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Thermal desorption: an experimental technique to assess liquid Hg in different soil matrices

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Aims

- Assess whether the different matrices were able to affect the release of Hg^0
- Verify whether the addition of liquid Hg was favouring the formation of new Hg species
- Study the dynamics of Hg species after incorporating Hg^0 into the soil.

Disadvantages

Advantages

High calibration stability

Temperature of the chamber was measured by a thermocouple

Fast mercury determination without its preliminary accumulation on a gold trap

Lumex 915M

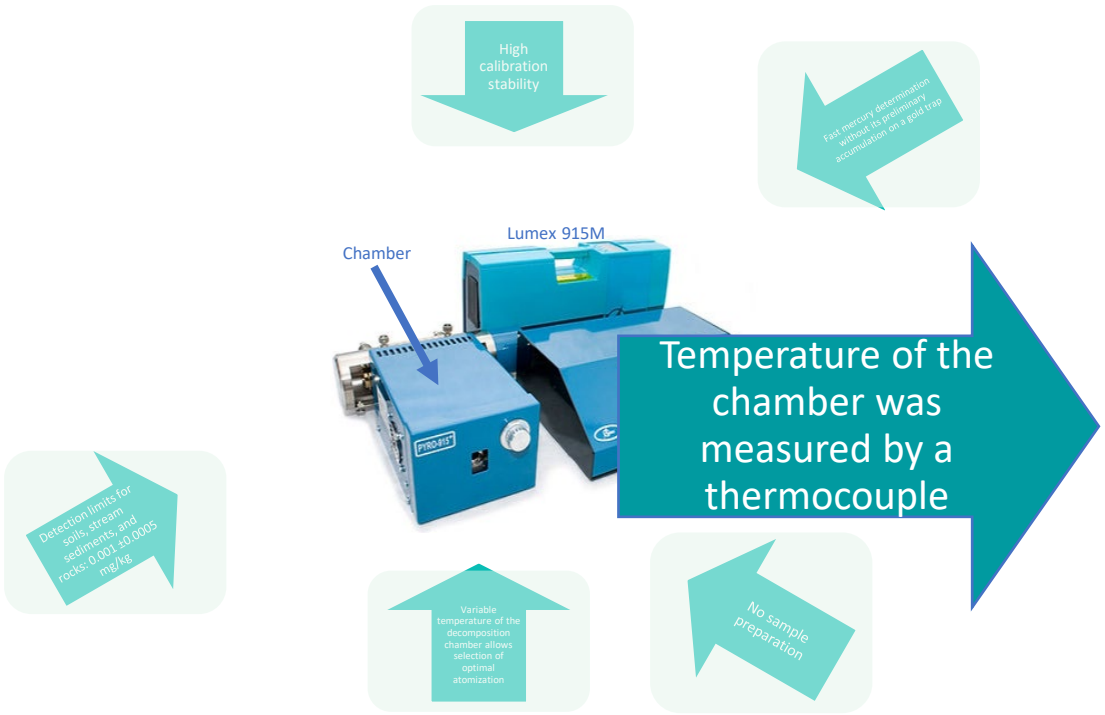
Chamber

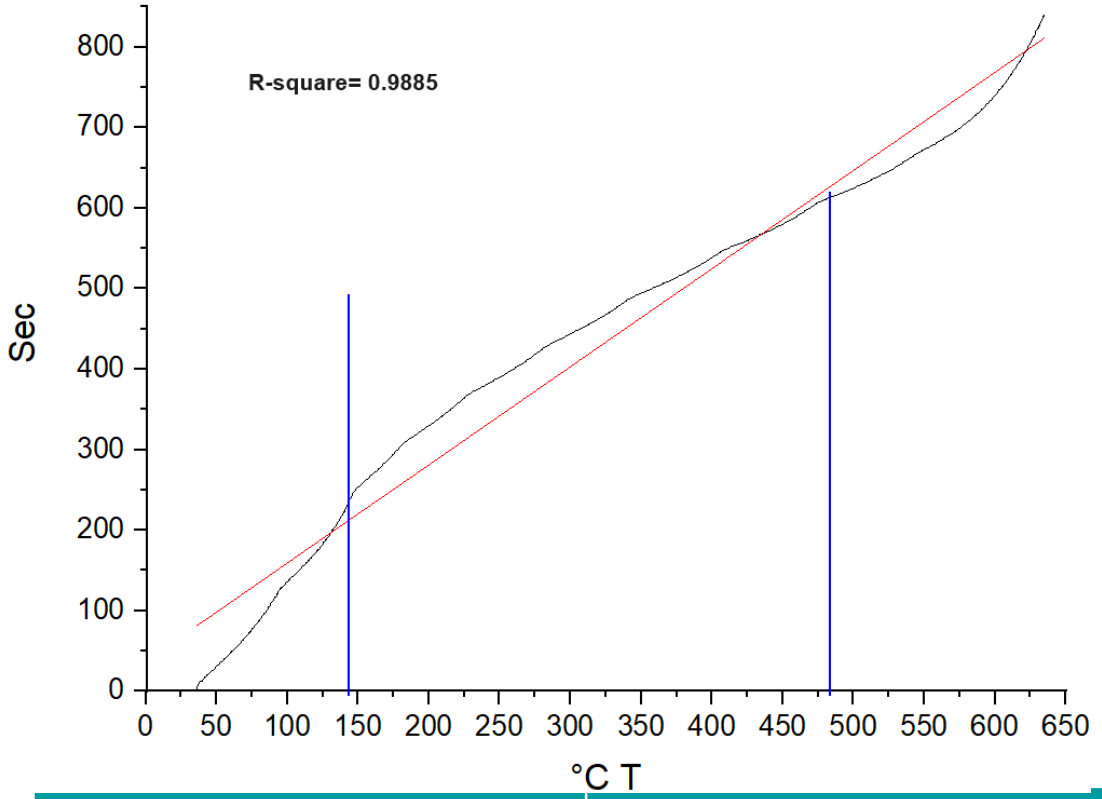
Detection limits for soils, stream sediments, and rocks: 0.001 ±0.0005 mg/kg

No sample preparation

Variable temperature of the decompositi on chamber allows selection of optimal atomization

