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The effect of manure, zeolite and soil ageing in the dynamics of hexavalent chromium in *Cichorium spinosum*

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Cr(VI): CrO_4^{2-} and $HCrO_4^{-}$ ⟶ Anion

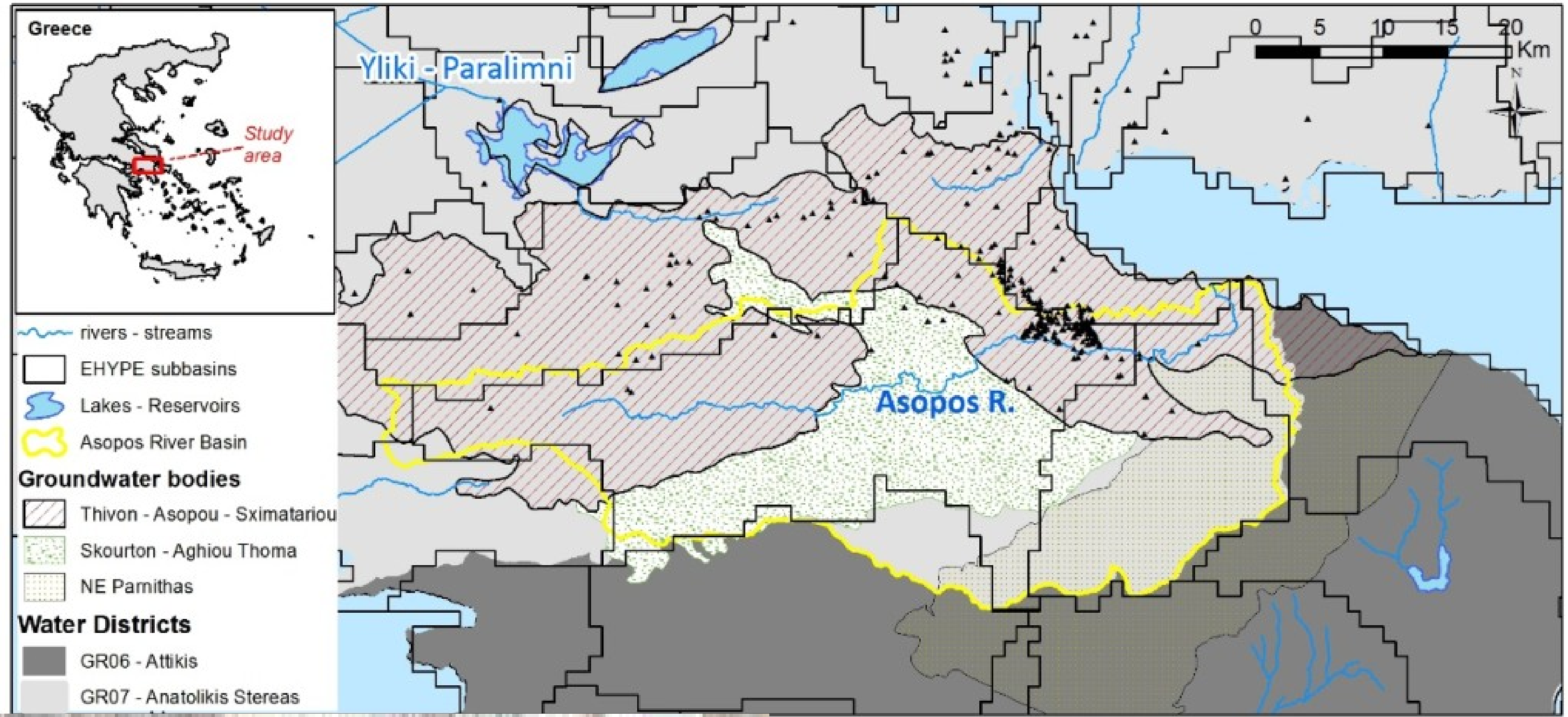
Not retained by soil colloids (mainly of negative charge)

Cr(VI): Highly toxic--easily mobilized in soil

Easily absorbed by plants

Mainly anthropogenic inputs (industrial waste-waters)

