Hg release and Hg nanoparticle formation upon flooding of an agriculturally used fluvisol.

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Soils in legacy sites of chlor-alkali and acetaldehyde production are point sources of mercury (Hg) to downstream eco-systems. Flooding and agricultural activities may influence the mobility of Hg by altering redox conditions, bioavailability, microbial activity and carbon budgets. However, the complex interplay between these parameters is still not well understood. As well, soil flooding is changing initial speciation of Hg in soils (e.g. by promoting reduction of Hg²⁺ to Hg⁰ and incorporation of Hg into the metallic Cu nano particles [1]).

We study the influence of flooding and agricultural practice on the fate of Hg in polluted soils. Here, we present data from a soil incubation experiment. We mimicked the effect of redox cycles (soil flooding/draining) and local agricultural practices (manure addition) to study the influence of these factors on the release/sequestration of Hg and the formation of Hg nanoparticles. Based on earlier observations we hypothesized that manure addition may enhance Hg release by reductive dissolution of Mn oxi-hydroxides [2] and Hg nano-particle formation by promoting sulphate reducing micro-organisms [1].

Our results show manure addition accelerated the release as well as the subsequent sequestration of Hg in pore water during flooding. Further, it enhanced the formation or release of Hg colloids in the range of 5 - 20 nm over the course of the experiment.

