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Serpentine mining wastes as geochemical barriers

for the soil remediation under the ongoing Cu-Ni pollution in the Russian Arctic

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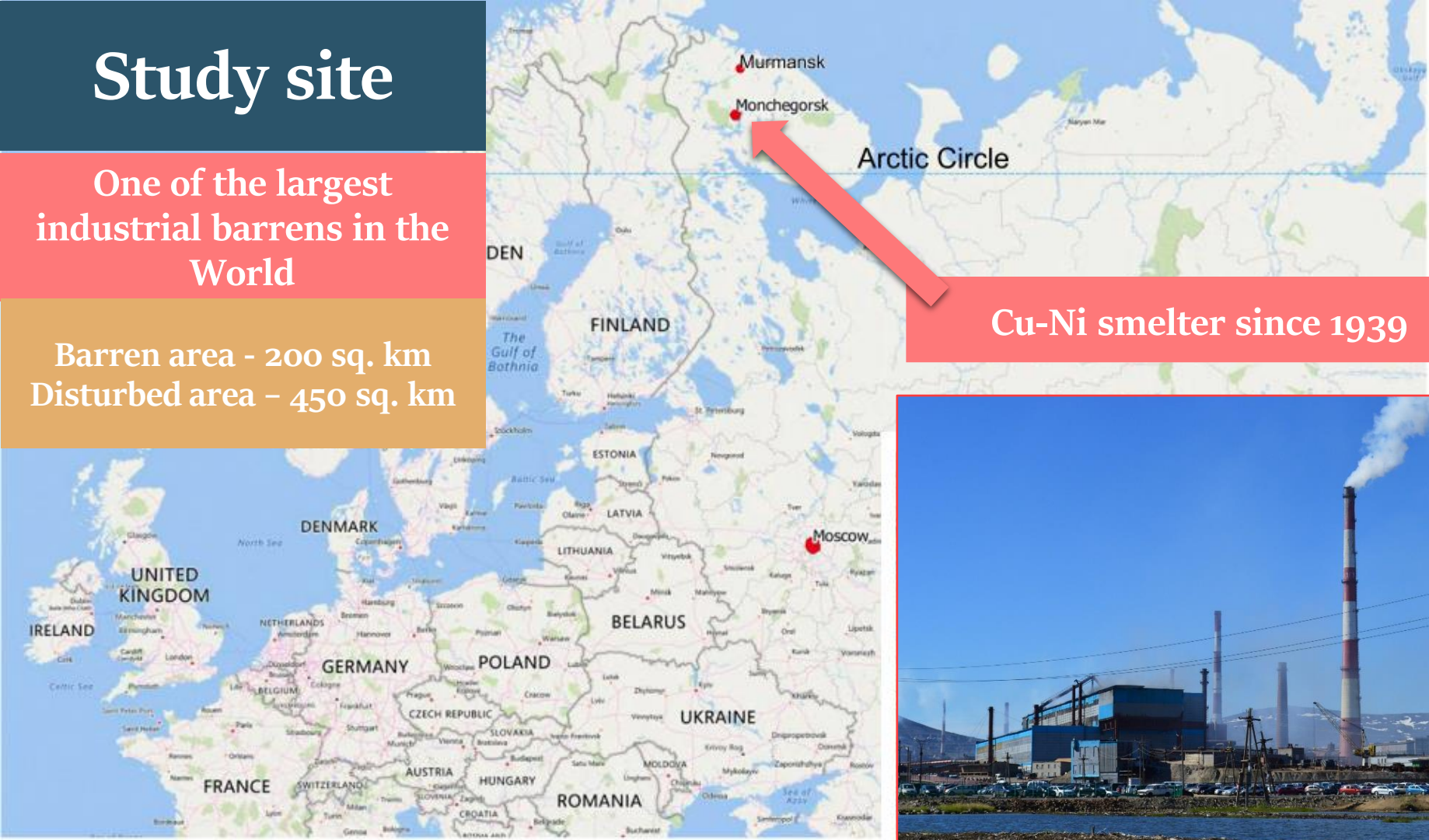
Study site

One of the largest industrial barrens in the World

Barren area - 200 sq. km
Disturbed area – 450 sq. km



Cu-Ni smelter since 1939

How did **industrial barrens** form?

