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EDTA application on agricultural soils affects microelement uptake of plants

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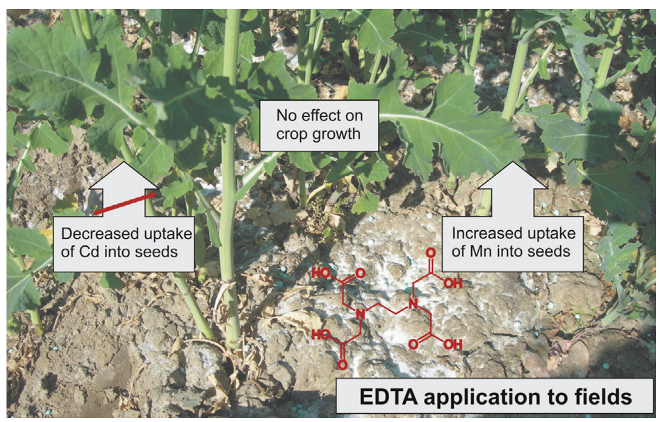
HIGHLIGHTS

- EDTA was still detectable in deeper soil layers 18 months after soil application indicating to its high persistence.
- High soil applied EDTA rates (up to 1050 kg ha^{-1} EDTA) did not affect plant growth under field conditions.
- High soil applied EDTA rates (550 - 1050 kg ha^{-1} EDTA) changed the macro- and micro-elemental composition of crop plants.
- Soil-applied EDTA decreased the Cd content in seeds of oilseed rape and grain of winter wheat.

GRAPHICAL ABSTRACT



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ABSTRACT

Chelates such as ethylenediaminetetraacetic acid (EDTA) enter soils via various sources but their effect on agricultural crops is mostly unknown. Sources of EDTA include industry, households, sewage water and agricultural practices. In a field experiment EDTA was applied in its free form at different rates (0, 150, 550, 1050 kg ha^{-1}) to study its translocation in the soil profile and to evaluate its effect on yield and mineral composition of the cultivated crop, both in the year of application (oilseed rape) and in the following year (winter wheat). The results indicate that EDTA was translocated from the soil surface to deeper soil layers in the time-frame of the experiment. EDTA was still detectable in the rooting zone 19 months after application, indicating its persistence in the soil. Only the highest EDTA rate (1050 kg ha^{-1}) reduced vegetative growth of oilseed rape until stem elongation, but seed yield was not affected by EDTA application. EDTA application changed the mineral composition of plants. Higher phosphorus (P), sulphur (S), iron (Fe) and manganese (Mn) and lower cadmium (Cd) concentrations were determined in the seeds of oilseed rape. No yield effects of residual EDTA were observed for the following crop, winter wheat, but the Cd content in seeds was still lower in plots where EDTA had been applied in the previous year. Data show that EDTA application affects the mineral uptake of cultivated crops under field conditions.

1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is a commonly used agent forming strong complexes with divalent and trivalent metals and

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alkaline earth metals such as the macronutrients calcium (Ca) and magnesium (Mg), and trace elements such as iron (Fe), copper (Cu), zinc (Zn), nickel (Ni) lead (Pb), and cadmium (Cd) (Eklund et al., 2002). The stability of the complexes is determined by the complex dissociation constant (log *K* value) which is characteristic for each element. For the investigated elements of the present study very stable EDTA complexes exist with Fe^{3+} (log $K = 25.1$), Cu^{2+} (log $K = 18.8$), and Ni^{2+} (log $K = 18.6$) followed by Pb^{2+} (log $K = 18.0$), Cd^{2+} and Zn^{2+} (log $K = 16.5$) and Mn^{2+} with the lowest value (log $K = 14.0$) (Mitchell, 1997). The capability to sequester metal ions is the reason why EDTA, diethylenetriaminepentaacetic acid (DTPA) or nitrilotriacetic acid (NTA) are used in high quantities in paper- and pulp-making industries, electroplating, photographic industries, textile finishing, and leather manufacturing (Oviedo and Rodriguez, 2003). In Germany, considerable quantities of EDTA have been used since phosphate limiting regulations came into force in 1980 (Anon, 2014; Evangelou, 2007). As a consequence, triphosphates were substituted in cleaning agents with complexing substances to increase their cleaning activity by reducing water hardness. In addition, EDTA was used as a preserving agent or stabilizer in cosmetics and in foodstuffs as food additive to promote color retention in dried and canned foods (Anon, 2014; Oviedo and Rodriguez, 2003). In agriculture, EDTA is applied in low quantities via micronutrient fertilizers such as Fe(III)-, Cu- and Zn-EDTA. In Germany, the annual consumption accounts for 3700 tons of EDTA and 1600 tons of DTPA (average from 2005 to 2009) and environmental loads originate to about 60% from industry and 40% from municipal sewage plants (Anon, 2012).