Heating ramp



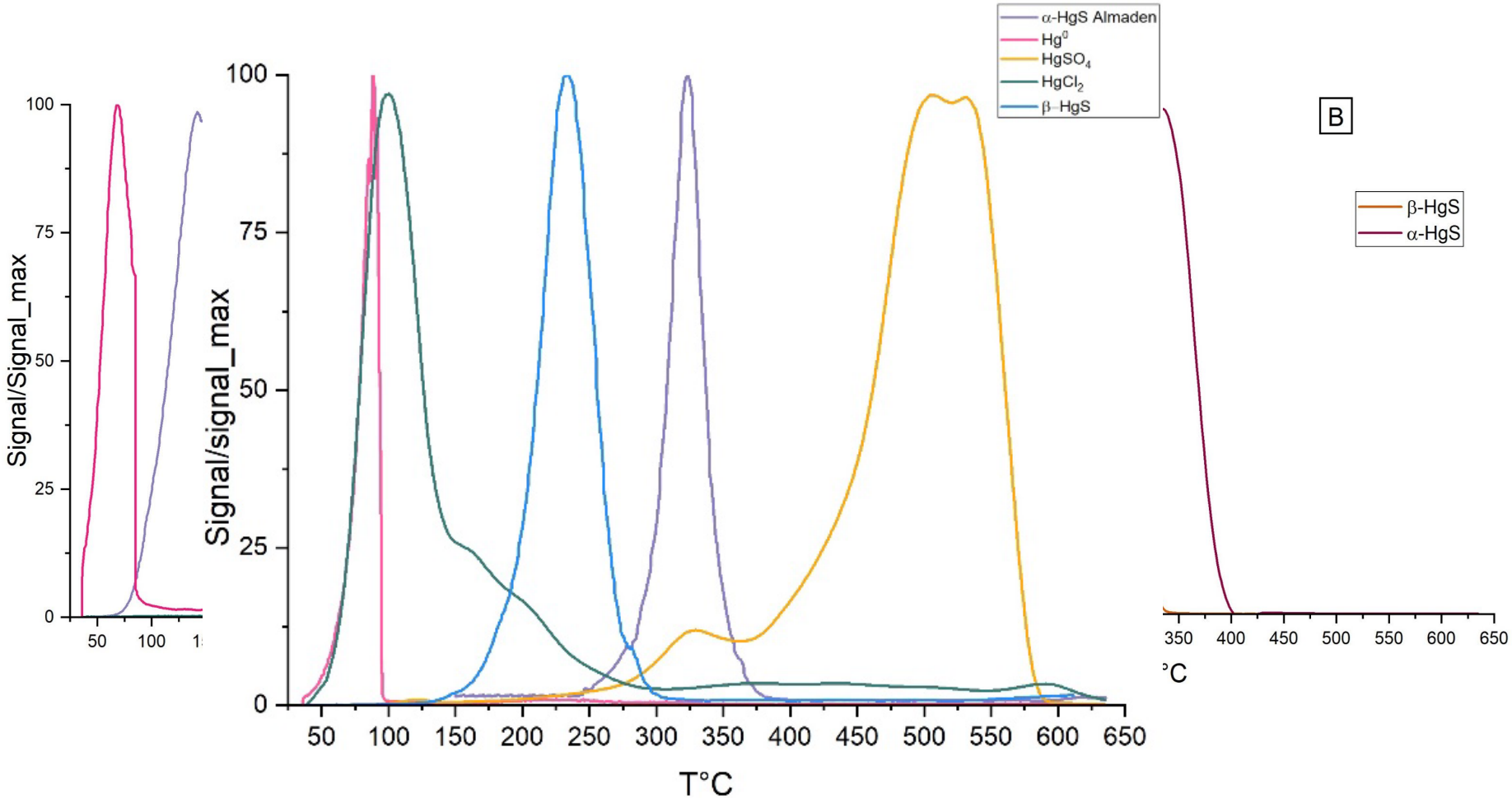


- ✓ The temperature in the first chamber: from 36 °C to 635 °C.
- ✓ Active carbon purified air was used as carrier gas at 3 L min^{-1}

Time (s)	Heating rate (°C/min)
0-140	28.8
140-480	40.8
480-840	49.8

Speciation analysis- Instrument calibration

✓ The certified material NIST 2711a was measured to guarantee quality control (RSD < 5%).