Activity of non-ferrous factories

High content of metals in **mobile fractions**

Degradation of plant cover and soil

Very long term / impossibility of ecosystem self-recovery

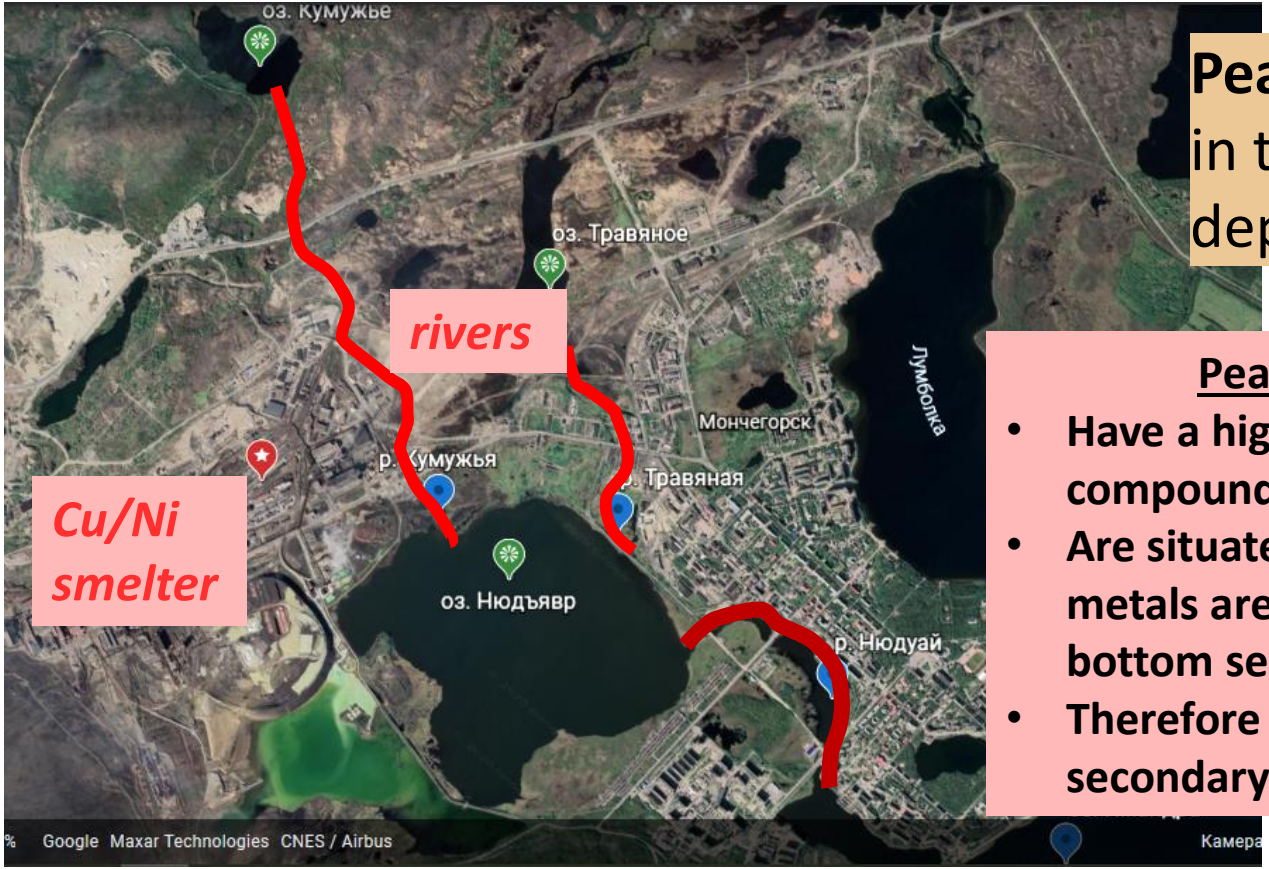
The need to develop remediation technologies