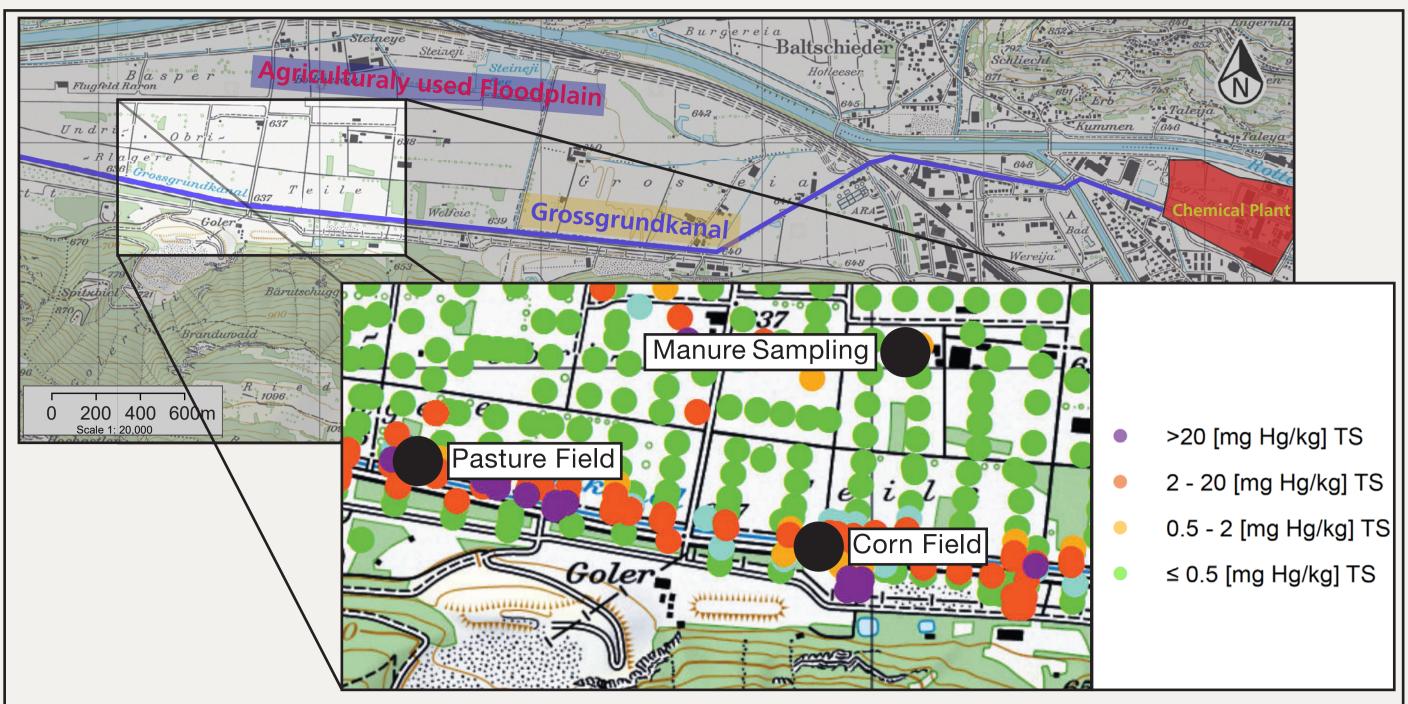


Fig.1 Samples were taken from a Hg contaminated legacy site down stream of a chemical plant. Organic manure for the experiments were sampled from a farm tilling the fields on the plain.



1. Study site

Our study site is situated on an agricultural flood plain downstream of a chemical plant (Visp, Switzerland) and is affected by historical pollution. The chemical plant emitted Hg through the discharging canal Gross-grundkanal. A preliminary screening assessed the Hg distribution on the floodplain (Fig.1). The major part of the area has Hg concentrations around the global background of ≤ 0.5 mg kg⁻¹. Soil Hg concentration increases gradually towards the discharging canal, with max. concentrations up to 65 mg kg⁻¹(own measurements).

For the incubation experiment, we chose two fields with different land use types (pasture and crops). Soils from the upper 10 cm were sampled. Fresh Manure (liquid) was sampled from a nearby farm.

There are contrasting reports on the inorganic speciation of Hg in soils from the study area. Hg is both reported to be present mainly as refractory Hg (e.g. HgS(s)) or to be mainly bound to Mn oxi-hydroxides and therefore highly exchangeable (up to 35% of the total Hg pool) [3, 4]. The initial Hg speciation in soils strongly influences the release and bioavaliability of the Hg upon flooding.

Fig. 2 The periodically flooded agricultural fields are mainly used as pasture sites as well as to grow corn. Liquid manure is routinely applied to increase fertility of the nutrient poor fluvisol.

