MICRONUTRIENTS AND CONTAMINANTS IN AERIAL PARTS OF DACTYLIS GLOMERATA GROWN ON 9 BARE CONTAMINATED SOILS AND MINE RESIDUES WITH AMENDMENT OF MODIFIED BAUXITE RESIDUE (MBR)

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Micronutrients and contaminants in aerial parts of *Dactylis glomerata* grown on 9 bare contaminated soils and mine residues with amendment of modified bauxite residue (MBR)

**Introduction**: how to cope with bare phytotoxic soils/mine tailings?

**Material and methods**
- soils and mine residues
- cultivation of *D. glomerata*
- speciation of immobilised elements

**Results**
- immobilisation of leaching fraction of elements, and
- concentration of elements in leafs
- speciation of the immobilisation of the elements (examples)

**Conclusion**
Introduction: bare soils and mine tailings and residues

Many abandoned mine sites contain sulfides and emit toxic acid water and contaminated dust.

According to the literature and own experiments, bauxite residue can be used to reduce the soluble fraction of toxic elements, and alleviate phytotoxicity of mine residues and aquatic toxicity of mine waters. Detailed methods and results are available in technical reports, and will be published in a series of papers.

This study presents summarized results of 4 years of experimentation at laboratory and pilot scale to immobilise contaminants modified bauxite residue (MBR, pH 8.5), from 9 soils and mine tailings, from initial pH 2.8 to pH 7.8.
Introduction: pyritic mine residues, acid mine drainage

Oxydation of sulfides in contact with O$_2$ by mining activities generates sulfuric acid that dissolves (phyto)toxic elements (acid mine drainage)
Saint Sébastien d’Aigrefeuille (Alès)
Former process residue basin (confidential)
Acid mine drainage (confidential)
Introduction: Immobilisation of elements: (i) adsorption by Fe/Al (hydr)oxides

Specific: inner-sphere complex

Non-specific: outer-sphere complex (include ionic exchange) (Bradl 2004)

Figure 5.4. A schematic portrayal of an inorganic hydroxyl surface, showing planes associated with surface hydroxyl groups ("s"), inner-sphere complexes ("a"), outer-sphere complexes ("β"), and the diffuse ion swarm ("d").

Sposito 1984
Introduction: Immobilisation of elements: (ii) precipitation and (iii) fixation

Precipitation:
- Growth of a 3-D solid
- With OH\(^-\), CO\(_3\)^{2-}, PO\(_4\)^{3-}, S^{2-}
- Function of metal concentrations, pH, redox and anions

Fixation:
- Diffusion of a species in a solid phase in 3-D

Bauxite residue contents
48% of iron (hydr)oxides → specific adsorption
12% of aluminum (hydr)oxides → specific adsorption
10% cancrinite and katoite → non-specific adsorption
1.5 M OH-/kg → precipitation
Materials and methods

Soils and mine residues
Control = thin clay soil on limestone (rendzina) with forest, from Aix-en-Provence (F)
Geze = excavated subsoil (10 m) from Marseille (F)
SME = heavily Cu polluted soil from a former wood treatment facility, Saint Médard D’Eyrans, Bordeaux (F)
SSAF = bare pyritic mine tailings in sandstone, high lead and zinc concentrations, Saint Sébastien d’Aigrefeuille, Alès (F)
Campo Pisano = flotation tailing dumps, Campo Pisano, Sardinia (I)
Escalette = mining residues and tailings, high As and Pb concentrations, Escalette, Marseille (F)
Sa Masa = marsh downstream of zone of mine tailings, Sa Masa, Sardinia (I)
Materials and methods

Soils and mine residues
SLLM = bare or with poor adapted vegetation acid mine tailings, Saint Laurent le Minier, Montpellier (F)
St Félix = bare pyritic artisanal mine tailings, high zinc, lead and cadmium concentrations, Saint Félix (F)
RM3-1 = processed residues of pyrite, high copper concentration, fine fraction, grey mud deposit, confidential (F).