Industrial barren at the Kola peninsula

Limiting factors:

- The loss of Mg and Ca
- High soil acidity
- High portion of exchangeable fraction of Cu and Ni

Peat soils' remediation



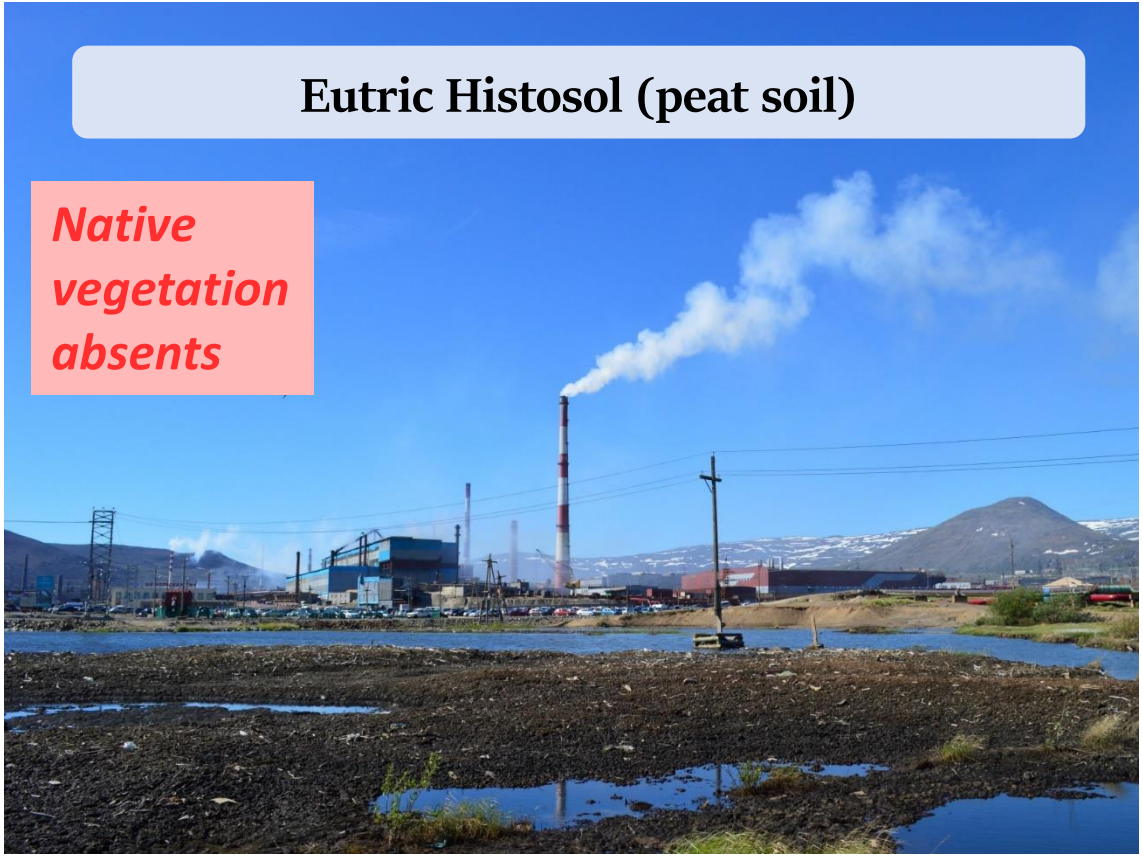
Peat soils are situated in the meso-relief depressions

Peat soils:

- **Have a high content of mobile metal compounds**
- **Are situated near water bodies, and metals are leaching into water and bottom sediments**
- **Therefore peat soils are the source of secondary ecosystem pollution**