In Greece: Assopos plain ↘ Vegetable producing area


Greece
Study area
Yliki - Paralimni
0 5 10 15 20 Km
Asopos R.
rivers - streams
EHYPE subbasins
Lakes - Reservoirs
Asopos River Basin
Groundwater bodies
Thivon - Asopou - Sximatariou
Skourton - Aghiou Thoma
NE Parnithas
Water Districts
GR06 - Attikis
GR07 - Anatolikis Stereas

$Cr(VI) \xrightarrow{\text{reduction}} Cr(III)$ (a likely reaction in soil)

↓

Cationic (Cr^{3+}), relatively inert, low availability

[#1] Mitigation practice: Allow time for ageing!

(applies when Cr(VI) is not continuously deposited)

[#2] Add organic matter ⟶ Accelerates reduction

[#3] Add positive-charge surfaces

e.g., surfactant-modified zeolites

Natural z. = negative charge ⟶ SMZ: Positive charge

Marked disadvantages of SMZ:

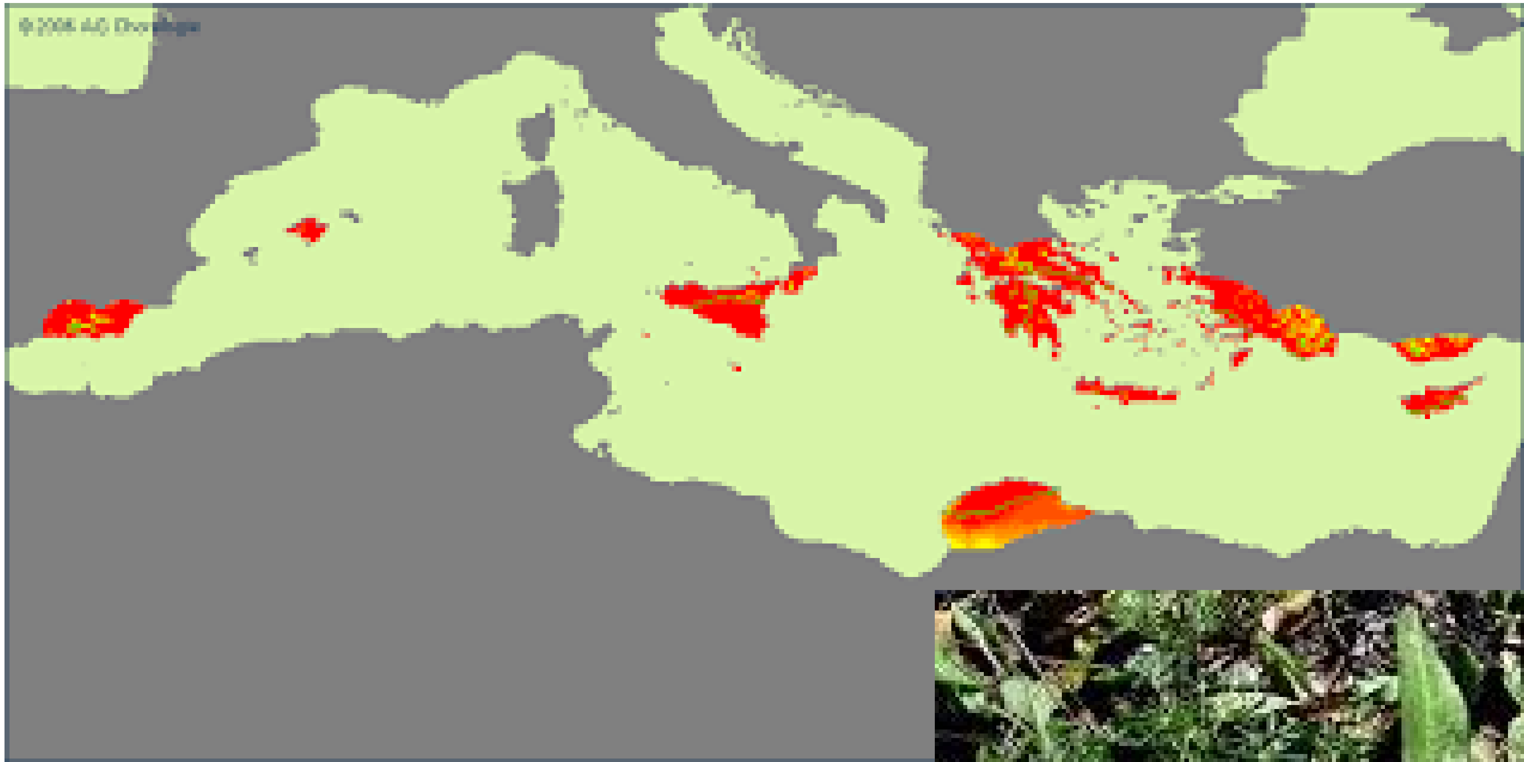
Marked disadvantages of SMZ:

