Life+ Environment Policy and Governance
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DIPARTIMENTO DI AGRARIA

CERMANU

SUMMER SCHOOL

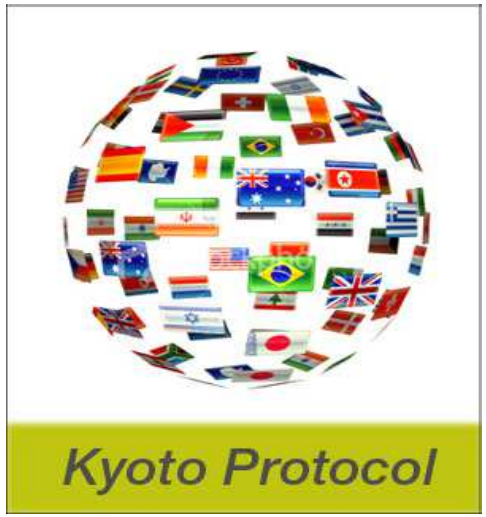
Organic matter and Biological Agriculture

3-6 July 2017

Innovative technologies for the soil organic carbon stabilization: the in situ biomimetic catalysis

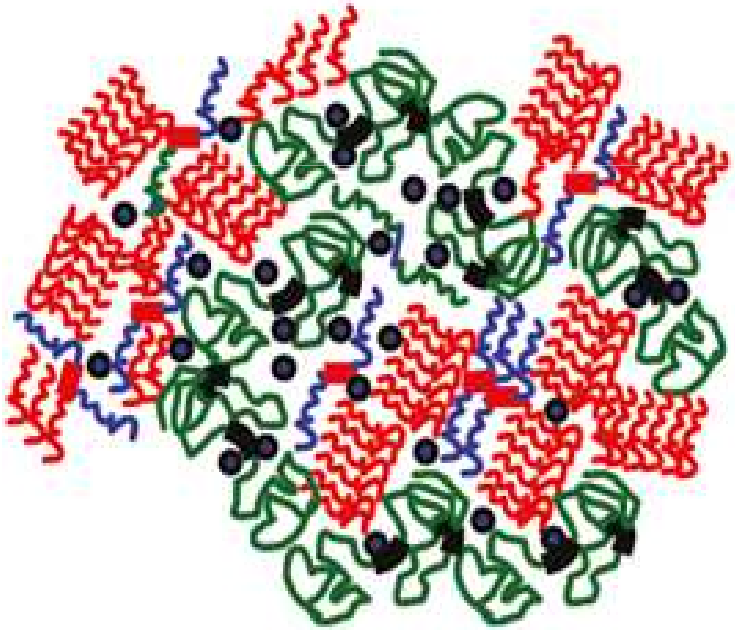
Dr. Assunta Nuzzo

Soil organic matter (SOM) is closely related to chemical, physical and biochemical soil properties



Carbon sequestration in terrestrial pools should be encouraged by adopting sustainable soil management practices that improve SOM incorporation and accumulation

THE HUMIFIED ORGANIC MATTER IN SOIL REPRESENTS THE LARGEST CARBON RESERVOIR IN TERRESTRIAL ECOSYSTEMS



Humic supramolecular structure

(Piccolo A. *Soil Science* **2001**, *166*, 810-833)
(Piccolo A. *Advances in Agronomy* **2002**, *75*, 57-134)

Catalyzed oxidative polymerization of aromatic humic molecules

Increase of the content of chemical energy

Enhancement of the metabolic threshold required by soil microorganisms to mineralize soil organic matter

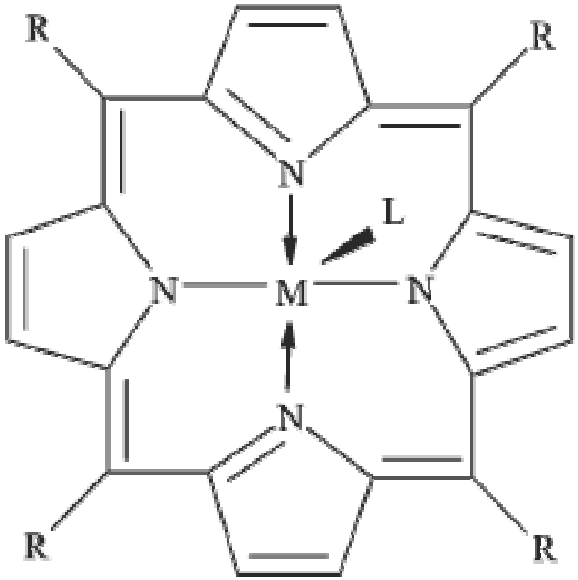
Decrease of soil organic matter mineralization

- **Soil carbon sequestration**
- **Reduction of CO_2 emissions from soil**

The oxidative polymerization of humic supramolecular associations

INNOVATIVE METHOD

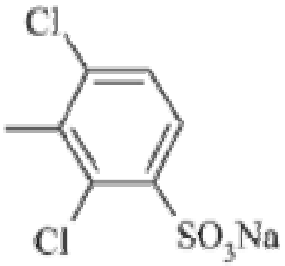
Biomimetic catalysis by using water-soluble **metal-porphyrins**