Experimental site,

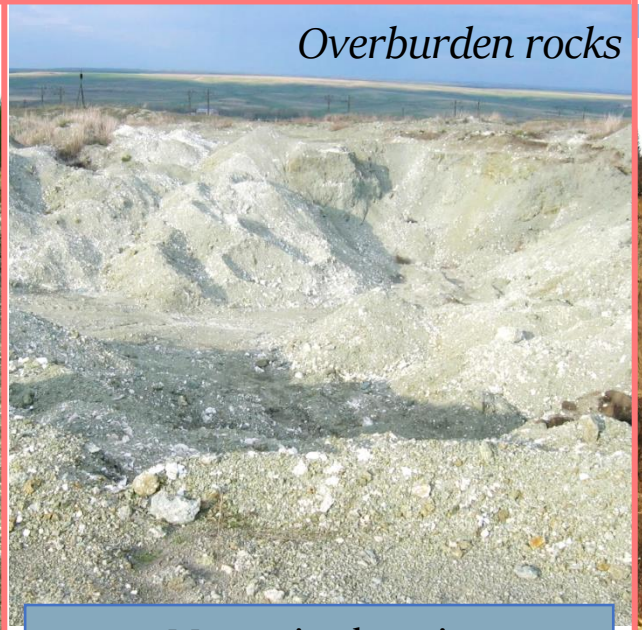
0.7 km from the Cu-Ni factory



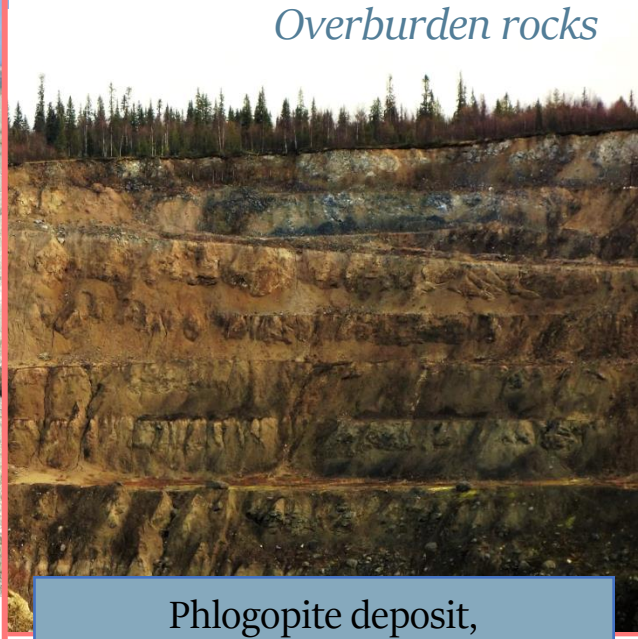
The surface of peat site after snow melting

Serpentine mining wastes as materials for soil rehabilitation

Olivinite deposit,
Murmansk reg. Russia



Magnesite deposit,
Orenburg reg. Russia



Phlogopite deposit,
Murmansk reg. Russia

Five serpentine mining wastes were used:

Initial (>2 mm)	Thermally activated	Initial (>2.5 mm)	Thermally activated	Initial (>2 mm)
L	Lt	SM	SMt	VL

Functions of serpentine mining wastes

Serpentines:
$X_{2-3}Si_2O_5(OH)_4$,
where **X** = Mg, Fe^{2+}, Fe^{3+}, Ni, Al, Zn, Mn

Domination of Mg in chemical composition

Mg and Si plant available compounds → **The enrichment of soil by macronutrients**

Alkaline environment → **Transfer of mobile metal compounds into insoluble form**

Sand texture (0.5-2.5 mm) → **Favorable for root development**

Design of experiment

Grass cover

Direct seeding
50 % of plots

OR

Rolled lawns
50 % of plots

Expanded Vermiculite, h=1 cm

Geochemical barrier

Soil covering
h=5 cm
(for initial wastes)

OR

Soil mixing
h=10 cm
(for therm. act. wastes)

Polluted Topsoil

Sustainable plant cover

2011

2019

Functioning as geochemical barriers

Soils were analyzed using sequential extraction procedure:

Mobile ability	Geochemical fraction	Extractant	Mechanism of extraction	Migration forms
Actually Mobile	**Water-extractable**	Water distilled	Dissolution	**Plant available**
	Exchangeable	Ammonium Acetate Buffer, pH 4.65 **(threefold treatment)**	Ion exchange, complexation	
Potentially Mobile	**Bound with Fe/Mn (hydr)oxides**	0,04 M NH_2OH-HCl in 25% CH_3COOH, pH 2	Destruction of carrier phases (reducible conditions)	**Strongly associated with carrier phases**
	Bound with Organic Matter	30% H_2O_2 + 0,02 M HNO_3, then - 3,2 M CH_3COONH_4	Destruction of carrier phases (oxidizable conditions)	
Strongly bound	**Residual**	1N HNO_3	Full autopsy	**Not migrate**

Metal deposition

Serp. waste layer

Cu: 200-1200 ppm

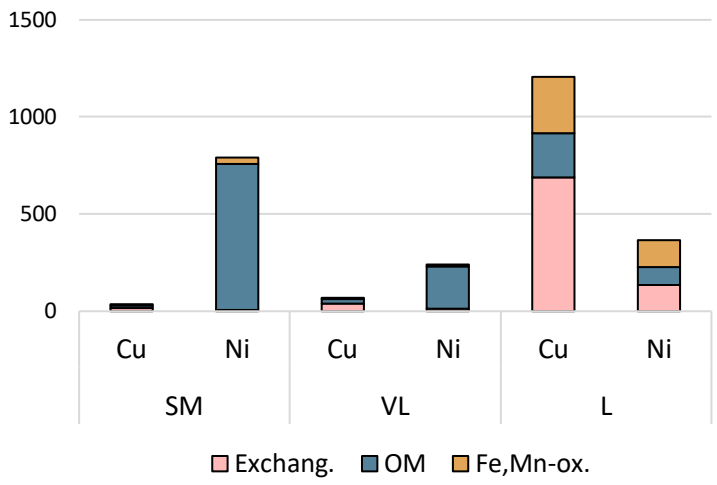
Ni: 400-2500 ppm

Total metal deposition

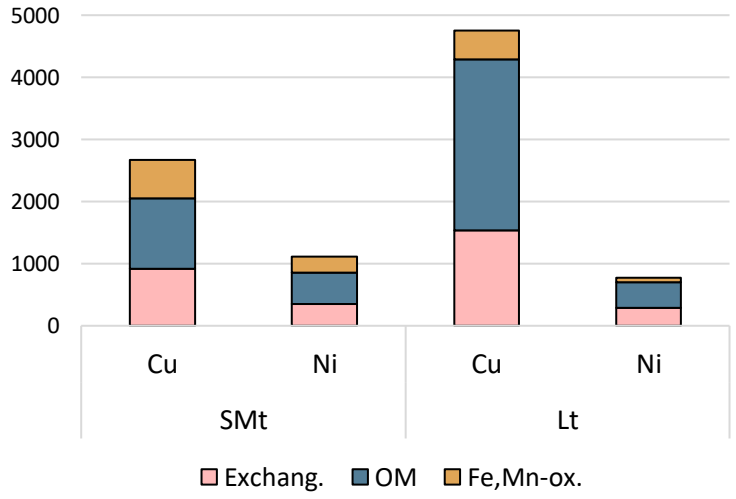
Therm/act. waste mix

Cu: 2700-4800 ppm

Ni: 780-1100 ppm

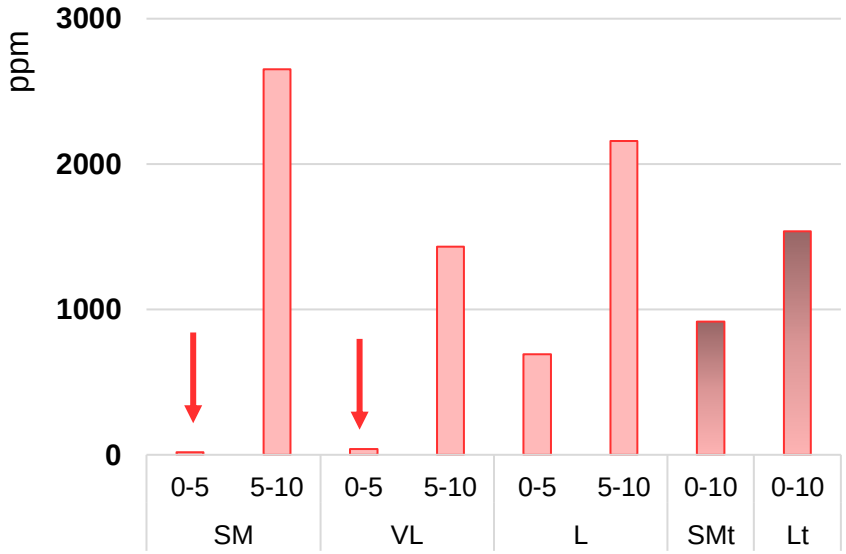


Potentially mobile fractions

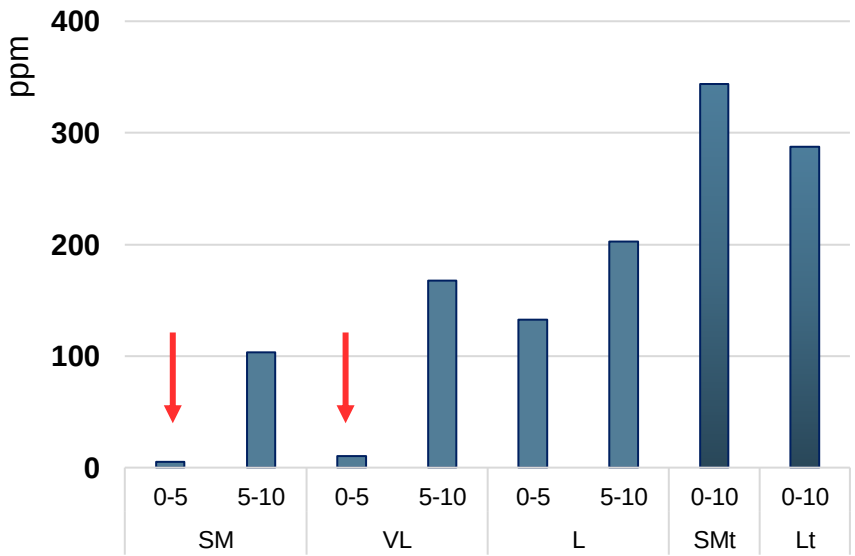


Exchangeable fraction

Cu >6000 ppm in initial peat soil



Ni >500 ppm in initial peat soil