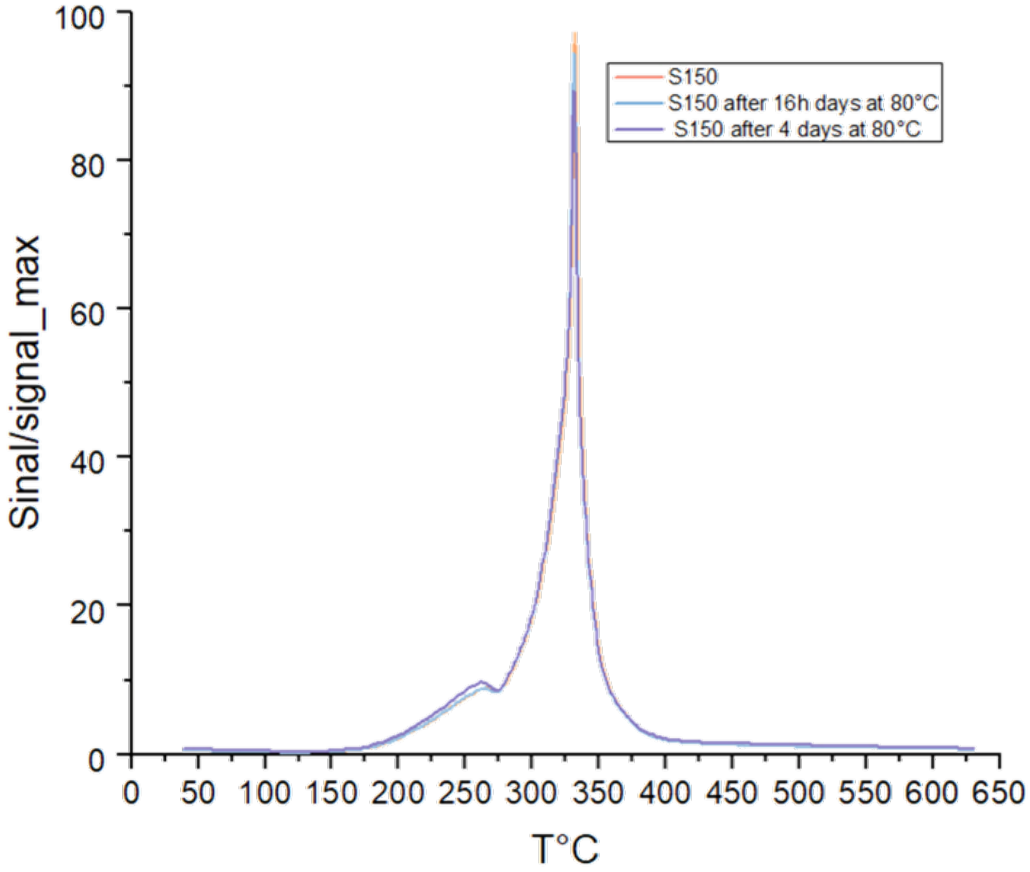
Liquid Hg (Hg_l)experiment

One of the challenges in the remediation of Hg-contaminated sites is the determination of the presence/absence of Hg^0 within the soils/sediments

The method of Hg^0 determination in soils and sediments previously proposed by ARPAT-Siena (gravimetry method) involved the determination of Hg after heating at 30 and 80 °C.

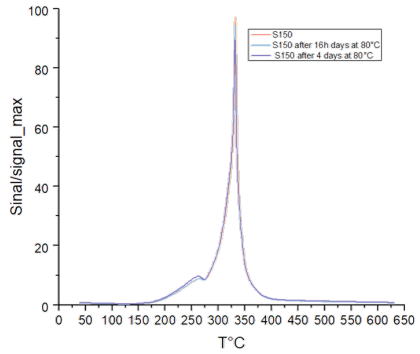
Hg_I experiment- First step

- The First Step of the experiment was to repeat the ARPAT-Siena method and observe what happened, in terms of Hg speciation, to a previously analyzed soil.
- After 16h or 4 days at 80 °C the analyzed soil did not reveal any change. Therefore, the method proposed by ARPAT is apparently not suitable for the determination of the Hg^0 content in a soil.



Hg_I experiment-Second Step

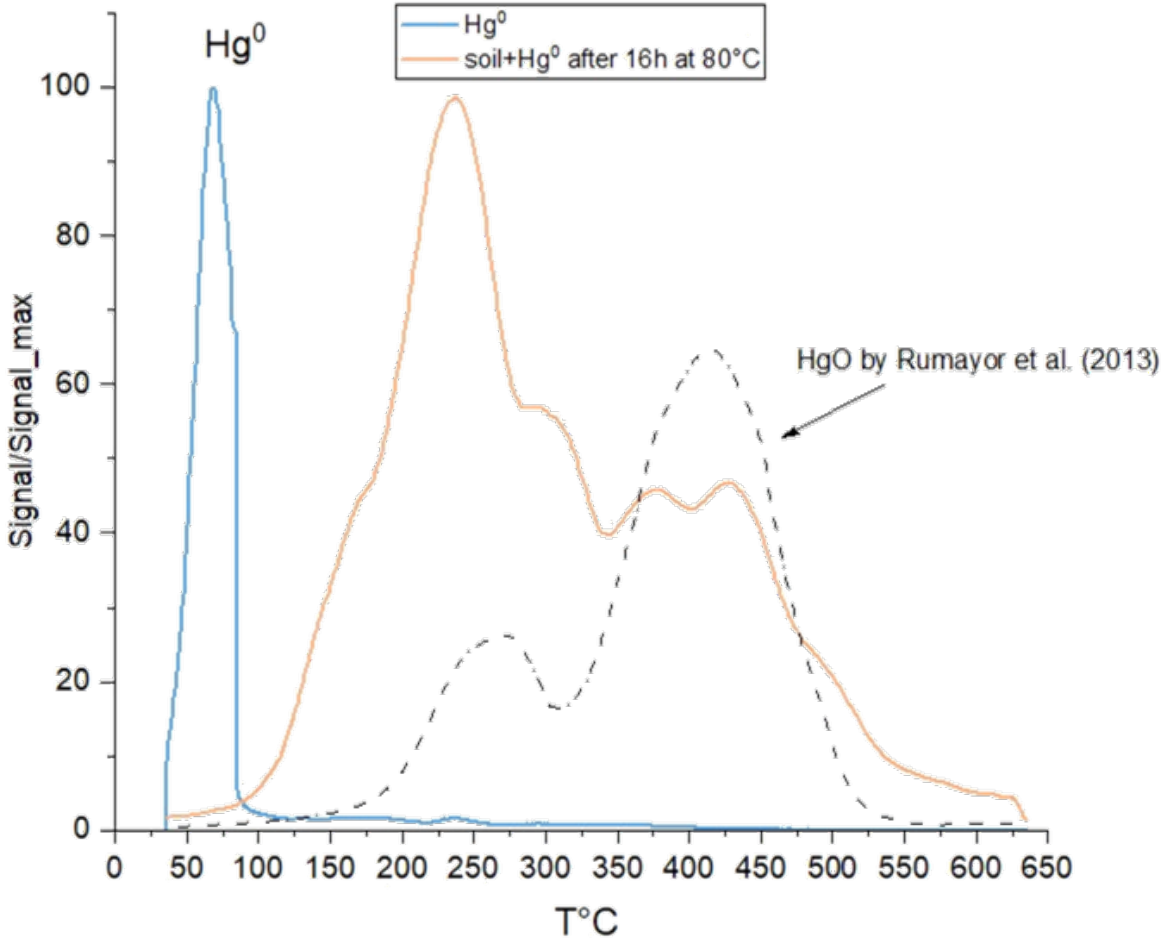
First Step



Observe what was occurring to soil previously mixed with liquid Hg when it was placed in an oven at 80 °C for 16 h and understand what the various peaks resulting post-heating might be associated with:

1) to peaks at 450 °C: thermal decomposition of HgO or $HgSO_4$

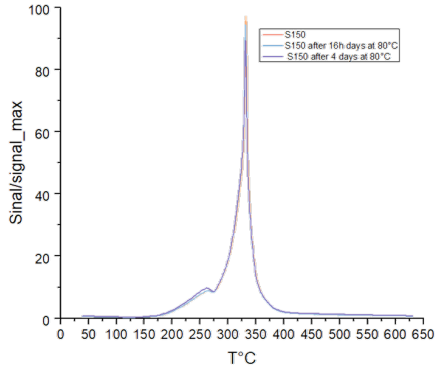
2) peak at 240 °C: formation of α-HgS or Hg-related organic matter or Fe/Al/Mn oxides/hydroxides?