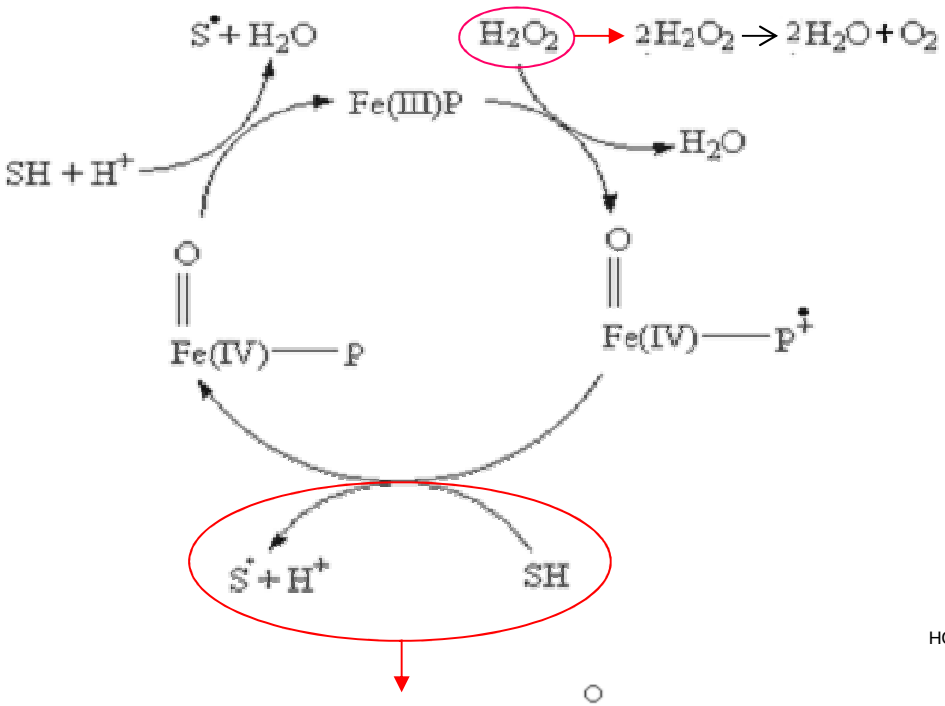
M = Fe, Mn

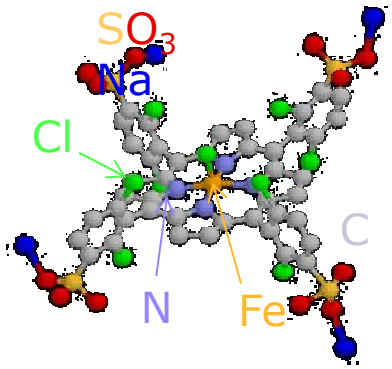
L = Cl

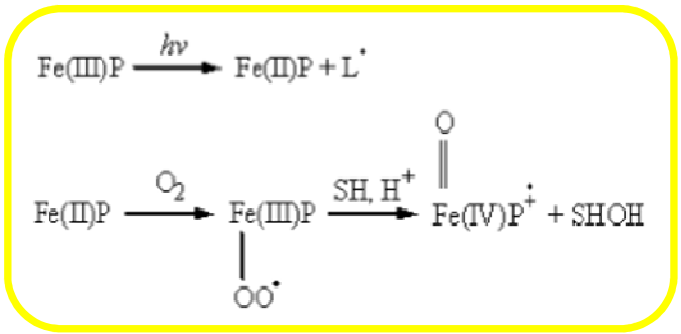
R =

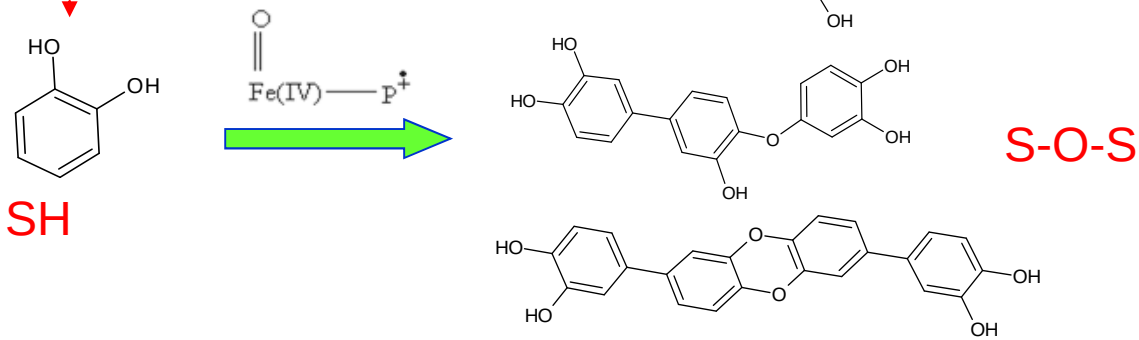


Metal-porphyrins









• Biomimetic catalysts such as iron- and manganese-porphyrins were shown to successfully catalyze oxidative coupling reactions of monomeric natural phenols such as catechol, caffeic and *p*-coumaric acid (Šmejkalová D., Piccolo A. *Environ. Sci. Technol.* **2006**, *40*, 1644-1649; Šmejkalová D., Piccolo A., Spiteller M. *Environ. Sci. Technol.* **2006**, *40*, 6955-6962; Šmejkalová D., Conte P., Piccolo A. *Biomacromolecules* **2007**, *8*, 737-743), as well as dissolved phenol-containing humic matter under a chemical oxidant (Piccolo A., Conte P., Tagliatesta P. *Biomacromolecules* **2005**, *6*, 351-358), or under photo-oxidation (Šmejkalová D., Piccolo A. *Biomacromolecules* **2005**, *6*, 2120-2125).

• Water-soluble iron-porphyrin was also employed to catalyze the photo-polymerization of humic molecules *in situ* in soil, with the aim to enhance the microbial stability of soil humus and, thus, reduce its mineralization and consequent CO_2 emission (Piccolo A., Spaccini R., Nebbioso A., Mazzei P. *Environ. Sci. Technol.* **2011**, *45*, 6697-6702).

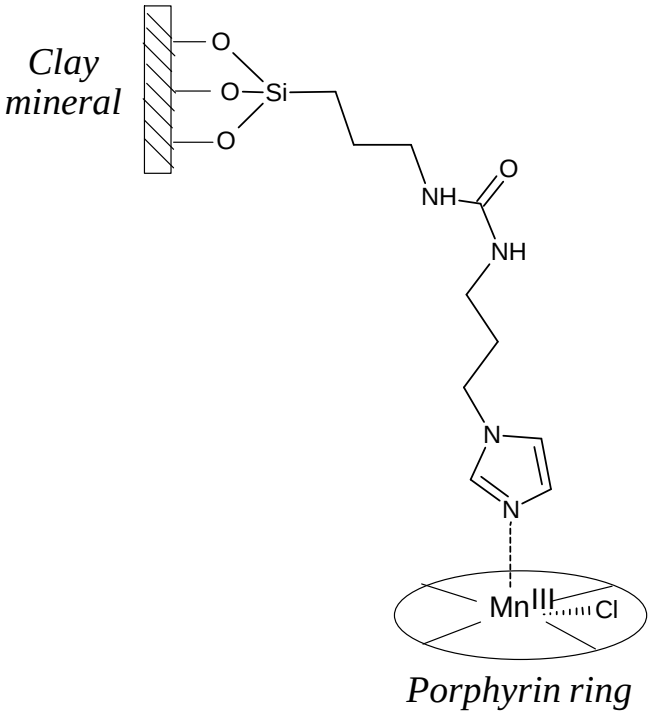
When water-soluble metal-porphyrins are used in soil systems their loss by leaching and their oxidative degradation may limit considerably their catalytic activity

STRATEGY

Immobilization of metal-porphyrins on adequate supports

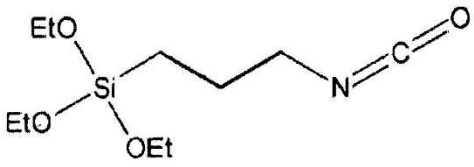
Heterogeneous biomimetic catalysts

Immobilization of a meso-tetra(2,6-dichloro-3-sulphonatophenyl)porphyrinate of manganese(III) chloride (MnPha) biomimetic catalyst on both kaolinite (K) and montmorillonite (M) clay minerals, following their functionalization with a molecular spacer to allow a coordinative interaction between the imidazole terminal of the spacer and the metal in the porphyrin ring