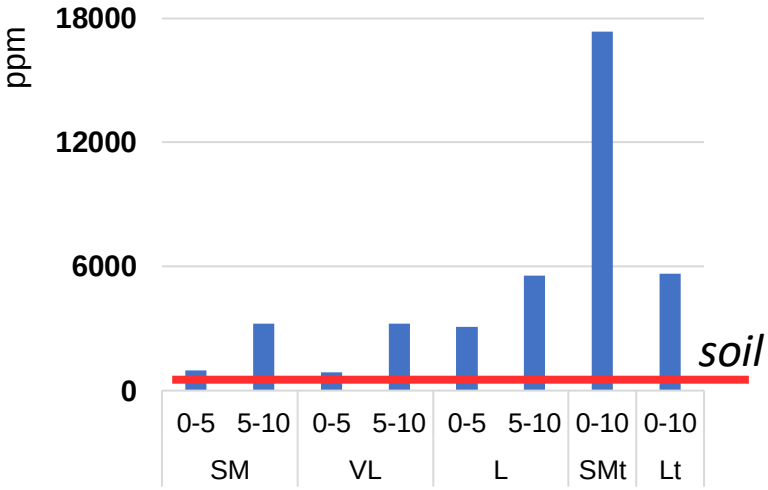


The BEST for plants:
Serpentinite-magnesite and Vermiculite-lizardite

Exchangeable fraction

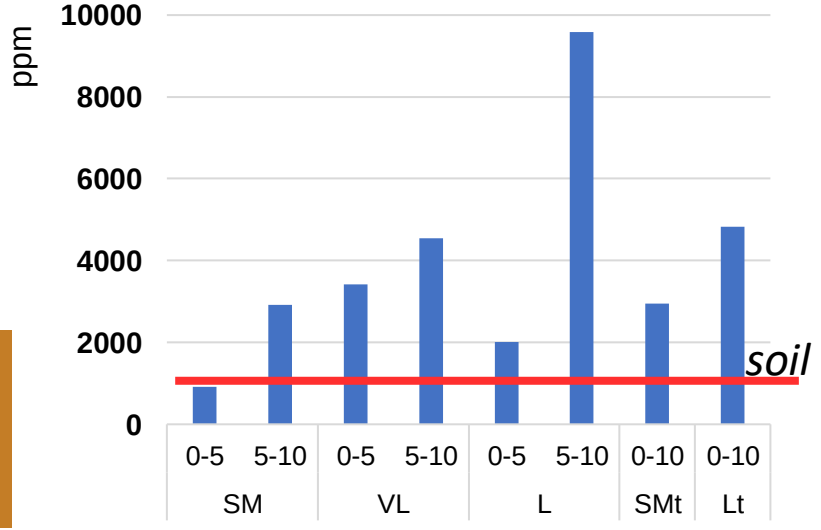
Mg

Max:
thermally activated



Ca

Min:
serpentinite-magnesite



Mg + Ca

Thermally activated > L, VL > SM

Assessment of phytotoxicity

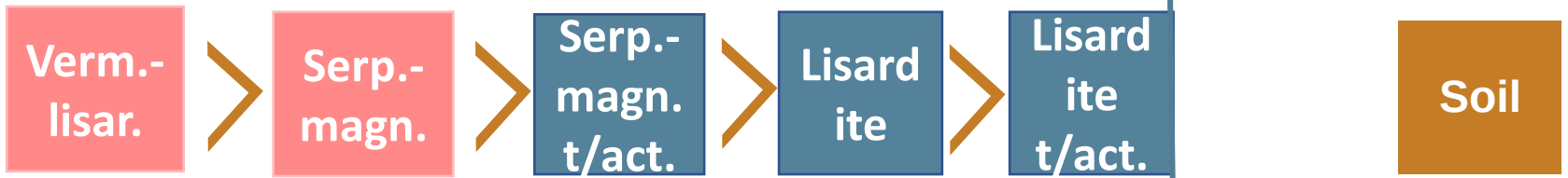
$$M_t = \frac{\nu_{Cu} + \nu_{Ni}}{\nu_{Ca} + \nu_{Mg}} \times 100$$

Affected:

- Plant biomass
- Fluorescence of chlorophyll *a*
- Content of photosynthetic pigments
- Soil CO_2 emission