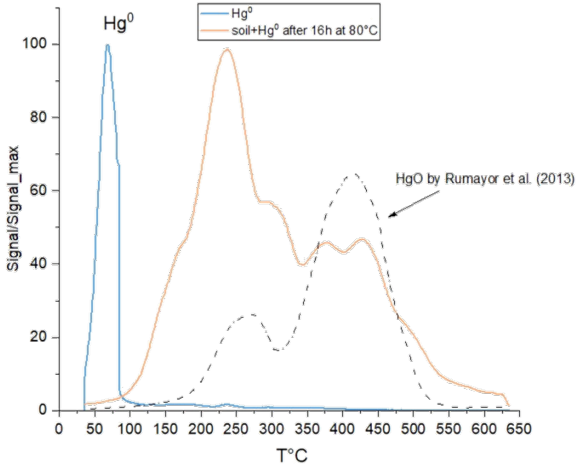
Hg_I experiment-Third step

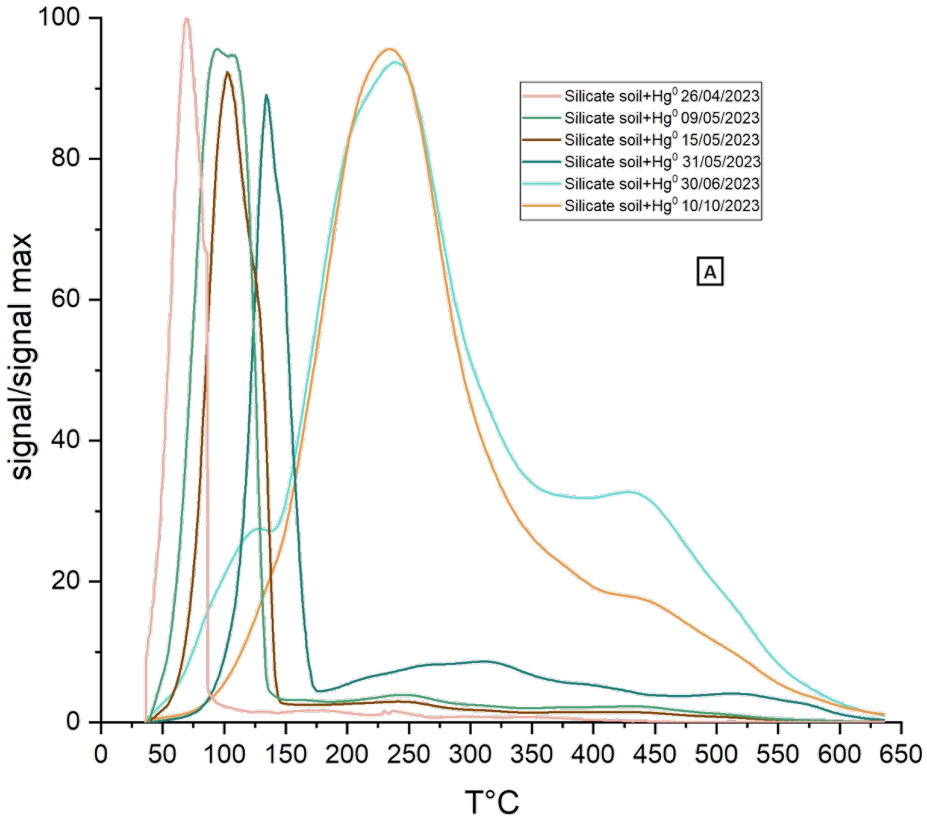
How long Hg^0 was achieved at room T in previous thermograms? Were new phases formed?