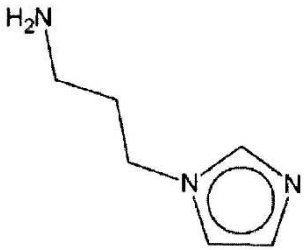
Nuzzo A., Piccolo A., *J. Mol. Catal. A: Chem.* **2013**, *371*, 8-14

SPACER SYNTHESIS

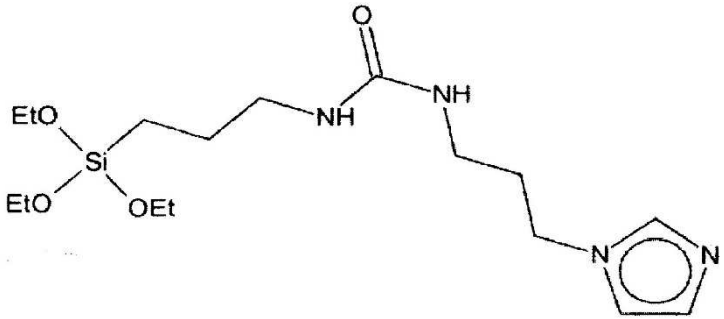


(3-isocyanatopropyl)triethoxysilane

+



N-(3-aminopropyl)imidazole

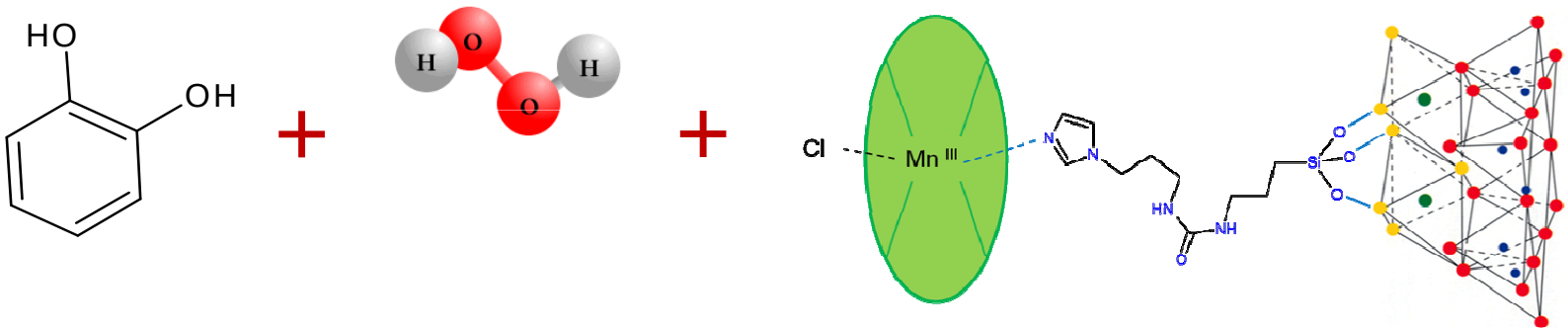


3-(1-imidazolyl)propylcarbamoyl-3
'-aminopropyl-triethoxysilane

Nuzzo A., Piccolo A., *J. Mol. Catal. A: Chem.* **2013**, *371*, 8-14

Catalyzed oxidative coupling of catechol

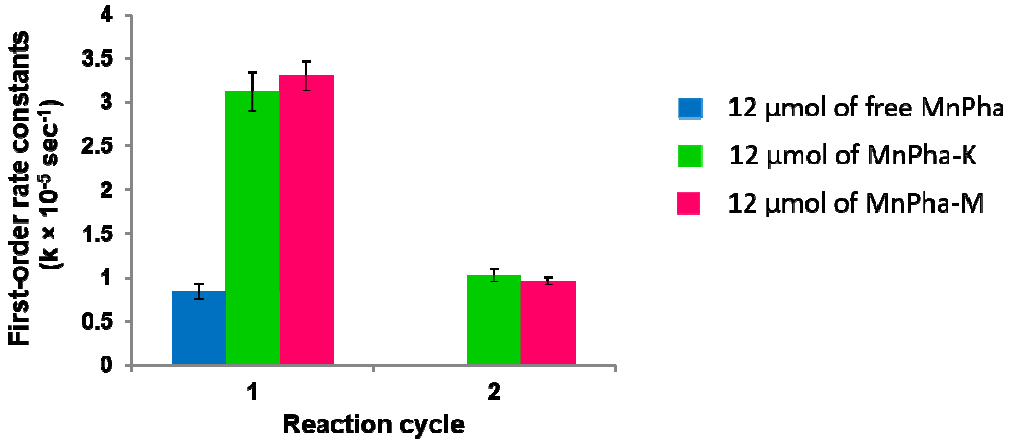
The activity of two heterogeneous catalysts was evaluated in the oxidative coupling reaction of catechol, a humic phenol, using H_2O_2 as oxygen donor

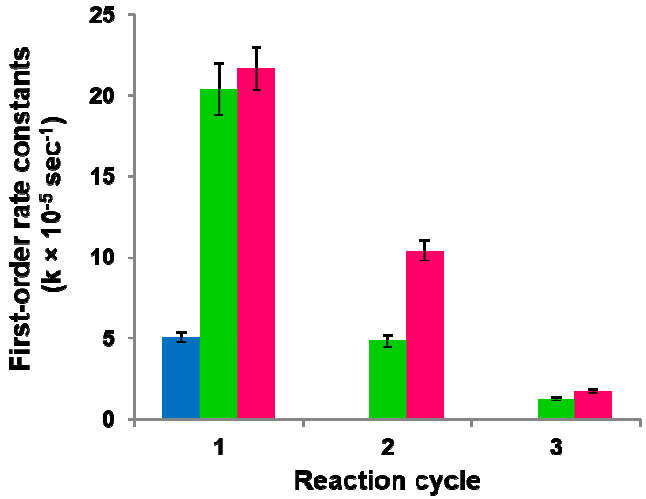


The progress of the reaction was followed by a HPLC system with a fluorescence spectrometer and a UV/vis detector

Nuzzo A., Piccolo A., *J. Mol. Catal. A: Chem.* **2013**, *371*, 8-14

First-order rate constants (5 h reaction course) calculated for catechol oxidation catalyzed by either 12 or 240 µmol of both the unbound MnPha catalyst and that immobilized on the spacer-functionalized K and M clay minerals, are reported for subsequent reaction cycles