2. Experimental setup

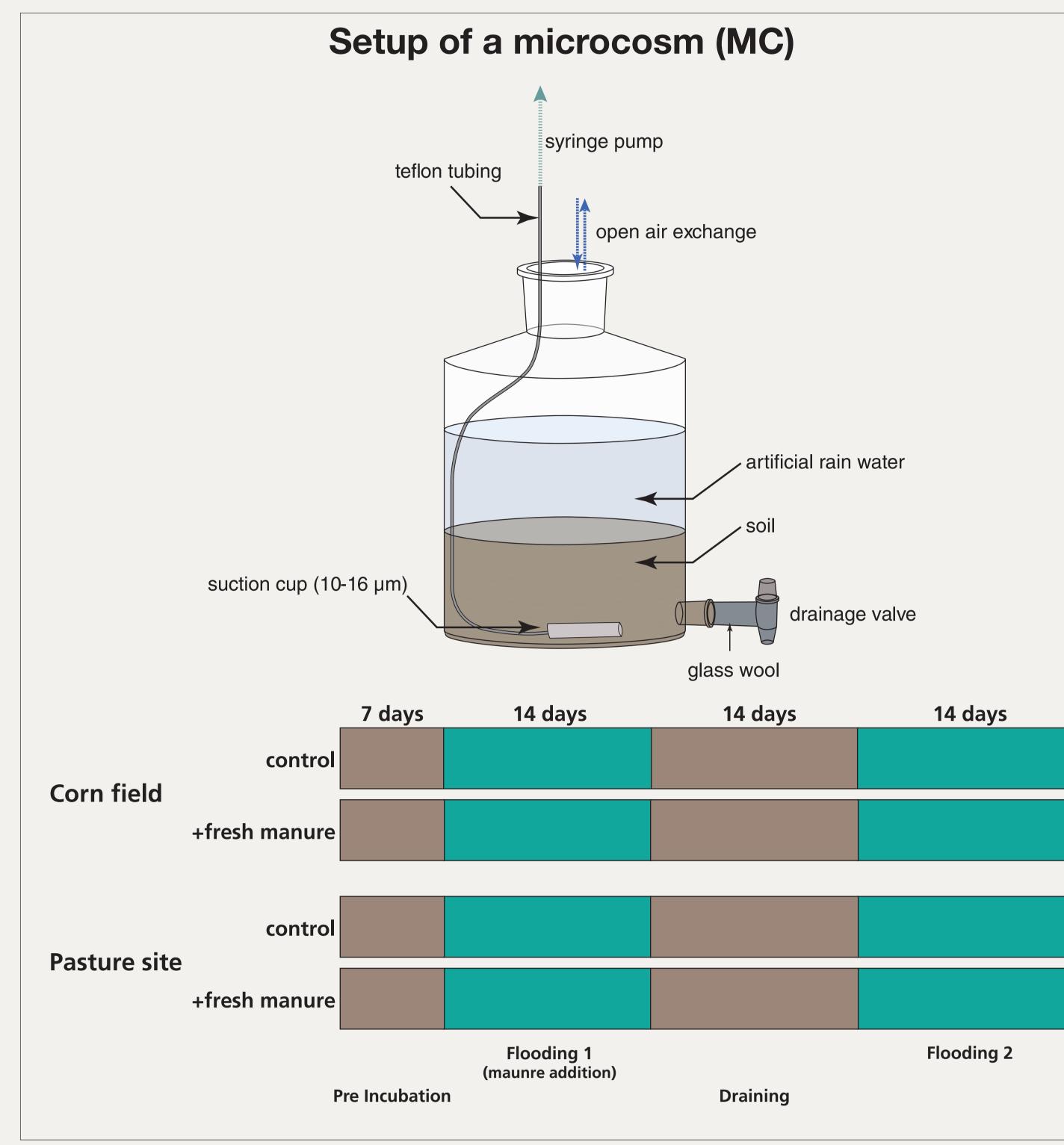


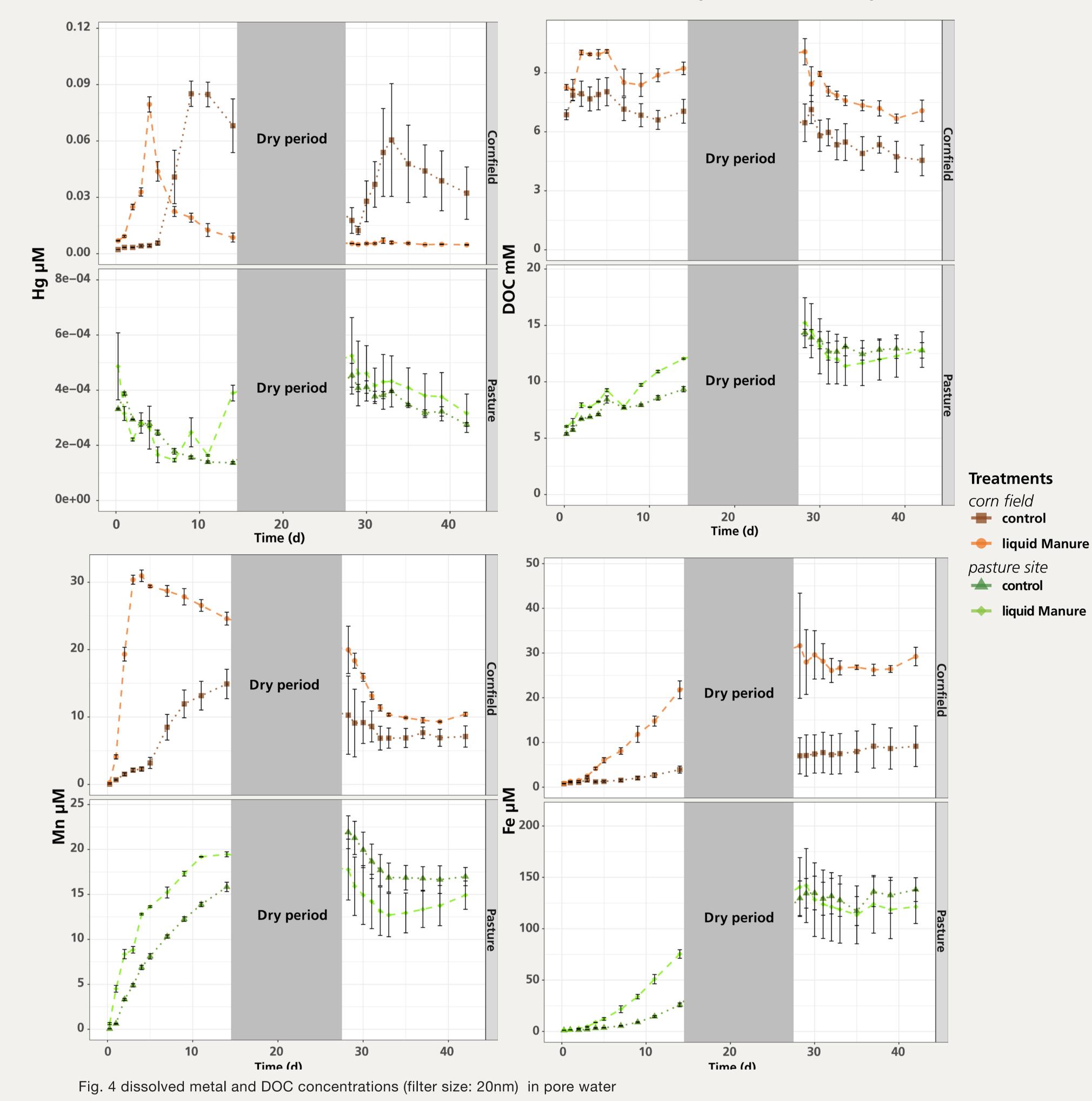
Fig. 3 Schematic of experimental setup

Fresh soils were passed to the incubator for a flooding-draining oscillation experiment (see Fig.3).

- Soil_{drv}:water ratio **1:1.4** (artificial rain water: *ionic strength = 0.3 mM*)
- Incubation at 22°C and 60% humidity in the dark.
- Treatment: 0.3 wt.% liquid manure was added after pre-incubation.
 - Treatments were run in triplicates.
- Repeated pore water sampling.
 - Filter sizes 0.45µm / 0.02µm
 - Analyses of Hg, DOC, pH, Eh, relevant metals (Fe, Cu, Mn) and major Cat-/Anions.
 - Analyses of colloids in filter fraction 0.45µm by AF4-ICP-MS for selected time points and replicates.
- Soil sampling before and after Flooding 1 and 2.
 - HgT analyses using DMA-80 evo

Landuse	SOM (wt. %)	Hg (mg * kg⁻¹)	Soil type
Corn field	1.5 ± 0.1	44.8 ± 0.5	Fluvisol (sandy loam)
Pasture site	4.3 ± 0.3	2.4 ± 0.1	Fluvisol (sandy loam)

3. Results Hg release



- Pore water: dissolved metal and DOC concentrations (filter size: 20nm)
- Reductive dissolution of Mn and Fe-oxides was accelerated and enhanced by the addition of liquid manure in both soils.

Corn field

- Hg follows the trend of Mn in both treatments.
 - Mainly Hg bound to Mn oxides is released during the experiment.
- The manure addition accelerates the release and subsequent decrease of Hg in pore water.
 - This suggest a fast resorption e.g. by binding to natural organic matter or by the formation of Hg bearing sulphides or metallic Cu(s) particles [1].
- A considerable amount of Hg is staying in solution for up to 14 days in MCs without manure addition.
 - Therefore, possibly staying available for longer time to micro-organisms and plants.

Pasture site

- No simultaneous release of Hg and Mn or Fe was observed in these MCs.
 - No considerable amount of Hg is bound to Mn- or Fe oxides.
- Hg concentration <1 nM through the whole experiment.
 - The water soluble fraction appears to be relatively small in the pasture site soil.