The pH of these materials was in the 2.4 – 8.3 range.
Aqua regia concentration were for some very high
As: 4 – 1300 mg/kg
Cd: 1 – 250 mg/kg
Cu: 1 – 10 000 mg/kg
Pb 10 – 20000 mg/kg
Zn 10 – 4000 mg/kg.
Materials and methods

Cultivation of plant in pot, lysimeter or field plot

*Dactylis glomerata* is grown in open air in 400 g pot of soil/mine residue laboratory material (dried at 40°C and crushed at 2 mm), with NPK fertiliser at agronomic dose, with daily restrained irrigation and free leaching, from February to June 2016 at Aix-en-Provence.

The growth was very poor to poor, and after 2 months, compost (1%) has been added and *D. glomerata* re-seeded.

For control, St Félix and MR3-1, *Dactylis glomerata* is grown in open air lysimeters of 50 l, without compost, with NPK fertiliser at agronomic dose, with regular irrigation and free leaching. The growth with addition of MBR was flourishing.
Materials and methods

Speciation of immobilised elements
Bearing phases were measured according to ISO/CD 12782-1 to 3:
- Amorphous iron
- Crystalline iron
- Reactive aluminum
Reactive carbon were assessed from TOC measurements from solid and liquid samples.

Samples were leached at 8 different pH from pH 2 to pH 12 (EN 14997) and solubilised elements were measured.

Geomodelling of the different fractions was done with LeachXS/Orchestra.
Results

Growth of *D. glomerata* in pots: example of St Félix

St Félix 10% RBM

![Bar graph showing growth of *D. glomerata* in different soil types and fertilization conditions. The x-axis represents soil treatments (Control, Soil, SoilMBR) and fertilization levels (no Fertilizer, Fertilizer). The y-axis represents the number of plants per pot.](image)
Growth of *D. glomerata* in lysimerer: example of St Félix

Left: without MBR
Right: with MBR

78 days after sewing
Growth of *D. glomerata* in plot: example of St Félix
Phytotoxicity: field trial 108 days after sewing (despite drought)
Phytotoxicity: field trial 458 days after sewing (summer)
Results

Growth of *D. glomerata* in pots: example of SSAF

Mine residue SSAF pH 3.5: MR, MR+Fertiliser, MR + 0.1% RBM + fertiliser, idem 0.3%, 1%, 3%, 10%, 30%
Growth of *D. glomerata* in pots: example of RM3-1
Growth of *D. glomerata* in lysimeter: example of RM3-1
Growth of *D. glomerata* in pots: other soils/MR

Left to right: Control, SLLM, SME, Escalette, Campo Pisano, Sa Masa, Geze

Upper to lower row: 0%, 10% and 30% MBR
Results

Leaching concentrations / Foliar concentrations: Cd

Leaching conc. (mg/kg)
- Control
- Geze
- SME
- SSAF
- C. Pisano
- Escalette
- Sa Masa
- SLLM
- St Félix
- MR3-1

Foliar conc. (mg/kg)
- Control
- Geze
- SME
- SSAF
- C. Pisano
- Escalette
- Sa Masa
- SLLM
- St Félix
- MR3-1

Leaching conc. (mg/kg):
- Cd

Foliar conc. (mg/kg):
- Cd
Leaching concentrations / Foliar concentrations: Cu

Leaching conc. (mg/kg)

0.0 0.001 0.003 0.01 0.03 0.1 0.3

Foliar conc. (mg/kg)

0 0.1 0.3 0.1+CaCO3

Control
Geze
SME
SSAF
C. Pisano
Escalette
Sa Masa
SLLM
St Félix
MR3-1
Leaching concentrations / Foliar concentrations: Zn

Leaching conc. (mg/kg)

- Control
- Geze
- SME
- SSAF
- C. Pisano
- Escalette
- Sa Masa
- SLLM
- St Félix
- MR3-1

Foliar conc. (mg/kg)

- Control
- Geze
- SME
- SSAF
- C. Pisano
- Escalette
- Sa Masa
- SLLM
- St Félix
- MR3-1

Legend:
- 0
- 0.001
- 0.003
- 0.01
- 0.03
- 0.1
- 0.3
- 0.1+CaCO3
Leaching concentrations / Foliar concentrations: As