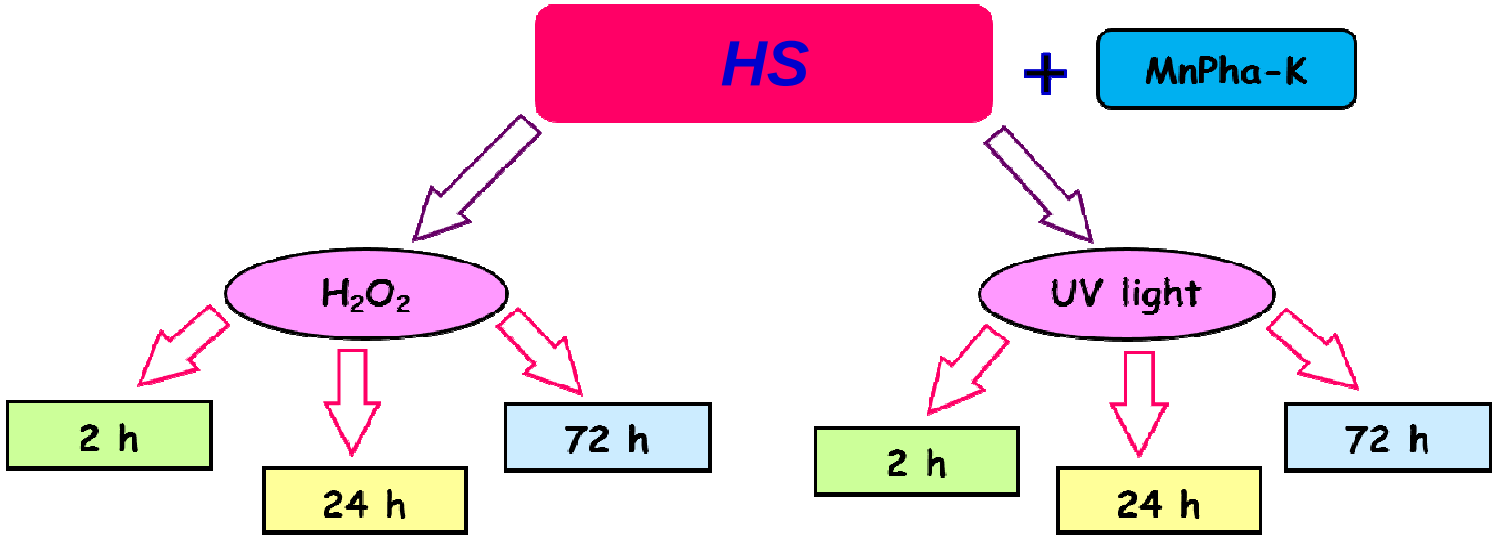




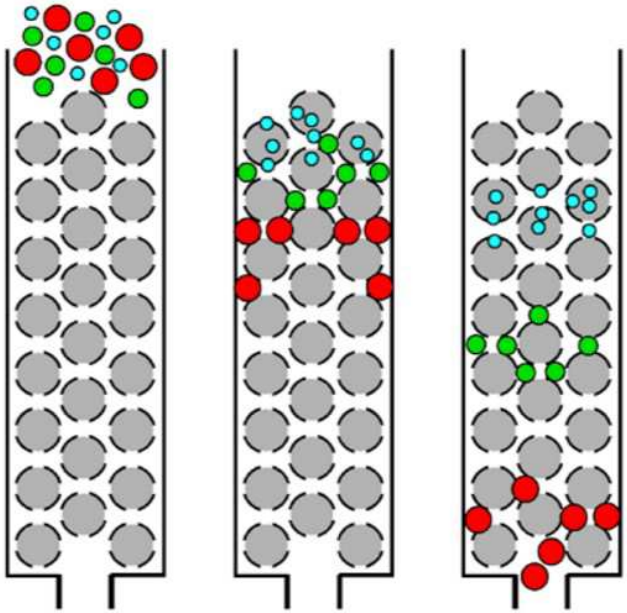
240 µmol of free MnPha
240 µmol of MnPha-K
240 µmol of MnPha-M

Nuzzo A., Piccolo A., *J. Mol. Catal. A: Chem.* **2013**, *371*, 8-14

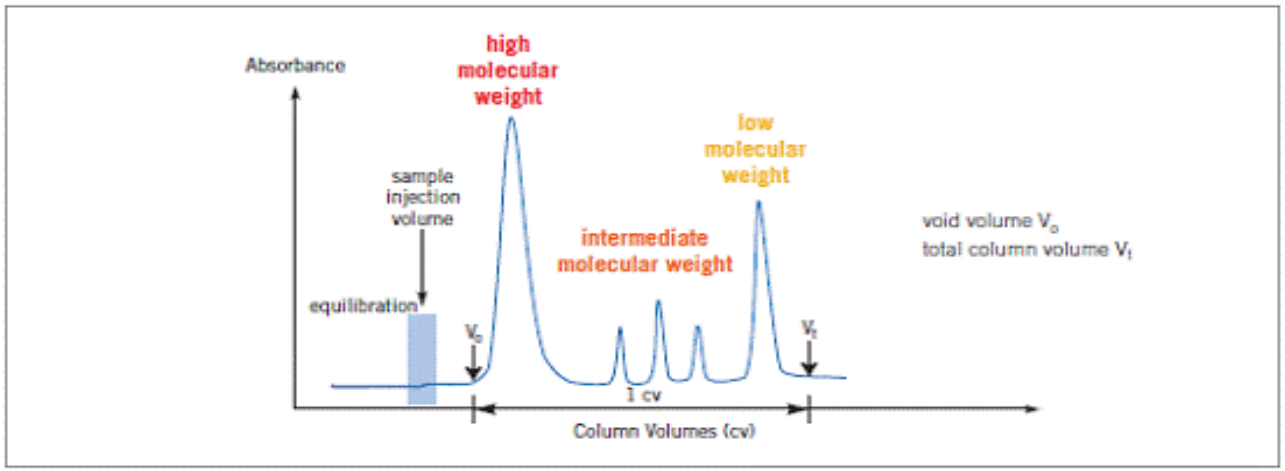
The MnPha-K was employed in the oxidative polymerization reaction of humic suprastructure (HS) with either chemical (H_2O_2) or UV-light oxidation