Hg Nanoparticle formation

Corn field

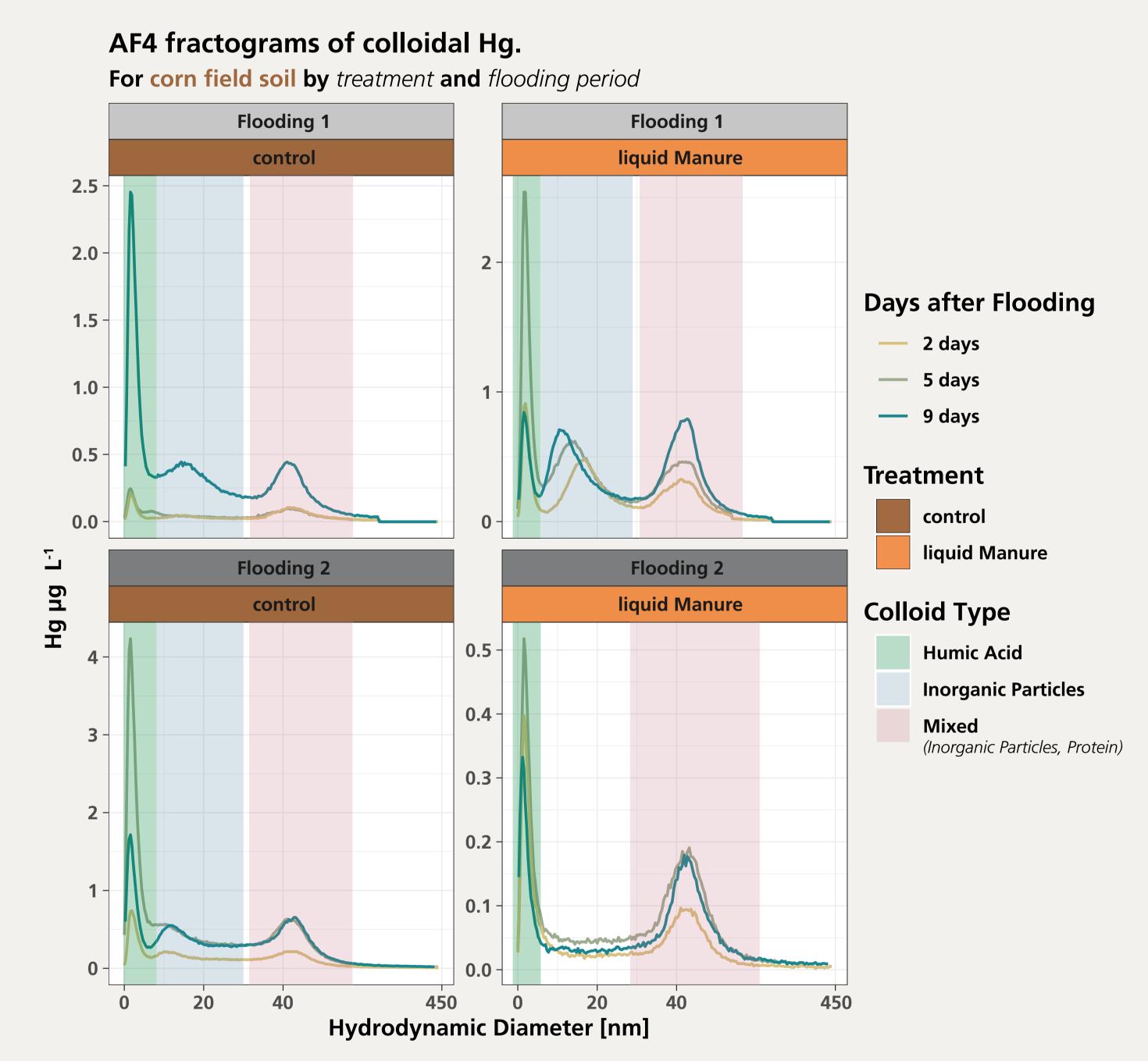
The colloidal fraction we defined as 450 nm. We analysed the colloidal fraction by both ICP-MS and AF4-ICP-MS.

