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Effects of organo-mineral glass-matrix based fertilizers on citrus Fe chlorosis

Biagio Torrisi[a,*], Alessandra Trinchera[b], Elvira Rea[b], Maria Allegra[a], Giancarlo Roccuzzo[a], Francesco Intrigliolo[a]

[a] Consiglio per la Ricerca e la sperimentazione in Agricoltura – Centro di ricerca per l'Agrumicoltura e le Colture Mediterranee (CRA-ACM), C.so Savoia 190, 95024 Acireale, Italy
[b] Consiglio per la Ricerca e la sperimentazione in Agricoltura – Centro di ricerca per lo studio delle Relazioni tra Pianta e Suolo (CRA-RPS), Via della Navicella 2-4, 00184 Roma, Italy

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ABSTRACT

Several citrus orchards develop symptoms of Fe deficiency when cultivated in calcareous and alkaline soils. In a field trial a new type of fertilizer, the glass-matrix based fertilizer (GMF, a by-product from ceramic industries) was applied. GMF is able to release nutrients, particularly Fe, on the basis of plant-demand, being nutrients not soluble in water, but only in acidic or metal complexing solutions. In our experiment, the effectiveness of GMF was tested on "Tarocco" orange trees of twenty years, severely suffering from Fe chlorosis, also by mixing GMF with meat meal (MM) or digested vine vinasse (DVV), thus comparing these treatments to the conventional Fe-chelate fertilization and the Fe-unfertilized control.

The GMF + DVV mixture showed to be able to supply adequately micronutrients (particularly Fe) on long term, reducing the chlorosis symptoms, increasing the leaf SPAD index, Fe concentration and decreasing Fe index. No significant effect on yield and fruit quality was noticed. Our results indicated that these innovative formulates, and in particular glass-matrix based fertilizer mixed with digested vine vinasse, could be used as an "environmental friendly" fertilizer, allowing not only to reduce the use of chemicals (such as Fe-chelate), but also to re-use industrial wastes and organic residues which gave an "adding value" to these novel organo-mineral formulates.

1. Introduction

Fe chlorosis is the most complex phenomenon in citrus orchard and one of major abiotic stresses affecting fruit tree crops in the Mediterranean area (Abadía et al., 2011; Pestana et al., 2003). One of the most common symptoms is the leaf blade yellowing, starting from apical leaves, which may progress and turn into necrosis (Tagliavini and Rombolà, 2001). It exhibits a temporal and spatial variability, requiring an efficient diagnosis system. Fe chlorosis is mainly caused by low Fe availability in soil, due to the presence of high amount of active lime and high soil pH (Lindsay and Schwab, 1982).

In general, tolerant genotypes of citrus rootstocks display an enhanced ability to reduce Fe(III) at root level (by the FCR enzyme), releasing protons into the rhizosphere under low external Fe availability (Bienfait, 1988; Mantey et al., 1994; Pestana et al., 2011), reducing and/or chelating substances such as phenols and flavins (Welkie and Miller, 1993; Susìn et al., 1994). Strategy I also includes morphological changes, such as the development of root hairs and transfer cells and increased rates of protons excretion (Lòpez-Millan et al., 2001).

Low Fe availability induces morphological changes in root epidermal cells that are similar to those induced by P deficiency. When Fe is limiting, root-hair formation and elongation increases. The extra root hairs that result from limited Fe availability are often located in positions that are occupied by non-hair cells under normal conditions (Lòpez-Bucio et al., 2003; Römheld and Marschener, 1981).

The prevention and cure of Fe chlorosis in fruit trees have been traditionally approached through the use of synthetic Fe chelates (Lucena, 2003). Soil application of Fe chelates aims to enhancing Fe availability for the following uptake at root level and represents an efficient prevention tool, due to the mechanism by which it is absorbed by the roots, transported and utilized by the leaves.

It should be remarked that Fe chelates generally applied to soil are water-soluble and thus easily leached out from the rhizosphere if excessive irrigation regimes are applied, or during the rainy season (Rombolà and Tagliavini, 2006). Moreover, a likely underestimated problem related to synthetic chelates is their potential to bind also undesired heavy metals (Grčman et al., 2001). In addition, the cost for treating or preventing Fe chlorosis in citrus orchards with the use of synthetic Fe chelates is very high, as to be

* Corresponding author. Tel.: +39 095 7653132; fax: +39 095 7653113.
E-mail address: biagiofrancesco.torrisi@entecra.it (B. Torrisi).

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Table 1
Main physical and chemical parameters of 0–30 cm soil (mean values).

Parameter	Value
Clay (g kg^{-1})	240
Silt (g kg^{-1})	180
Sand (g kg^{-1})	580
pH	8.7
Available Fe (g kg^{-1})	5.2
EC1:2 (dS m^{-1})	0.26
Active lime (g kg^{-1})	165
Total $CaCO_3$ (g kg^{-1})	530
Organic matter (g kg^{-1})	20

Table 2
Elemental composition (g kg^{-1}) of fertilizers utilized in different treatments (a), and amount of nutrients (g tree^{-1}) distributed yearly during the trial (b).

	N	P as P_2O_5	K as K_2O	Fe
(a) Treatment				
GMF	–	295	198	83
GMF + DVV	8	238	161	66
GMF + MM	14	265	158	88
Fe chelate	30	–	150	60
(b) All	370	200	300	15[a]

[a] In all GMF treatments, the three years' Fe amount (45 g) was distributed in the first year; no Fe addition in the control.

applicable only to high value crops, corresponding to more than 400€ ha^{-1} (Rombolà and Tagliavini, 2006).