First Step



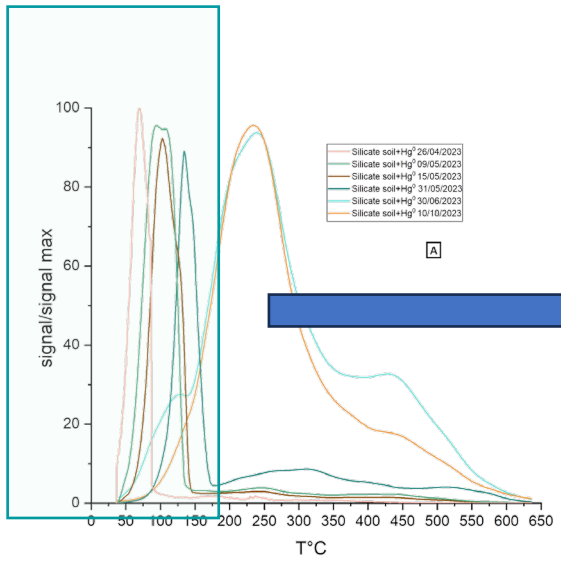
Second Step

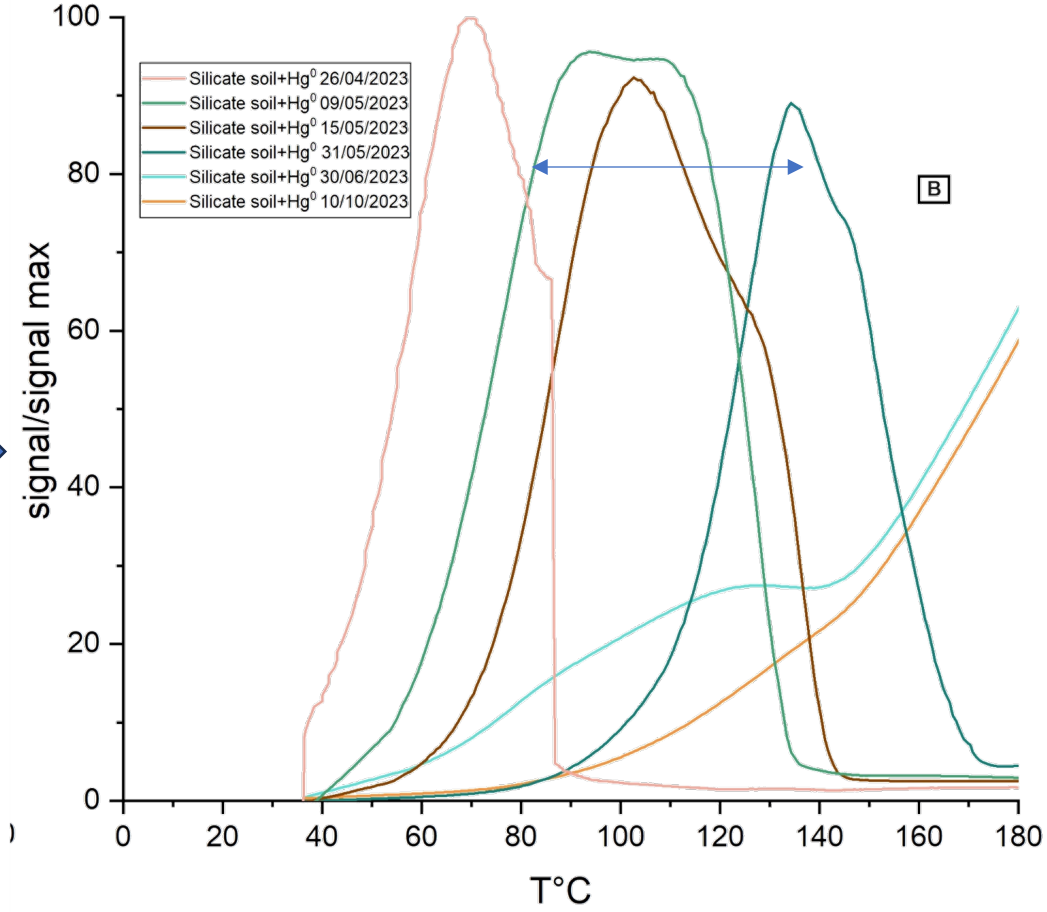




Hg_I experiment-Third step

$Hg^0 \rightarrow Hg^+ \rightarrow Hg^{2+}$





$$t_{1/2} = ln\frac{2}{K}$$

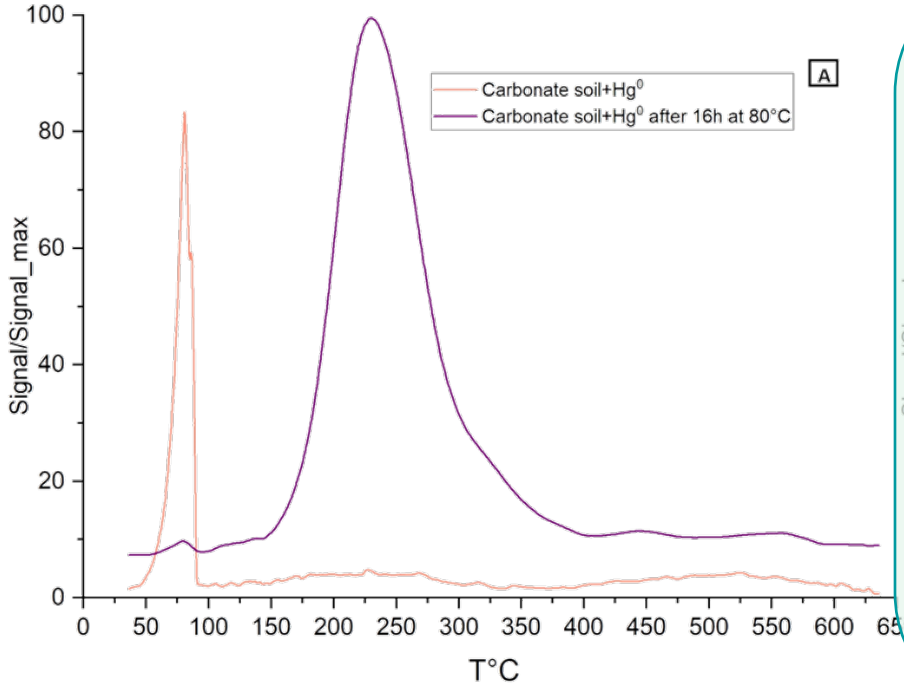
K=angular coefficient of the linear fit

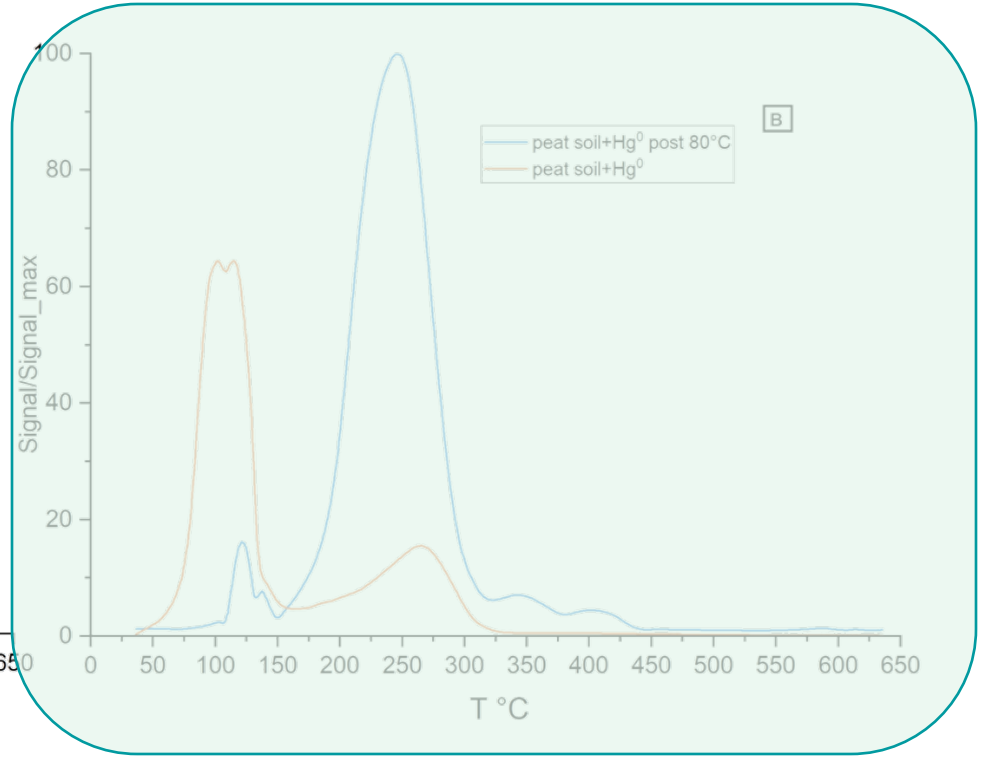
$t_{1/2}$= 42 days

99.2% of Hg^0 oxidized into Hg^{2+} in almost three months

Hg_I experiment

What's happen if we change the soil composition?