Mt = 0.5 - 20

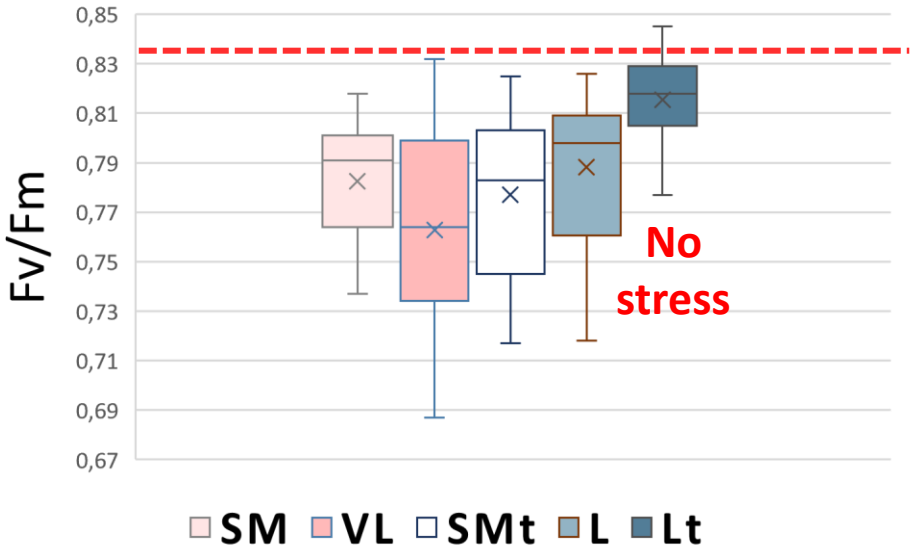
Mt = 200



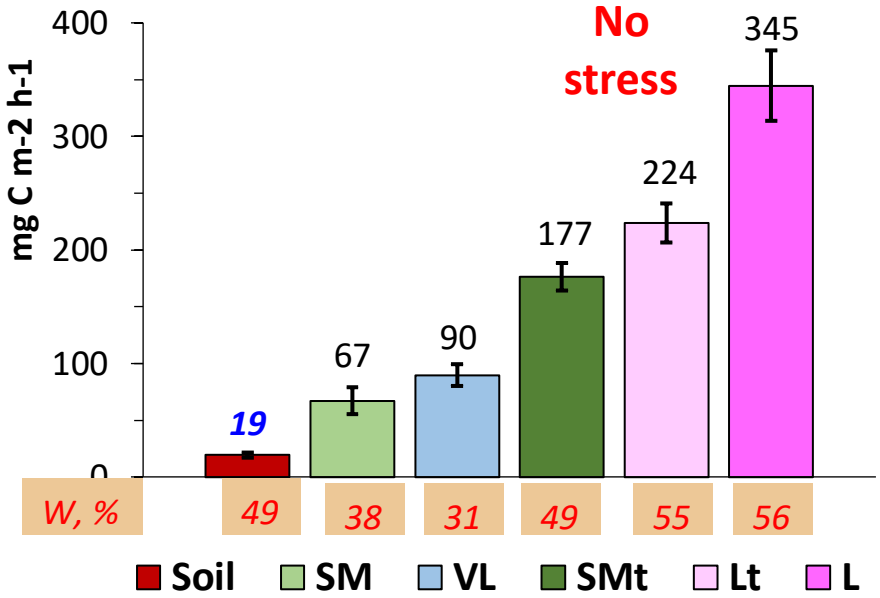
Slukovskaya et al. 2017. *Non-ferrous Metals, 2*:20-26.

Assessment of phytotoxicity

Fv/Fm (maximum photochemical efficiency)



CO_2 emissions



Thermally activated variants: high humidity and contents of Mg and Ca compensated toxic effect of Cu and Ni

Peat soils' remediation

Thermally activated serpentine materials

Peat Soil

- Have high adsorptive properties
- Are more alkaline in comparison with initial wastes
- Have high content of plant available Mg and Ca, which are essential elements in the study area and provide the higher thresholds of phytotoxicity for Cu and Ni

Remediation

Indicator	Peat soil	Podzol soil
		
Humidity, vol. %	50 %	20 %
Total Cu, ppm	8 500 - 10 400	600
Total Ni, ppm	5300	1000 – 1300
Approach suggested	**Mixing with thermally activated serpentine materials**	**Covering by serpentine-reached materials**

Take home messages

Serpentine mining wastes can perform the role of **alkaline geochemical barriers** and substrate for plant development
Thermally activated materials highly affected the polluted soil

- Mining wastes enriched with serpentine minerals **are suitable for the remediation** of highly polluted soils under continuing atmospheric emissions
- These materials are capable to change chemical composition and pH of soils

The following methods of remediation are proposed:
For podzol soil: soil covering by serpentine mining wastes
For peat soil: mixing of soil with thermally activated materials

Thank you for your attention!

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