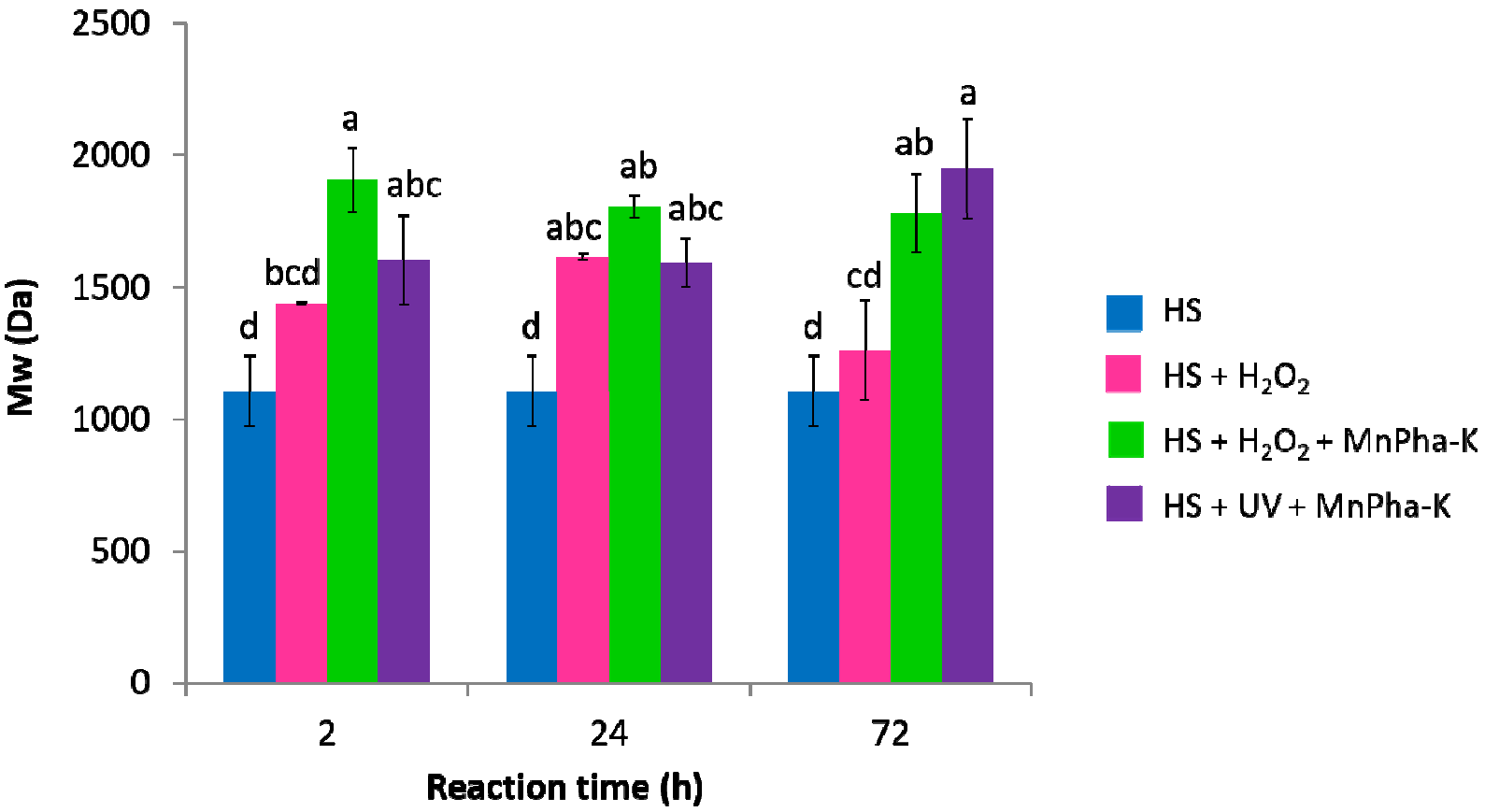
Nuzzo A., Piccolo A., *Biomacromolecules* **2013**, *14*, 1645-1652



High-performance size-exclusion chromatography (HPSEC)

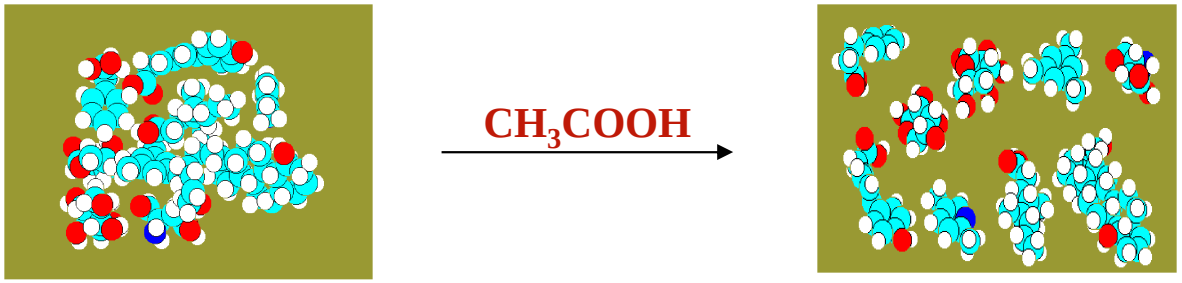


Mw values calculated from RI-detected size exclusion chromatograms for HS, before and after polymerization under heterogeneous catalysis by MnPha-K and oxidation by either H_2O_2 or UV-light irradiation

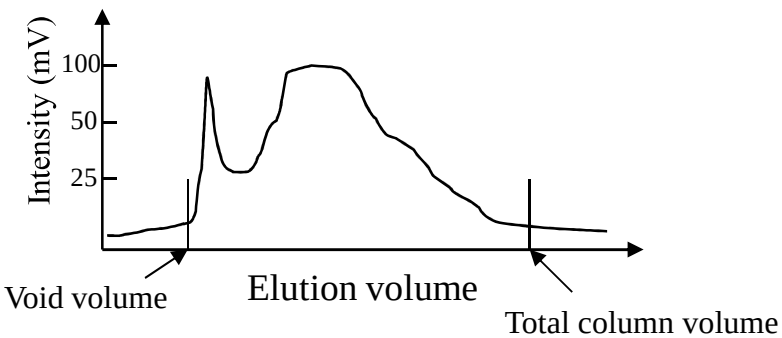


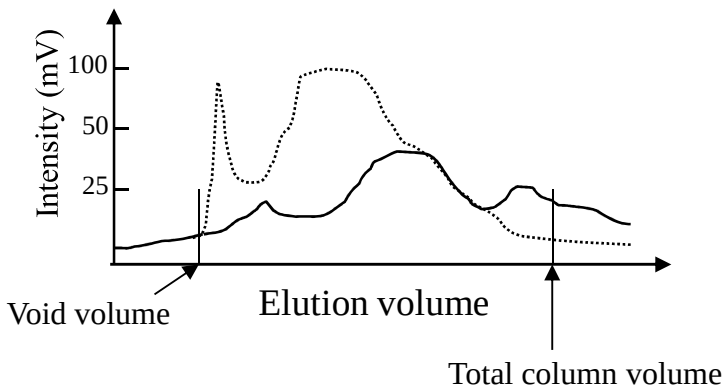
Nuzzo A., Piccolo A., *Biomacromolecules* **2013**, *14*, 1645-1652