Glass-matrix based fertilizer (GMF), obtained by altering the crystalline structure of a mineral natural substance through a physical process by mixing different salts and oxides, represents a new typology of fertilizer, characterized by the specific attitude to release nutrients on the basis of plant-demand, being nutrients not soluble in water, but only in acidic or in metal complexing solutions (~99%), similar to those exuded by plant roots (Pinton et al., 2007; Trinchera et al., 2009).

The GMF ability to release large amounts of macro and microelements, in particular Fe, when applied alone or in combination with small amounts of organic amendments, was already tested in laboratory under different extractive conditions (0.2% and 2% citric acid; 0.1% and 1% HCl) (Trinchera et al., 2009, 2011), confirming its attitude to solubilize nutrients in presence of complexing acidic solutions. On the basis of such previous laboratory results, in this field trial these fertilizers were tested in field as a suitable alternative to synthetic Fe chelates to cure Fe chlorosis.

The aim of our work was to evaluate if glass-matrix based fertilizer, alone or in combination with two alternative organic materials, could act on the prevention and treatment of nutrient deficiency and, in particular, of Fe chlorosis in field conditions, in comparison with the use of a common synthetic Fe-chelate fertilizer.

2. Materials and methods

2.1. Orchard description

The research was realized in a farm located in the Eastern Sicily (Italy), where twenty years old "Tarocco" orange trees [*Citrus sinensis* (L.) Osbeck] grafted on sour orange rootstock [*C. aurantium* (L.)] were cultivated with a planting distance of 6 m × 4 m (416 trees ha^{-1}). The area is characterized by high summer and low winter temperatures. The rainfalls are concentrated in the autumn–winter season. During the experimental period total rainfall had typical values of this Mediterranean region. The irrigation was carried out with two micro-sprinklers per plant with an average annual water supply of 3360 m^3 ha^{-1}. Soil of citrus orchard was a sandy-loamy soil, with a low content of organic matter, high contents of active lime and total calcium carbonate, low content of available Fe (Suppl. Ord. G.U. No. 248, 21.10.1999, Method IX.3). Main chemical–physical soil parameters are reported in Table 1 (soil sampled at 0–30 cm of depth, layer most explored by citrus roots).

Before treatments (early spring season, 2008), plant leaves showed typical symptoms of Fe deficiency by green discoloring, in particular the intervenial leaf yellowing, starting from apical leaves. Trees canopy showed symptoms of Fe chlorosis throughout the year, but they were more evident in spring, when shoot growth is faster and the bicarbonate concentration in the soil solution buffers the soil pH in the rhizosphere and root apoplast (Rombolà and Tagliavini, 2006; Torrisi and Intrigliolo, 2009). Results reported in this paper are related to three years of field trial (2008–2010).

2.2. Experimental design

The trial was realised by adopting a system with two randomized blocks; within each block 3 plants per treatment were identified, for a total of 6 index plants per treatment. To evaluate the effect of three GMF treatments, in comparison with a standard treatment with a Fe-chelate fertilizer and a Fe-untreated control, five treatments were applied: GMF (100% glass mineral fertilizer, powdered at 0.1 mm), GMF + DVV (80% glass mineral fertilizer + 20% digested vine vinasse, powdered at 0.1 mm), GMF + MM (80% glass mineral fertilizer + 20% meat-meal, powdered at 0.1 mm), NK fertilizer containing Fe-EDDHA [ethhylenediamine-di(o-hydroxyphenylacetic) acid], and the control Test (treatment without Fe supply).

GMF composition was determined for P_2O_5 (295.1 g kg^{-1}), K_2O (198.2 g kg^{-1}), Fe_2O_3 (118.5 g kg^{-1}), CaO (100.2 g kg^{-1}), MgO (56.8 g kg^{-1}), MnO (45.7 g kg^{-1}), ZnO (45.3 g kg^{-1}), B_2O_3 (25.6 g kg^{-1}), CuO (9.1 g kg^{-1}), SiO_2 (73.8 g kg^{-1}) and Al_2O_3 (28.8 g kg^{-1}).

Besides, main parameters of DVV and MM were also determined: pH (8.4 and 6.4), C_{org} (155 g kg^{-1} and 415 g kg^{-1}), N_{tot} (41 g kg^{-1} and 81 g kg^{-1}), P_2O_5 (9 g kg^{-1} and 125 g kg^{-1}), K_2O (16 g kg^{-1} and 10 g kg^{-1}), Fe_2O_3 (no detectable content and 1.5 g kg^{-1}), respectively. No detectable amount of heavy metals were recorded in GMF, DVV and MM (Table 2). To prepare the fertilizing mixtures, GMF and organic matrices (DVV and MM) were dried in a oven at 40 °C for 18 h, weighted and then mixed at the ratio GMF/organic matrix = 80/20 (w/w).

All the trees received the same NPK amount (370 g N, 200 g P_2O_5 and 300 g K_2O per tree), applied each year on the 2nd decade of March. In the control treatment and in all other treatments, to complete the annual requirements of N, P and K, single nutrient fertilizers were added as urea, simple superphosphate and sulphate of potash, respectively. The total Fe three years' request (45 g per tree) was applied in one rate at the beginning of the first year (2nd decade of March) for all the GMF treatments, whereas the Fe chelate one was fractionated in yearly applications (15 g per tree per year), added on the 2nd decade of March. Treatments with the addition of DVV or MM alone were not performed because of the negligible Fe supply respect to that added with GMF fertilizer (see Table 2).

The fertilizers were applied every year under canopy projection on the soil, whereas glass-matrix based fertilizers, with or without addition of organic materials, were applied as powder the first year, to add the overall Fe amount, inside two trenches dug at soil depth of 20 cm at a distance of about 150 cm from the trunk under the canopy projection and without any soil tillage. In particular, the depth at 20 cm for trenches was chosen in order to draw up the GMF fertilizers with fine roots (particularly active in