1. Costly to modify → Not for field scale
2. Creates hydrophobic surfaces in soil

[#3] Use of natural zeolite

Possible physical entrapment of anions in pores

Cichorium spinosum Thorny chicory



- Wild vegetable species ⟶ Edible shoots
- Tolerates harsh conditions (draught, salinity)
- Suspected tolerant species in Cr(VI)-contaminated soils

Aims of our study:

to test addition of manure,

addition of zeolite

soil ageing

as Cr(VI) mitigation practices

in a soil cultivated with *C. spinosum*.

Materials and Methods

Pot experiment

Soil with OM 1.3%, pH 7.5

5 treatments (x 5 replicates):

(a) C: Control soil, with no additions

(b) S: Soil added with 100 mg Cr(VI) kg^{-1}

(c) Z: Soil added with 100 mg Cr(VI) kg^{-1} and 1% w/w zeolite

(d) M: Soil added with 100 mg Cr(VI) kg^{-1} and 1% dry farmyard manure

(e) AS ("aged soil"): The same soil, amended one year before the experiment with 100 mg Cr(VI) kg^{-1} was used.

2-L pots

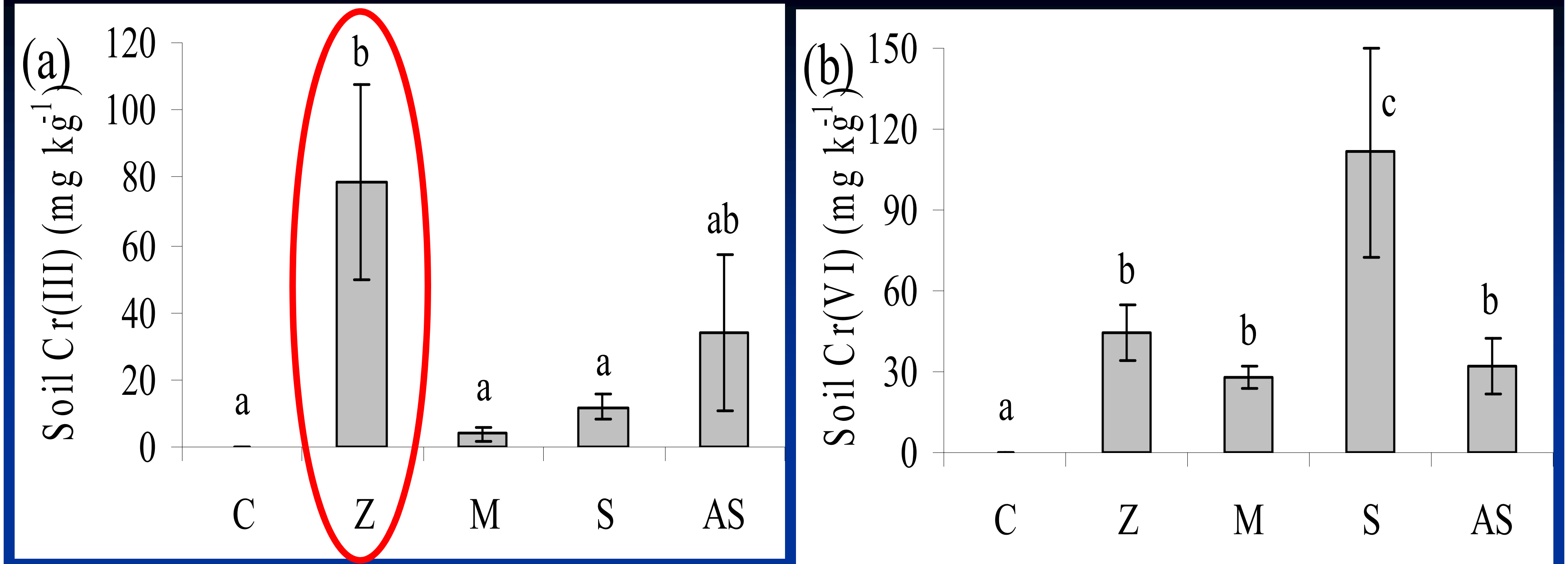
Duration = 60 days

At end: Harvested aerial biomass-obtained soil sample

Plant: Oven-dried, biomass weighed, dry-ashed (500 ^{0}C for 5 *h*), extracted with 20 mL 20% HCl

Soil: Extracted for Cr(III) (with DTPA)

Cr(VI) (with 0.01 *M* KH_2PO_4)