The acetic acid treatment is reported to disrupt the loose humic associations held together by weak bonds, and the consequent conformational changes are reflected in HPSEC profiles



SIZE EXCLUSION CHROMATOGRAPHY



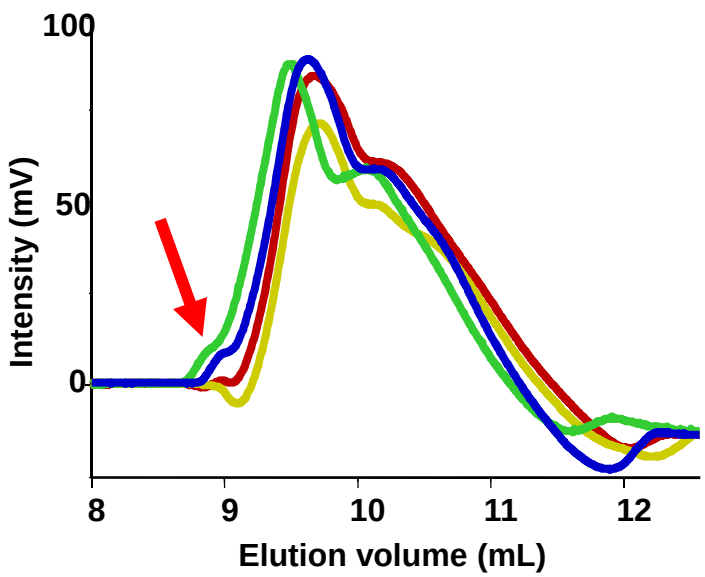


Conversely, it has been observed that the addition of acetic acid hardly modifies the original HPSEC profile of a humic solution after the humic conformation has been stabilized by new intermolecular covalent bonds induced by the oxidative polymerization catalyzed by metal-porphyrins