EDTA shows very low biodegradability in natural environments (Allard et al., 1996; Kari and Giger, 1996) causing a high environmental persistence. Only a few bacterial isolates have been identified that are able to degrade EDTA on a laboratory scale (Chistyakova et al., 2003; Dedyukhina et al., 2008; Nörtemann, 1999, 2005; Weilenmann et al., 2004). Environmental contaminations mainly occur via waste water effluents. As early as 1983, EDTA was detected as a new water contaminant in monitoring programs (Dietz, 1985) and is currently a prevalent anthropogenic compound in European water specimens (Oviedo and Rodriguez, 2003). Photolysis is the only effective elimination process for Fe-EDTA in surface waters (Kari, 1994). Hardly any degradation of EDTA takes place in sewage treatment plants and EDTA is still present in the effluents at concentrations of >5000 μg L^{-1} (18 μM) (Eklund et al., 2002; Kari and Giger, 1996). EDTA was detected in groundwater, lake and river water with mean concentrations of 2–100 μg L^{-1} (Bergers and De Groot, 1994; Kari and Giger, 1995; Oviedo and Rodriguez, 2003) and in drinking water with concentrations of up to 15 μg L^{-1} (~50 nM) (Brauch and Schullerer, 1987). In some rivers extremely high EDTA concentrations were determined, for example 900 μg L^{-1} in a river in Jordan and 1120 μg L^{-1} in the river Glatt in England (Kari and Giger, 1995; Oviedo and Rodriguez, 2003). High concentrations of EDTA, DTPA and NTA were also found in Canadian sewage treatment plants and pulp mill effluents, with maximum values of 1282, 2880, and 6090 μg L^{-1}, respectively (Lee et al., 1996).

Because of its low biodegradability alternative compounds were studied (Evangelou, 2007) and EDTA was partly replaced by equally effective but readily biodegradable chelating agents such as *S,S′*-ethylenediaminedisuccinic acid (EDDS) and iminodisuccinic acid (IDS) in cosmetics and other consumer products (Katata et al., 2006). Meanwhile, the industrial release of EDTA is regulated by law in many countries since the nineties. Consequently, a 44% reduction of EDTA inputs was observed in recent years in the Rhine watershed (Germany) (Anon, 2012).

EDTA itself is rated as being relatively harmless for humans and mammals at environmental concentrations. A concentration of 2200 μg L^{-1} was determined by the European Union Risk Assessment as the no-effect concentration for EDTA in water (European Chemicals Bureau, 2004). Higher concentrations can be toxic for soil and water organisms, as well as plants. Toxic environmental effects were attributed to the ability of EDTA to increase the bioavailability and phytotoxicity of heavy metals in sewage sludge or contaminated soils by changing the permeability of cell membranes (Bergers and De Groot, 1994; Grčman et al., 2001; Hugenschmidt et al., 1993; Sillanpää et al., 1995; Vassil et al., 1998). Moreover, a change in permeability takes place and cells become more vulnerable to many substances, due to the loss of Ca^{2+} and Mg^{2+} from plasma membranes and lipopolysaccharides (Hancock, 1984; Bergan et al., 2001). The toxicity of EDTA in its free form is much higher than when chelated with micronutrients (Hugenschmidt et al., 1993).

In plant science EDTA was paid special attention because of its ability to increase the metal uptake of plants which made EDTA an interesting agent for improving phytoextraction (Blaylock et al., 1997; Epelde et al., 2008; Panwar et al., 2011; Piechalak et al., 2003; Vassil et al., 1998). Vassil et al. (1998) reported a 75-fold higher Pb uptake by Indian mustard when EDTA was present in hydroponic solution at a minimum concentration of 250 μM. Mobilized heavy metals and EDTA complexes are either translocated into the groundwater, or cause a higher uptake by crops. By this means free EDTA interferes with one of the most important soil functions, to act as a filter for xenobiotics and heavy metals.

To the best of our knowledge no studies are available where EDTA was applied as free acid in graded rates on agricultural soils. The presented experiment was conducted to show direct effects of EDTA application on growth and on macro- and microelement uptake of agricultural crops under field conditions.

2. Material and methods

2.1. Field experiment

From 2008 to 2010 a field trial was conducted at the experimental station of the Julius Kuehn-Institut (JKI) in Braunschweig (E 10°27′, N 52°18′). The climate is temperate and characterized by frequent changes in temperature, humidity, and winds. The soil type is a Cambisol with a loamy sand soil texture (6.5% clay, 47% sand) with a water retention capacity of 33 vol% and a high leaching rate (for further soil characteristics see supplementary materials Table A.1).

Four different EDTA application rates were investigated: 0, 150, 550 and 1050 kg ha^{-1} EDTA. EDTA was applied to the soil in its acidic form as a powder (GKCH GmbH, Mannheim, Germany). The solubility of this product in water was low, ≤0.5 g L^{-1} at 25 °C, and it took >3 months until no more traces of the applied EDTA powder were detected at the soil surface. The acidic form of EDTA was chosen to prevent contamination of the soil by Na ions on the one hand (if a Na-EDTA product would have been added) or the input of further nutrients such as K or Fe which were investigated in the trial. Only the effect of EDTA on nutrient and element mobility was in the focus of the present study.

The field trial was conducted in a completely randomized design with 4 replicates and a plot size of 80 m^2. EDTA rates were split into two doses. A first dose of 50 kg ha^{-1} was applied to all plots except the control at sowing of oilseed rape (*Brassica napus*, var. *Ladoga*) in September 2008. This first application was performed to follow up any phytotoxicological effects of the product as hardly any information is available on the impact of EDTA applied in this form directly to agricultural crops. As the plants displayed no symptoms of toxicity neither on leaves nor roots, the main dose (100, 500, 1000 kg ha^{-1}) was applied in April 2009, after application of N and S in the form of an ammonium nitrate fertilizer containing 13% S (ENTEC® 26) delivering 156 kg ha^{-1} N and 78 kg ha^{-1} S to the soil. Potassium (K) was applied at an equal rate of 160 kg ha^{-1} as Korn Kali® and P at a dose of 40 kg ha^{-1} as triplesuperphosphate. EDTA doses were calculated at a rate to trigger plant response based on typical though high EDTA concentrations found in industrial sewage water of up to 20 mg L^{-1} EDTA (reported by the Hessian Agency for Nature Conservation, Environment and Geology), in combination with high irrigation volumes of 1000 to 5000 L m^{-2} per year that are used on irrigation fields in Germany