in silk (5.7 ng g$^{-1}$) was little smaller than in leaves (7.3 ng g$^{-1}$) which had a longer growing season. As parts of the wind pollinating flowers that release and capture pollen from the atmosphere, tassel and silk have relatively large surfaces exposed to the air, which might explain some of their efficiency in adsorbing Hg from the atmosphere. In contrast, foliage of deciduous tree species, surface adsorption has only played a minor role ranging from 1.6% to 4% of total Hg uptake (Laacouri et al. 2013). Niu et al. (2014) had found about double the concentration in maize leaves grown under elevated Hg concentrations in air (10 ng m$^{-3}$) compared to plants exposed to background air values (<2 ng m$^{-3}$). In maize grown on contaminated soils (with Hg concentrations of 345 and 458 ng g$^{-1}$), and therefore probably also under enhanced atmospheric Hg concentrations due to soil Hg emissions (Osterwalder et al. 2019), Fu et al. (2014) had found Hg concentrations in leaves (41 ± 6 ng g$^{-1}$), that were several times higher than our highest Hg concentration in leaves measured at the end of the growing season (7.3 ng g$^{-1}$). However, the relative differences in
Hg concentration between the different parts of the maize plant at harvest were similar, with the highest values in leaves, much lower values in cob, kernels, and stems, and those of husks in between. Lower concentrations in husks as compared to leaves could result from the husks tight wrapping around the corncob and consequently smaller area exposed to the atmosphere.

The total Hg content of a maize plant increased throughout the growing season (Figure 3). Nearly all of the total Hg content of the plant was found in only four of the seven analyzed parts. By the end of the sampling period (17th of September), leaves had the highest Hg content among maize parts by far (83%) followed by husk (9%), silk (5%), and tassel (3%). More than 70% of the final Hg content accumulated between the 5th and the 26th of August. During the following three weeks, until the 17th of September, where only the kernels continued to grow, no further net accumulation of Hg was observed. Only tassel and silk continued to

Figure 2. Change in Hg concentration in different parts of the maize plant during the main growth period, in which the plants accumulated 84% of their final dry mass. Linear trendlines fitted to the data indicate accumulation rates of 0.2 ng g\(^{-1}\) d\(^{-1}\) in the tassel (black line, \(R^2 = 0.99\)) and half that rate in the silk (red line, \(R^2 = 0.94\)). In contrast, Hg concentrations in leaves and husk increased in a similar manner as did the dry mass of these parts.

Figure 3. Development throughout the growing season of the Hg content in a maize plant, differentiated by its major parts.
accumulate Hg. Yet, due to their small contribution to the overall dry mass, their additional contribution did not markedly affect the overall Hg budget during that period. At harvest, the aboveground parts of a plant contained 411 ng Hg. With a typical crop density of 8 plants m$^{-2}$ this results in a net uptake of 3.3 µg m$^{-2}$ over the growing season. More graphically, an area half the size of a football field and planted with maize had absorbed the equivalent of a liquid Hg droplet 1 mm in diameter (7.1 ng).

Although leaves constituted only 12% of the aboveground dry mass at the end of the vegetation period, they contained 83% of all accumulated Hg. By the end of the vegetation period, over-proportionally large amounts of Hg were also present in the tassel and the silk. Their Hg concentration was 10 and 5 times larger than that of all aboveground plant material pooled together. In contrast, stalk, cob, and kernels harbored 81% of the total dry mass, but only 1% of the total Hg. Husks had close to average Hg concentrations (6% of total dry mass, 9% of total Hg). To summarize, the maizes (Zea mays L.) leaves to low-level air and soil mercury exposures. Environ Pollut. 250:944–952. doi:10.1016/j.envpol.2019.03.093.

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