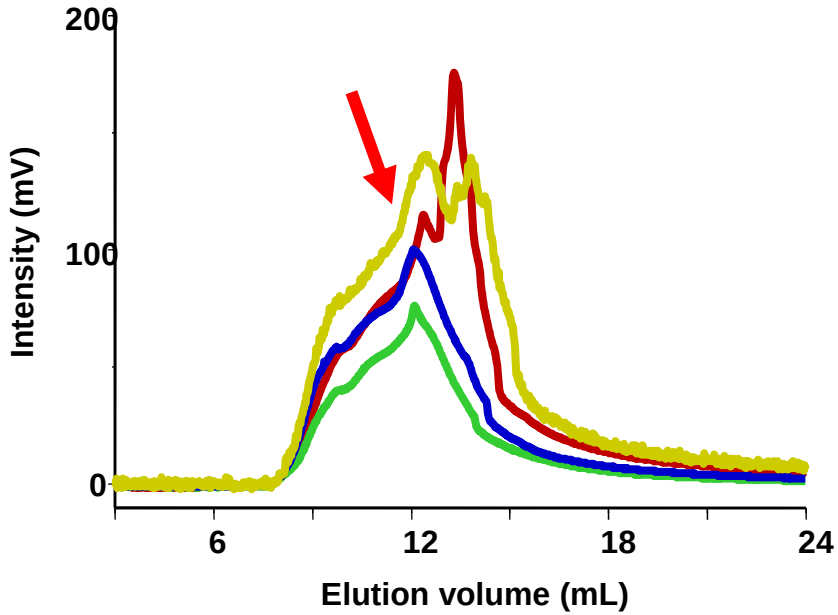
Conformational stabilization

- HS + CH_3COOH
- HS + H_2O_2 + CH_3COOH
- HS + H_2O_2 + MnPha-K + CH_3COOH
- HS + UV + MnPha-K + CH_3COOH

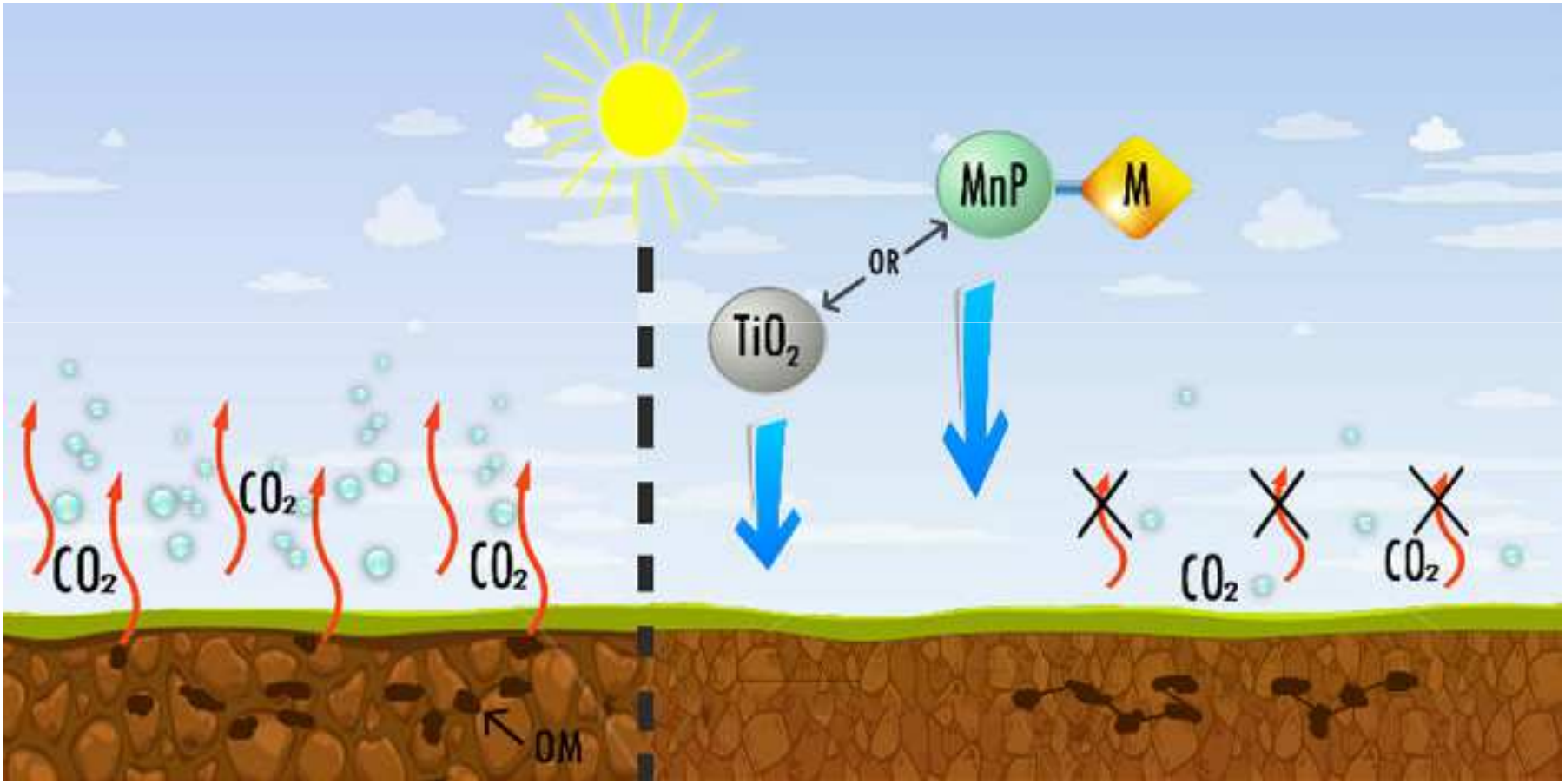
RI-HPSEC



UV-HPSEC

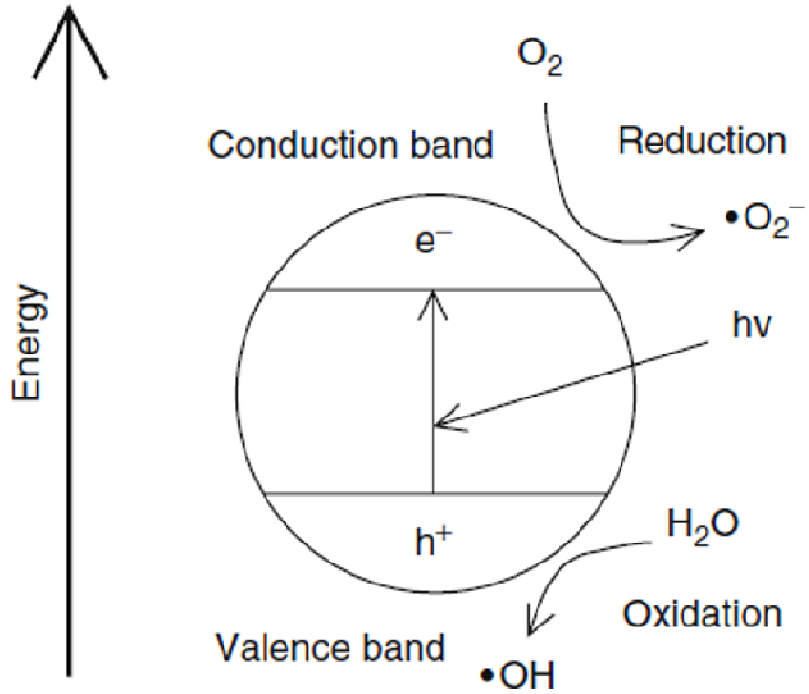


Nuzzo A., Piccolo A., *Biomacromolecules* **2013**, *14*, 1645-1652

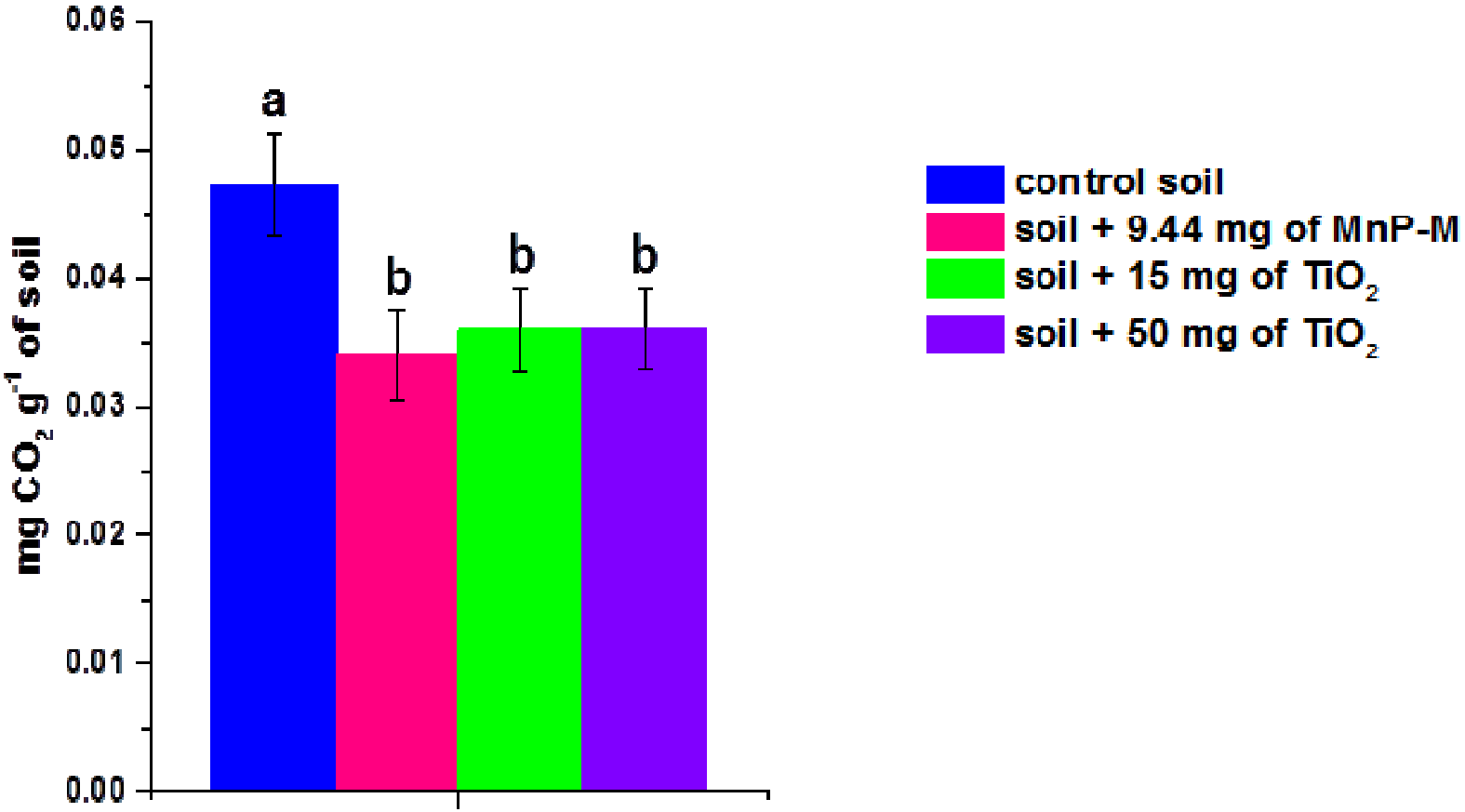

MnP
M
OR
TiO2
CO2
CO2
CO2
CO2
CO2
OM

We proved that the titanium dioxide (TiO_2) nanoparticles are capable to catalyze the photo-oxidative coupling of humic molecules in solutions of natural organic matter, as it does the manganese-porphyrin when immobilized on clay minerals (Nuzzo A., Madonna E., Mazzei P., Spaccini R., Piccolo A. *Biol. Fertil. Soils* **2016**, *52*, 585-593)