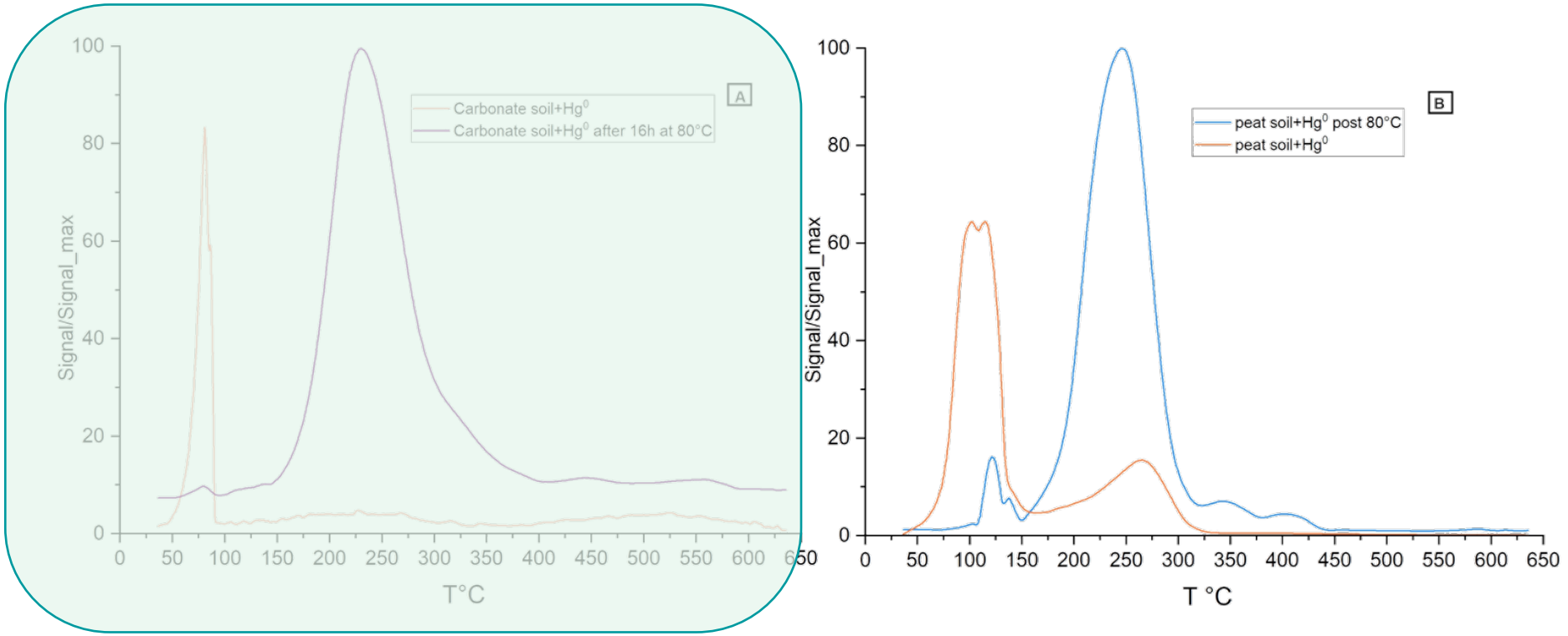




- No formation of peak at 450°C

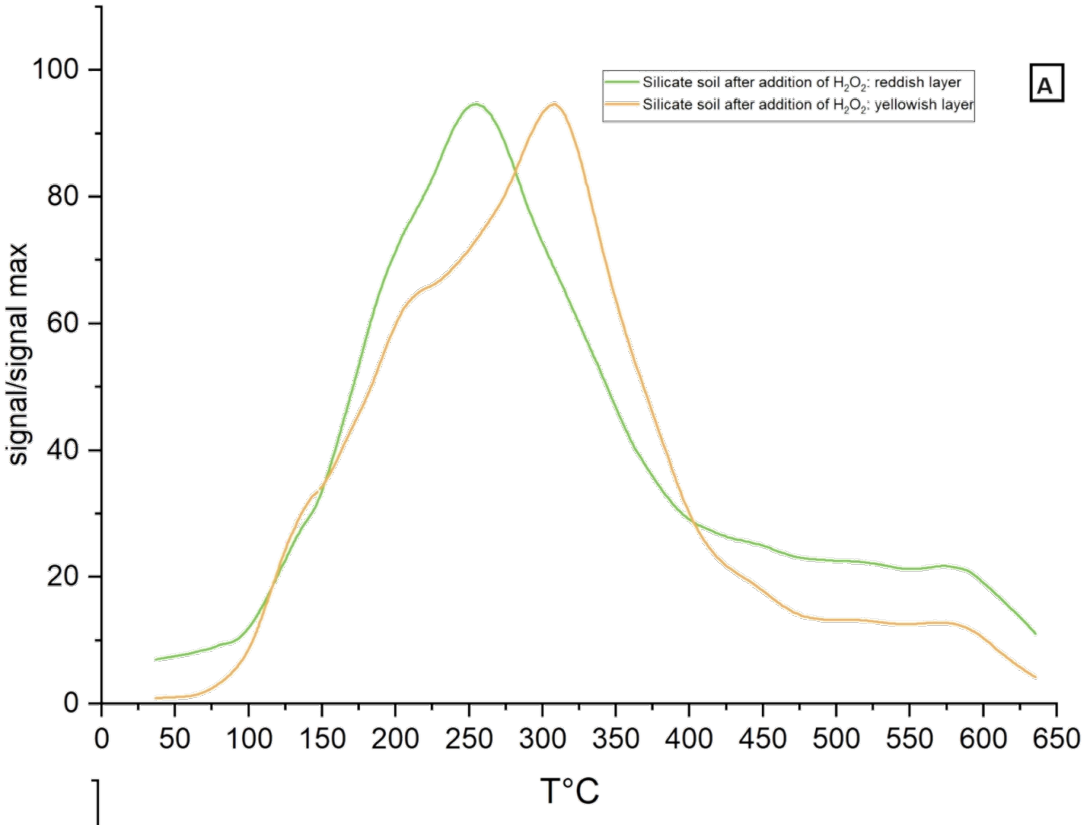
Hg_I experiment

What's happen if we change the soil composition?