AF4-recovery (%) = (HgT_{AF4-ICP-MS}/HgT_{ICP-MS}) x 100)

We consider *AF4-recovery* as the relative amount of Hg not passing the 1kD membane.

control

- Hg mainly present as dissolved Hg (< 1kDa) or bound to humic acids (HA). (Fig.5 and 6)
- Truly dissolved Hg (< 1kDa) represents 70 30 % 450nm filtrates throughout the experiment (exception day 2). (Fig.6)
 - This is an unexpectedly high amount considering the high concentration of DOC (>6mM) in the pore water.
- During the first flooding Hg was released at day 9 mainly as HA bound Hg and Hg colloids **5 20 nm**.
 - This relative contribution of these two fraction remained the same in the second flooding phase.



liquid manure addtiton

- Fast formation of Hg colloids or sorption of Hg to other colloids in two distinct size ranges **a.**) **5 20 nm** and **b.**) **30 450 nm** (hydrodynamic diameter).
 - During first flooding period Hg associate to a.) and b.) increased with a simultaneous decrease of Hg bound to HA.
 - During the second flooding colloidal Hg consisted to similar parts of b.) and HA bound Hg.
- Only 0 30% is truly dissolved Hg (< 1kDa) throughout the experiment. (Fig.6).

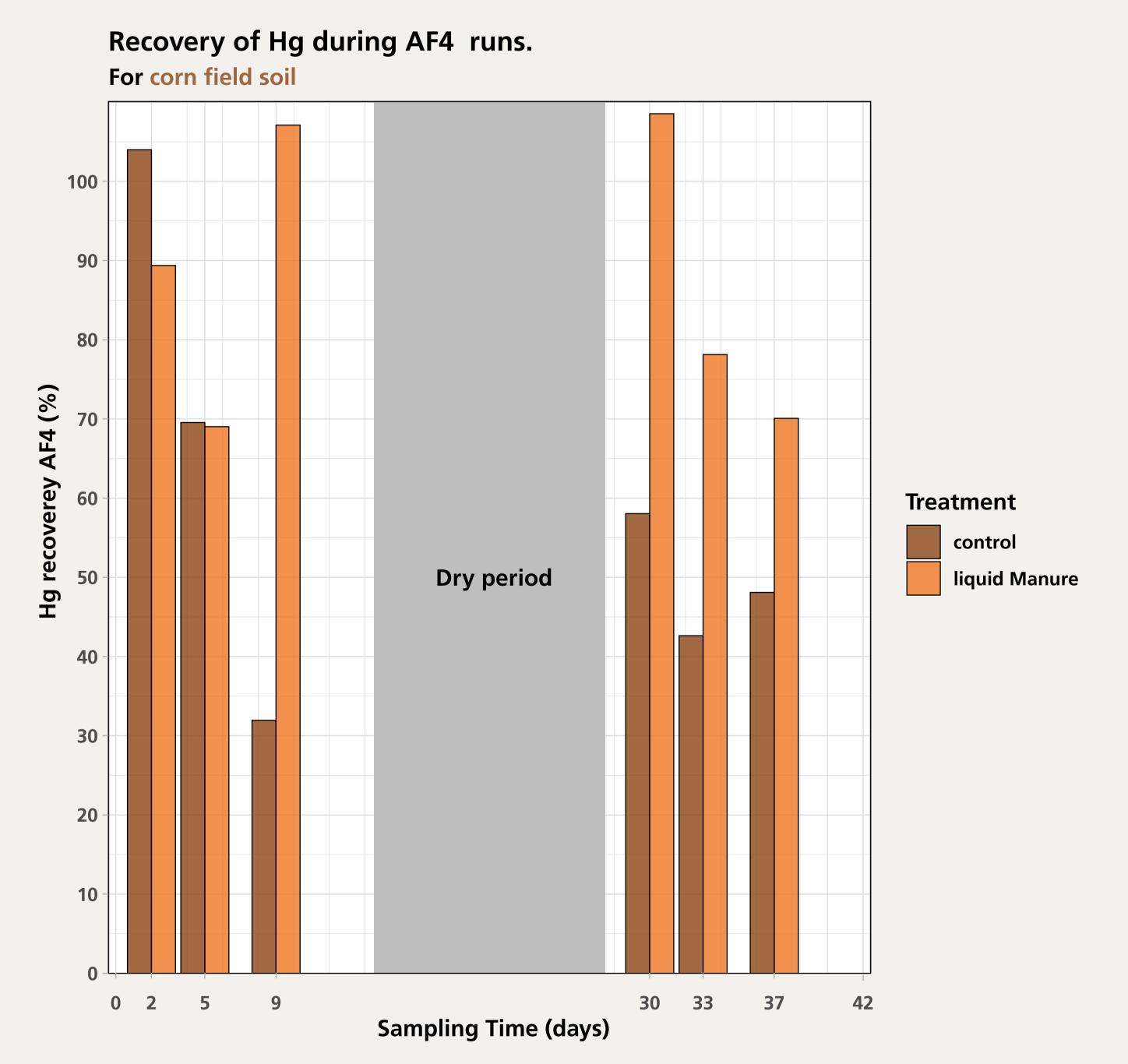
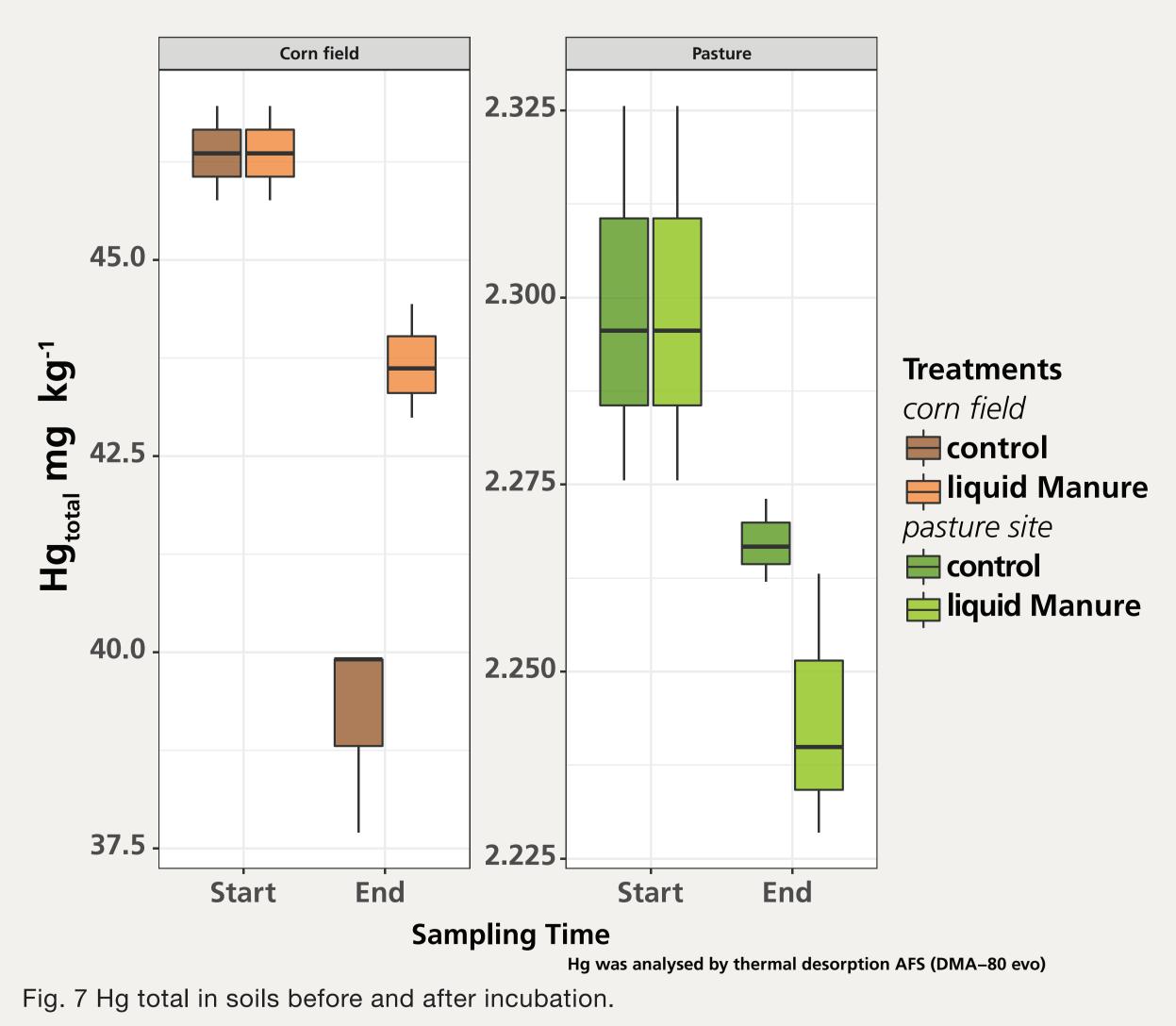