TiO_2 photo-catalysis

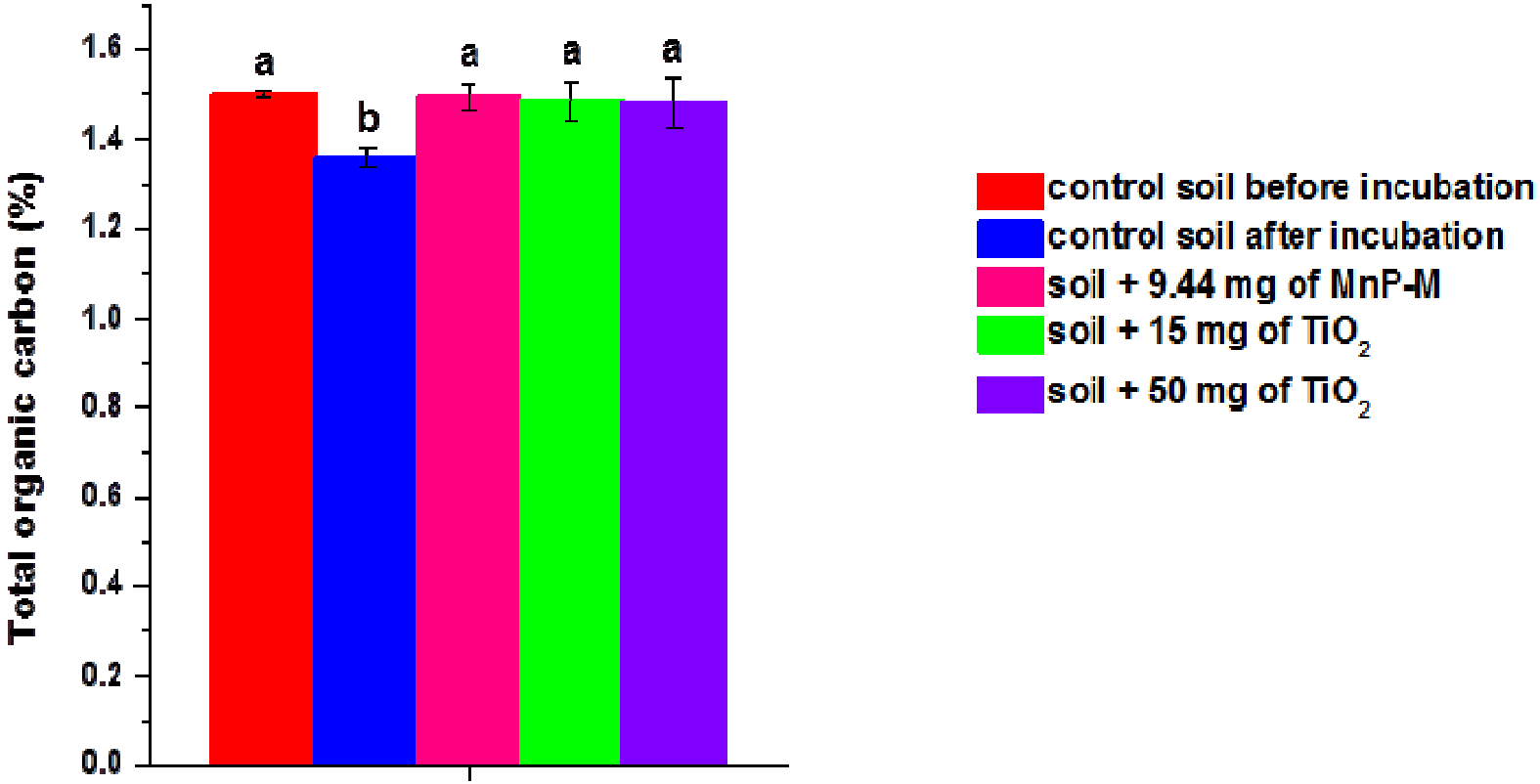


Soil respiration (mg CO_2 g^{-1} of soil) before and after catalyst-assisted *in situ* photo-polymerization treatment, following 27 days incubation:



Nuzzo A., Madonna E., Mazzei P., Spaccini R., Piccolo A., *Biol. Fertil. Soils* **2016**, *52*, 585-593

Percent of total organic carbon content in soil samples with and without *in situ* photo-polymerization catalyzed by either MnP-M or TiO_2, following 27 days incubation:



Nuzzo A., Madonna E., Mazzei P., Spaccini R., Piccolo A., *Biol. Fertil. Soils* **2016**, *52*, 585-593

- Manganese-porphyrin catalyst immobilized on spacer-functionalized kaolinite or montmorillonite clay minerals, significantly increased the rate of oxidative coupling of catechol, a humic phenolic precursor, as compared to the corresponding free catalyst (Nuzzo A., Piccolo A., *J. Mol. Catal. A: Chem.* **2013***, 371*, 8-14)

- The manganese-porphyrin immobilized on spacer-functionalized kaolinite also successfully promoted both oxidative and photo-oxidative polymerization of dissolved phenol-containing humic matter (Nuzzo A., Piccolo A., *Biomacromolecules* **2013***, 14*, 1645-1652)

- The photo-polymerization reaction of humic molecules under biomimetic catalysis was also shown to occur within the soil complex matrix. In fact, a manganese-porphyrin immobilized on spacer-functionalized montmorillonite were found to operate directly in soil by photo-oxidation under solar radiation, thus resulting in a significant reduction of soil respiration and CO_2 emissions to the atmosphere (Nuzzo A., Madonna E., Mazzei P., Spaccini R., Piccolo A., *Biol. Fertil. Soils* **2016***, 52*, 585-593)

Soil treatments with heterogeneous biomimetic catalysts, synthesized by immobilizing metal-porphyrins on the surface of spacer-functionalized clay minerals, may represent an innovative and useful technology for carbon sequestration in soil and for reducing greenhouse gases emissions from soil to the atmosphere

Thank you for your attention