Leaching conc. (mg/kg)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Control</th>
<th>Geze</th>
<th>SME</th>
<th>SSAF</th>
<th>C. Pisano</th>
<th>Escalette</th>
<th>Sa Masa</th>
<th>SLLM</th>
<th>St Félix</th>
<th>MR3-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaching conc. (mg/kg)</td>
<td>0 0.001 0.003 0.01 0.03 0.1 0.3</td>
<td></td>
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</table>

Foliar conc. (mg/kg)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Control</th>
<th>Geze</th>
<th>SME</th>
<th>SSAF</th>
<th>C. Pisano</th>
<th>Escalette</th>
<th>Sa Masa</th>
<th>SLLM</th>
<th>St Félix</th>
<th>MR3-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foliar conc. (mg/kg)</td>
<td>0 0.1 0.3 0.1+CaCO3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

0.1 1 10 100 1000
Leaching concentrations / Foliar concentrations: Cr

Leaching conc. (mg/kg)

Control  Geze  SME  SSAF  C. Pisano  Escalette  Sa Masa  SLLM  St Félix  MR3-1

Foliar conc. (mg/kg)

Control  Geze  SME  SSAF  C. Pisano  Escalette  Sa Masa  SLLM  St Félix  MR3-1
Leaching concentrations / Foliar concentrations: Sb

**Foliar conc. (mg/kg)**

- Control
- Geze
- SME
- SSAF
- C. Pisano
- Escalette
- Sa Masa
- SLLM
- St Félix
- MR3-1

**Leaching conc. (mg/kg)**

- Control
- Geze
- SME
- SSAF
- C. Pisano
- Escalette
- Sa Masa
- SLLM
- St Félix
- MR3-1
Leaching concentrations / Foliar concentrations: Pb

- **Leaching conc. (mg/kg):**
  - Control
  - Geze
  - SME
  - SSAF
  - C. Pisano
  - Escalette
  - Sa Masa
  - SLLM
  - St Félix
  - MR3-1

- **Foliar conc. (mg/kg):**
  - Control
  - Geze
  - SME
  - SSAF
  - C. Pisano
  - Escalette
  - Sa Masa
  - SLLM
  - St Félix
  - MR3-1

Legend:
- 0
- 0.001
- 0.003
- 0.01
- 0.03
- 0.1
- 0.3
- 0.1+CaCO₃
Leaching concentrations / Foliar concentrations: Fe

Leaching conc. (mg/kg)

- Control
- Geze
- SME
- SSAF
- C. Pisano
- Escalette
- Sa Masa
- SLLM
- St Félix
- MR3-1

Foliar conc. (mg/kg)

- Control
- Geze
- SME
- SSAF
- C. Pisano
- Escalette
- Sa Masa
- SLLM
- St Félix
- MR3-1

Concentrations for Fe:
- Leaching: 0.001, 0.003, 0.01, 0.03, 0.1, 0.3
- Foliar: 0, 0.1, 0.3, 0.1+CaCO3
Leaching concentrations / Foliar concentrations: Al

Leaching conc. (mg/kg) vs. Foliar conc. (mg/kg) for different locations and treatments.

- Control
- Geze
- SME
- SSAF
- C. Pisano
- Escalette
- Sa Masa
- SLLM
- St Félix
- MR3-1
Leaching concentrations / Foliar concentrations: Mn

Leaching conc. (mg/kg)
Mn
0 0.001 0.003 0.01 0.03 0.1 0.3

Foliar conc. (mg/kg)
Mn
0 0.1 0.3 0.1+CaCO3
Results: Chemical speciation of Zn (extractible pH 2) of St Felix:
At pH 7.6, 93% of Zn on FeOxide (84% without MBR)

Phase distribution of Zn+2

At pH 7.6
- Free: 1.3%
- DOC-bound: 0.5%
- POM-bound: 4.9%
- FeOxide: 93.1%
- Clay: 0.2%
Results: Chemical speciation of Pb (extractible pH 2) of St Felix + 10% MBR:

At pH 7.6
- Free: 0.0%
- DOC-bound: 0.2%
- POM-bound: 2.0%
- FeOxide: 97.8%
- Clay: 0.0%
- Pb2SiO4: 0.0%
- Pb3[VO4]2: 0.0%
- PbMoO4[c]: 0.0%