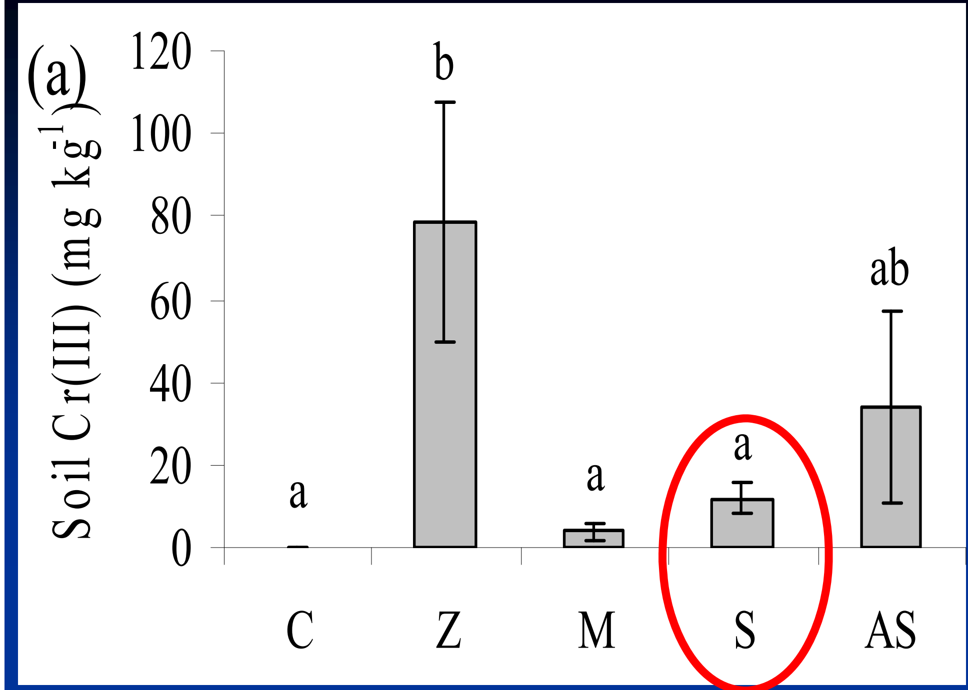
No Cr (either III or VI) in control

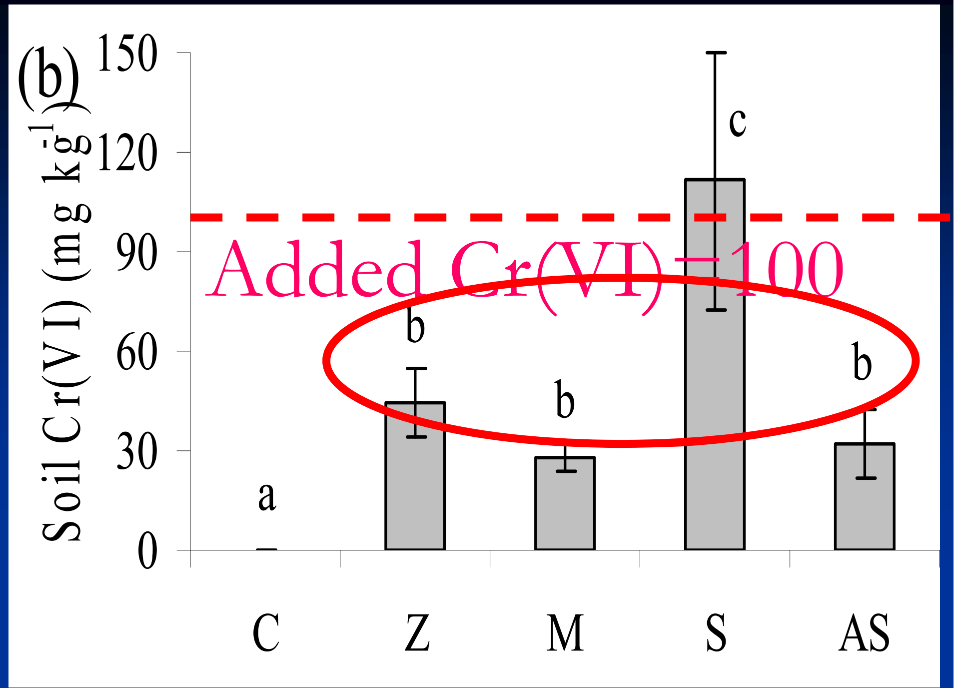
Cr(III): Z sign. higher than other treatments

Cr(III) only from Cr(VI) reduction

Produced Cr(III) entraped in z. pores...

...released slowly ...lasts longer in soil

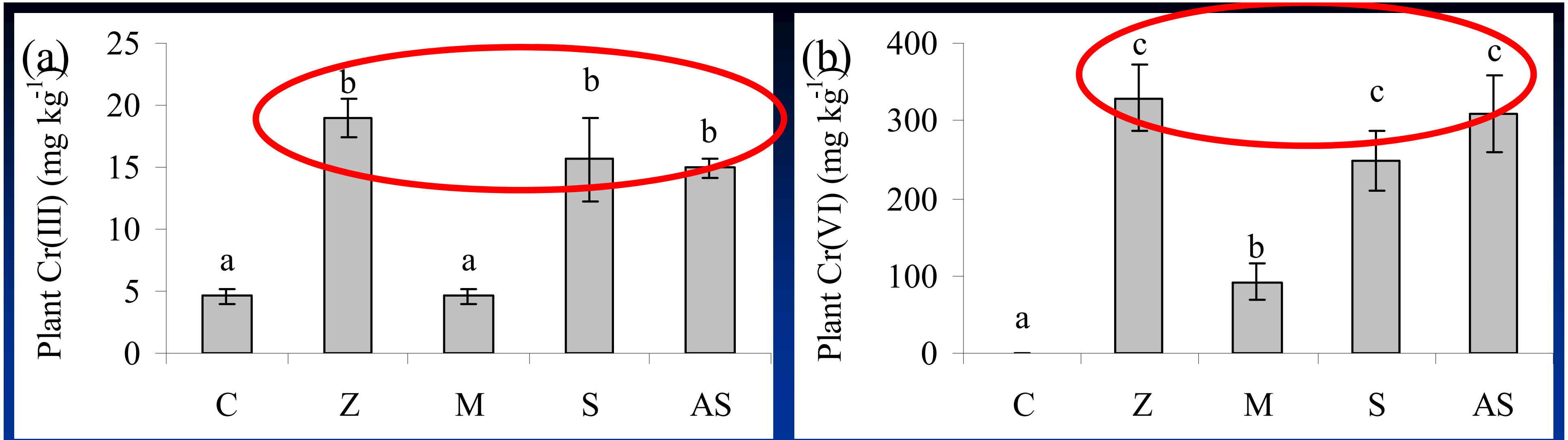




Cr(VI) at S: minimal reduction

Concurs with low Cr(III) at S

Cr(VI) decreased at Z, M, and AS (no sign. diff.)



C: Some minimal Cr(III), but no Cr(VI)

Same Cr(III) to Z, S, and AS (lower at M)

Similar for Cr(VI): Z, S, AS: Same (lower at M)

Thus (combing soil and plant data):

Z in soil helped at Cr(III) evolution...