- No formation of peak at 450°C
- Formation of peak at 125°C in peat soil probably related to not-fully-oxidized form of Hg^{2+}

Hg_I experiment- Soils+ H_2O_2



The peak at 240 °C is associated with Organic Matter?

Silicate Soil

Tiny reddish layer of alteration in upper part and yellowish in lower part

Speciation in both layer

Reddish Layer a new peak, shifted by about 50 °C is formed

$HgS_s + 4H_2O_2 \rightarrow Hg^{2+} + SO_4^{2-} + 4H_2O$

Hg^{2+} probably adsorbed on Fe-Al, or Mn Oxides

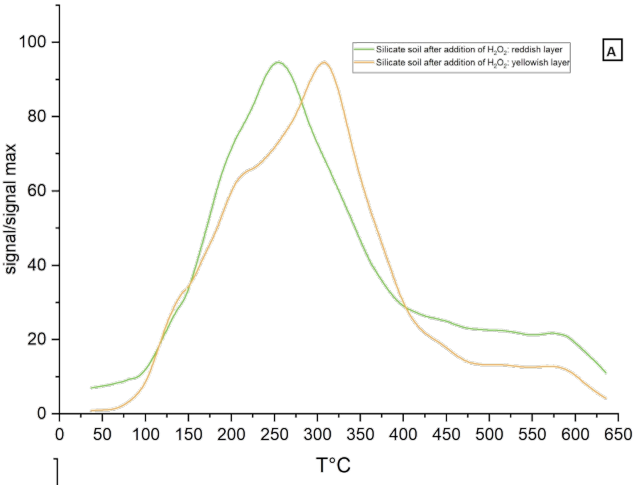
Peak at 240°C was still present in a **yellowish layer**