Phase distribution of Pb+2

Concentration (mg/L) vs. pH
Chemical speciation of Pb (extractible pH 2) of SSAF:

Phase distribution of Pb+2

Concentration (mg/L)

pH

Free
DOC-bound
POM-bound
FeOxide
Clay
ettr_ss
Pb2V2O7
Pb3[VO4]2
Chemical speciation of Pb (extractible pH 2) of SSAF + 10% MBR:

Phase distribution of Pb+2

Concentration (mg/L) vs pH

Free, DOC-bound, POM-bound, FeOxide, Clay, ettr_ss, Pb2V2O7, Pb3[VO4]2, PbMoO4[c]
Conclusions

Modified bauxite residue addition reduces the leaching concentration (10 liter deionised water/kg DM) of all elements, up to concentration of the control soil, or to the limit of quantification, depending on the amount added.

In pots, growth is poor (frequent death of plants for pots without MBR) to moderate (for 0.3 parts of MBR). Foliar concentrations are reduced with the MBR addition.

In lysimeters and plot, growth is flourishing foliar and concentrations are reduced up to the control concentration for all elements, excepted for lead (3 mg/kg for control, 62 mg/kg for St Félix and 8 mg/kg for MR3-1).

The simple leaching concentrations (with deionised water) can be used to test soil improvers, with the exception of lead.

The elements are immobilised primarily by iron and aluminum (hydr)oxides. Without acidity input or reductive conditions, immobilisation should be stable.
Acknowledgements

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Thank you...
Merci...
• **Introduction**

• Some contaminated soils and mine tailings or residues are so phytotoxic that they bare or with a very scarce vegetation for decades. They are prone to sheet erosion, gully erosion, wind erosion, and contaminated surface and underground water emissions.

• Due to large iron and aluminum (hydr)oxide content, clay content, and alkalinity content, the soil improver “modified bauxite residue” (MBR) immobilizes elements and, with agronomic fertiliser input, and
**Summary of mine residues and sub-soil treatment: Ratio final/initial leachable concentration**

Leachable concentrations up to inert waste landfill acceptance criteria

<table>
<thead>
<tr>
<th>Résidu/sol</th>
<th>Dose</th>
<th>pH i</th>
<th>pH f-i</th>
<th>Pb</th>
<th>Zn</th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
<th>As</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMR3-1</td>
<td>10% + CaCO3</td>
<td>2.43</td>
<td>6.51</td>
<td>0.1095</td>
<td></td>
<td></td>
<td>0.0010</td>
<td>0.0672</td>
<td>0.0645</td>
<td>0.1519</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AMR3-2</td>
<td>3%*</td>
<td>2.55</td>
<td>4.89*</td>
<td>0.3873</td>
<td></td>
<td></td>
<td>0.0113</td>
<td></td>
<td></td>
<td>0.9</td>
<td>0.9</td>
<td></td>
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</tr>
<tr>
<td>AMR2</td>
<td>1%</td>
<td>3.50</td>
<td>6.50</td>
<td>0.3427</td>
<td>0.0203</td>
<td></td>
<td></td>
<td>0.1498</td>
<td>1</td>
<td>1</td>
<td>1</td>
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</tr>
<tr>
<td>AMR1-1</td>
<td>10%</td>
<td>3.54</td>
<td>7.08</td>
<td>0.0159</td>
<td>0.0008</td>
<td>0.0385</td>
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<tr>
<td>AMR1-2</td>
<td>10%</td>
<td>6.80</td>
<td>7.60</td>
<td>0.0222</td>
<td>0.0052</td>
<td>0.0048</td>
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<td></td>
<td>1</td>
<td>1</td>
<td>2</td>
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<tr>
<td>Sub-soil</td>
<td>0.10%</td>
<td>7.74</td>
<td>6.95</td>
<td>0.6000</td>
<td></td>
<td></td>
<td>0.0714</td>
<td></td>
<td>0.0606</td>
<td>0.9</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*une dose de 10% (pH 7.0) a été adoptée pour les essais de végétation

Underlined = LOQ after treatment