AS in soil decreased Cr(VI)...

...but remaining Cr(VI) equally available

M was successful

Two mechanisms: (a) Cr(VI) reduction to Cr(III)

(b) organic ligands

If (a) was true: Cr(III) should increase in soil and plant

At M Cr(III) was the lowest of treatments

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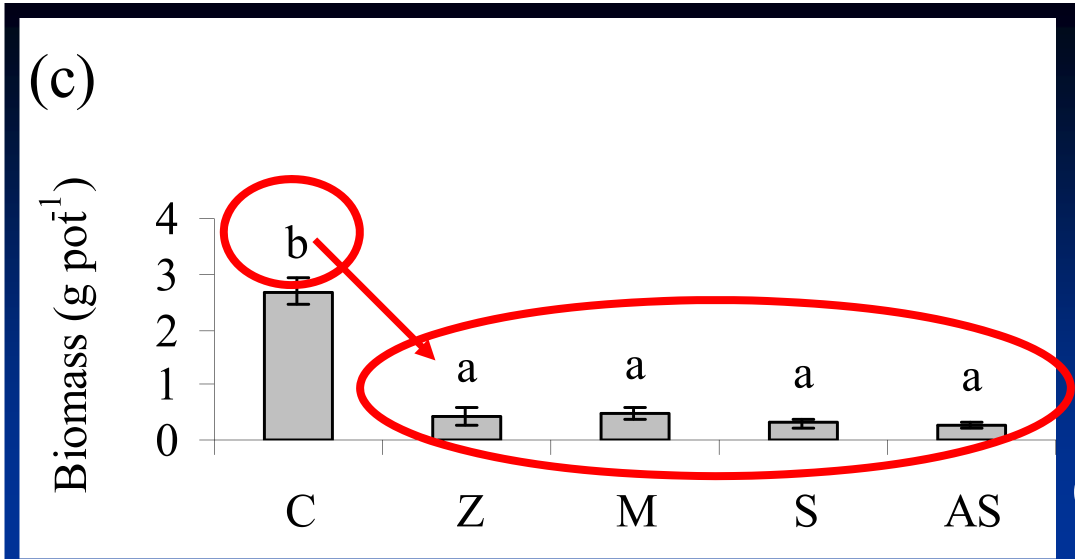
(a) = false. (b) must be true...

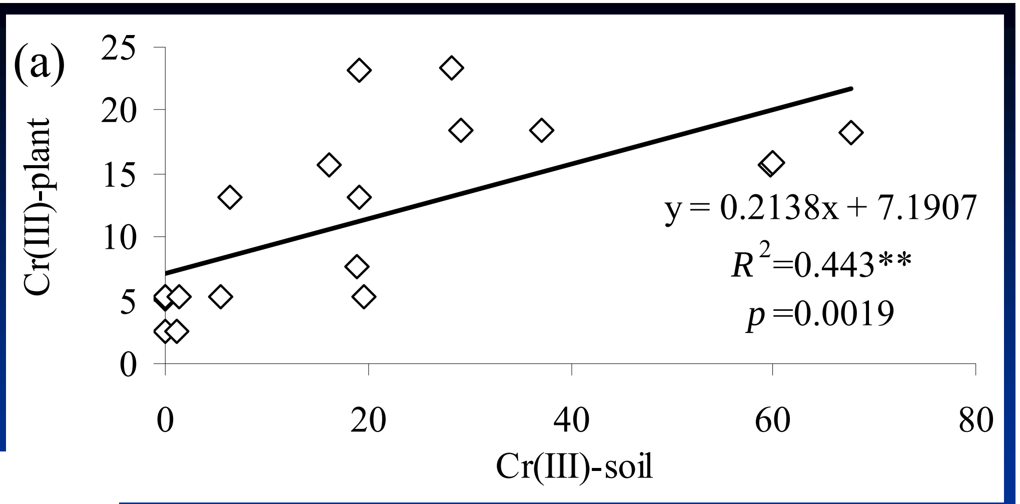
...but we can not prove it (at the moment)