Fig. 6 *AF4-recovery* for colloidal Hg by day and treatment. *AF4-recovery* is defined as the relative amount of Hg not passing the 1kD membane.

Hg loss

Soil Hg_{total} concentrations before and after incubation



- A substantial amount of Hg was lost during the experiment:
 - **Corn field:** 4.7 ± 0.9 mg for control and 1.7 ± 0.4 mg for manure addition.
 - **Pasture:** 0.02 ± 0.02 mg for control and 0.03 ± 0.01 mg for manure addition.
- This can not be solely explained by the loss through pore water sampling (*in range of 10² ng*).
- We suggest a Hg loss due to Hg²⁺ reduction during the course of the experiment.
- Consequently, the percentage of bioavailable Hg for reduction could represent up to **15%** of the total Hg pool in the contaminated soils.

4. Conclusions

- In highly contaminated soils with relatively low SOM (corn field soil)
 - Mn-oxides are a relevant binding partner for Hg.
 - Hg in soil solution maybe present as truly dissolved Hg (<1kD) up to weeks.
- Manure addition
 - accelerates the release of Hg as well as its subsequent sequestration in the soil solution.
 - decreases the relative amount of truly dissolved Hg (<1kD).
 - enhances the formation (or release) of Hg carrying nano particles between 5 20nm (hydrodynamic diameter).
- In the corn field soil higher loss in Hg_{total} in the control suggests
 - 1.) a lower bioavailablility of Hg to Hg reducing micro-organisms. Which might be caused by a comparably lower fraction of dissolved Hg (<1kD).
 - 2.) that manure addition shifts the abundance of Hg reducing micro-organisms.
 - ... a.) quantification of GEM and b.) the analysis of soil microbial taxonomy are needed to proof this hypotheses.

References

- [1] Hofacker, Anke F.; Voegelin, Andreas; Kaegi, Ralf; Kretzschmar, Ruben (2013): Mercury mobilization in a flooded soil by incorporation into metallic copper and metal sulfide nanoparticles. In Environmental science & technology 47 (14), pp. 7739–7746. DOI: 10.1021/es4010976.
- [2] Gygax, Sebastian; Gfeller, Lorenz; Wilcke, Wolfgang; Mestrot, Adrien (2019): Emerging investigator series: mercury mobility and methylmercury formation in a contaminated agricultural flood plain: influence of flooding and manure addition. In Environmental science. Processes & impacts 21 (12), pp. 2008–2019. DOI: 10.1039/c9em00257j.
- [3] Grigg, Andrew R. C.; Kretzschmar, Ruben; Gilli, Robin S.; Wiederhold, Jan G. (2018): Mercury isotope signatures of digests and sequential extracts from industrially contaminated soils and sediments. In The Science of the total environment 636, pp. 1344–1354. DOI: 10.1016/j.scitotenv.2018.04.261.
- [4] Shetaya, Waleed H.; Osterwalder, Stefan; Bigalke, Moritz; Mestrot, Adrien; Huang, Jen-How; Alewell, Christine (2017): An Isotopic Dilution Approach for Quantifying Mercury Lability in Soils. In Environ. Sci. Technol. Lett. 4 (12), pp. 556–561. DOI: 10.1021/acs.estlett.7b00510.
- [5] Deonarine, Amrika; Hsu-Kim, Heileen (2009): Precipitation of Mercuric Sulfide Nanoparticles in NOM-Containing Water. Implications for the Natural Environment. In Environ. Sci. Technol. 43 (7), pp. 2368–2373. DOI: 10.1021/ es803130h.

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