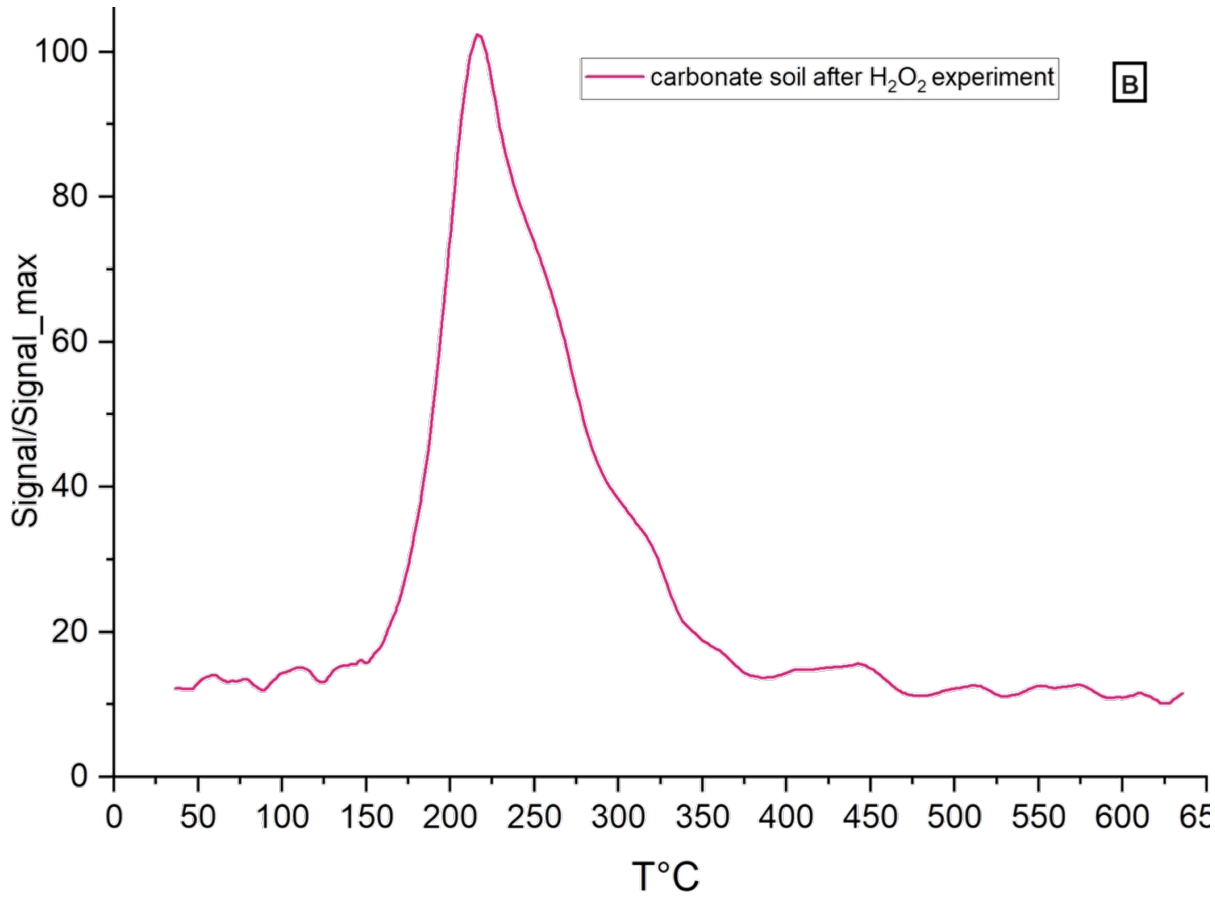
Hg^{2+} not linked to Organic Matter

Fe=9.7 wt.%; SOM:8 wt.%

Hg_I experiment-Soils+ H_2O_2

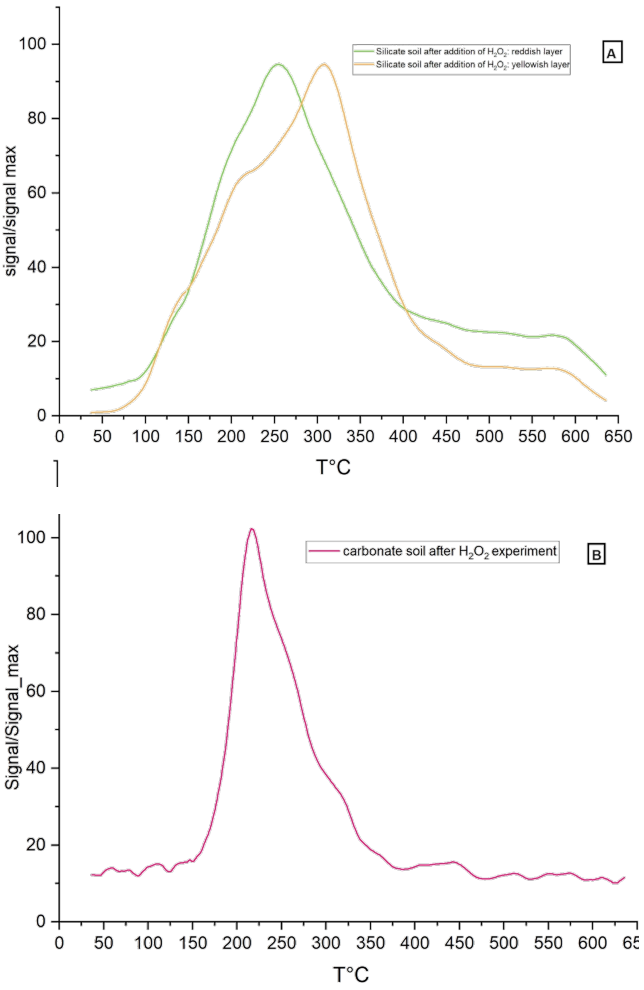
The peak at 240 °C is associated with Organic Matter?



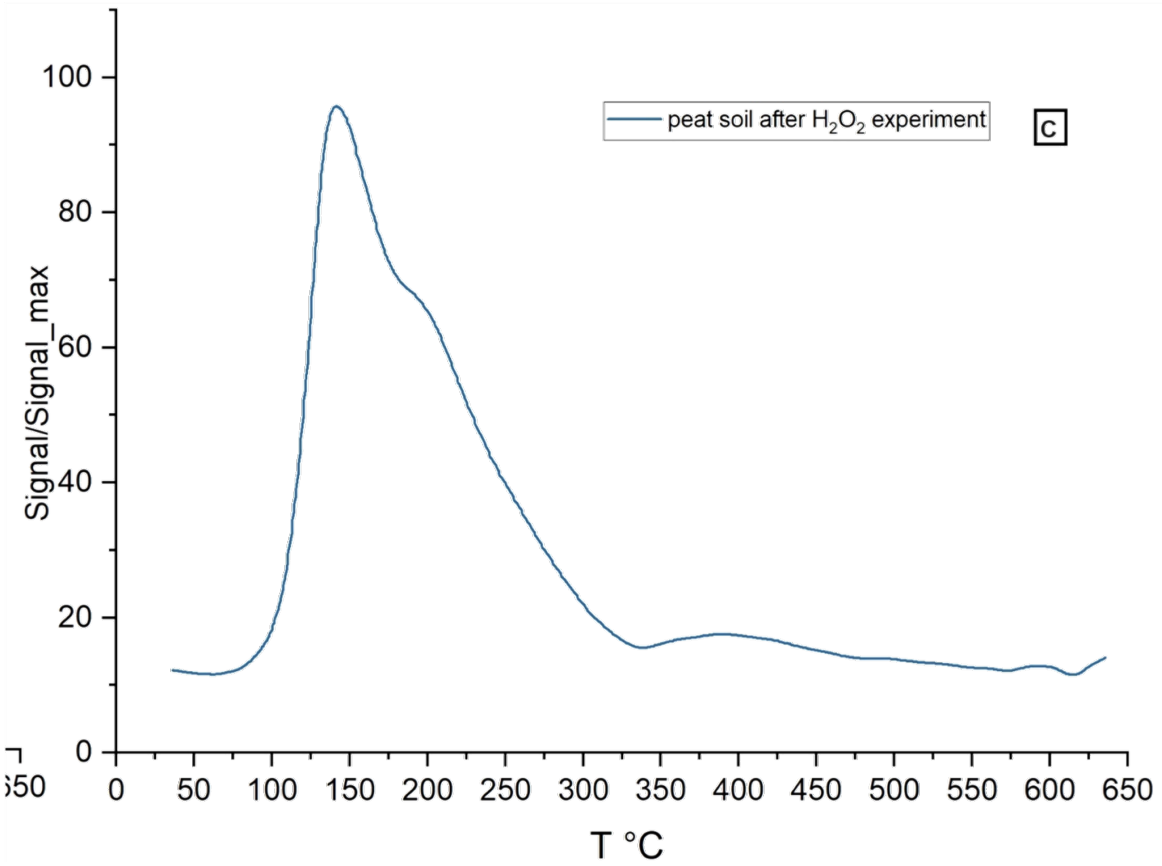


SOM: 4 wt.%

Hg_I experiment-Soils+ H_2O_2



The peak at 240 °C is associated with Organic Matter?



SOM of about 75 wt.% and presence of a new peak at 150°C

Conclusion and future studies

The experiments carried out with liquid Hg with different soil matrices highlighted that Hg^0 suffers oxidation processes to form more stable species (e.g. Hg^{2+}) in a relatively short time (~ 42 days).

New studies may be needed to understand the dynamics of Hg in different climatic contexts and with different soil types

Nevertheless, these results are expected to have important implications during soil remediation activities in areas where mercury has been used for industrial purposes or exploited from presently decommissioned mining activities. According to the different Hg-species occurring in soil, cautions are to be used during inertization processes or in-situ or ex-situ treatments.

The presence of Hg^0 and/or unstable products may produce unwanted reactions that may jeopardize the quality of the resulting material.

Thank you

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