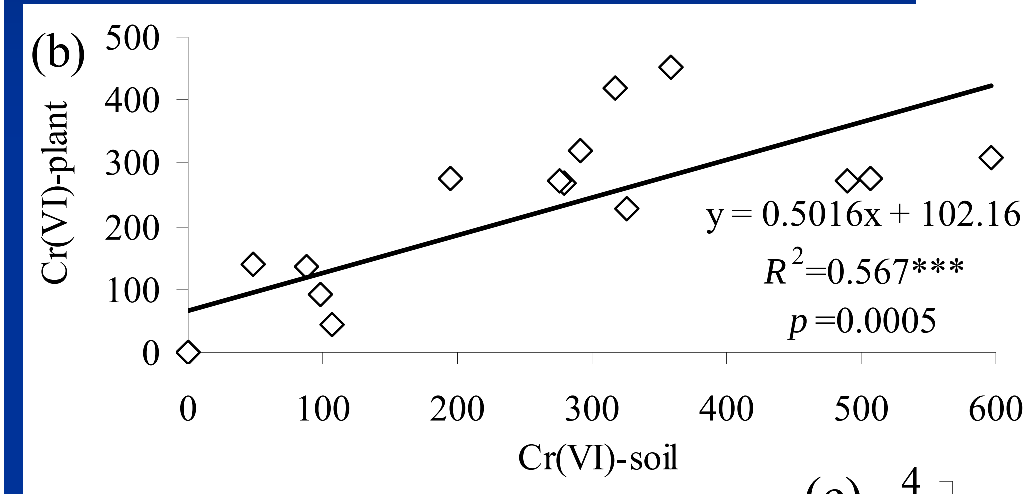


Cr(VI) toxicity indicated

Regression analyses...

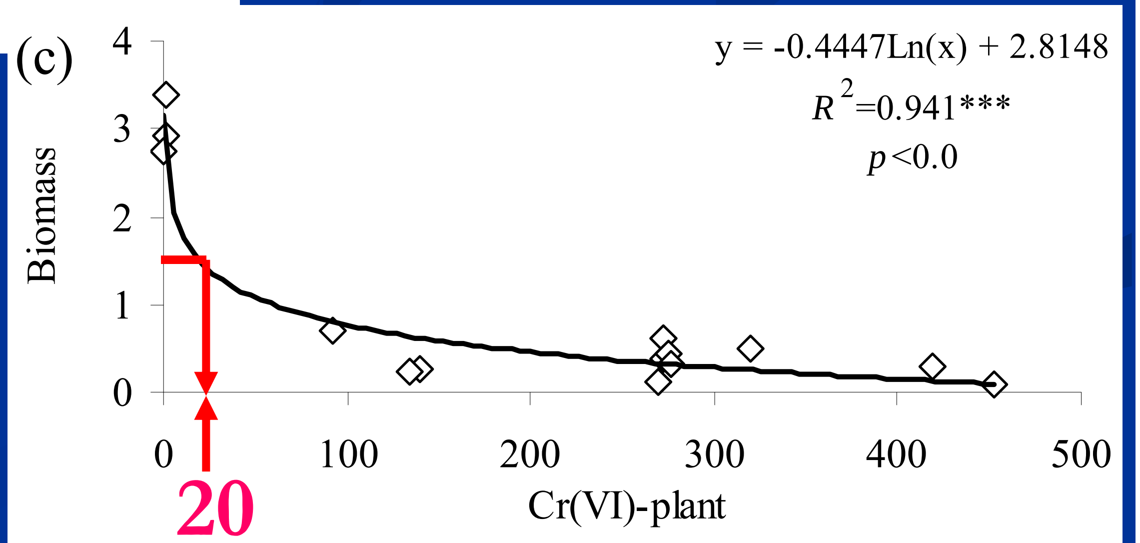
Cr(III) soil vs. plant





Cr(VI) soil vs. plant

Cr(VI)-plant vs. biomass



<u>Conclusions:</u>

The addition of organic matter (here, manure) is the best practice to minimize the Cr(VI) effects to *C. spinosum*.

<u>Thank you for your attention</u>