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ORIGINAL ARTICLE

# The combined treatment of Mn and Al alleviates the toxicity of Al or Mn stress alone in barley

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**Abstract** Aluminum (Al) and manganese (Mn) toxicity commonly coexists in acid soil, so the crop cultivars suitable for planting in acid soil should show high tolerance to both elements simultaneously. However, it is still not clear if the toxicity of Mn and Al on plant growth is antagonistic or synergistic, and the plants with Al tolerance are also tolerant to Mn toxicity. In this study, three barley genotypes (one Tibetan wild and two cultivated), differing in Al tolerance, were characterized for growth and physiological responses to Al or Mn toxicity as well as the combined treatment of the two toxic elements. Interestingly, it has been found that the combined treatment of both metals was less affected in comparison with Al or Mn treatment alone, in terms of plant growth, Al or Mn concentration in plant tissues, and photosynthetic parameters, indicating antagonistic interaction of Al and Mn for their effect on plant growth and physiological traits. The results also showed that there was a dramatic difference among barley genotypes in Mn toxicity tolerance and XZ16 showed much higher tolerance than other two genotypes. High Mn tolerance is mainly described to less Mn uptake and lower Mn concentration in plants, and Mn tolerance is independent of Al tolerance.

**Keywords** Acidic soil · Aluminum · Interaction · Manganese · Tolerance

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## Introduction

Almost half of potential arable land belongs to acidic soil, causing huge losses to crop production in the world (Von Uexküll and Mutert 1995). On the most acid soils, numerous detrimental factors coexist, including toxicity of aluminum (Al) and manganese (Mn), low availability phosphorus (P), calcium (Ca), magnesium (Mg), and some micronutrients (Kochian et al. 2004). However, Mn toxicity and P deficiency are the most dominant factors, resulting in reduced crop yield besides Al toxicity in acid soil.

With the decline of soil pH, active Al enhanced, which is phytotoxic and greatly accumulated, thus causing a severe toxicity to plant roots (Delhaize et al. 1993; Foy 1984, 1988). There is a distinct difference among plant species or genotypes within a species in Al toxicity tolerance. It is well documented that active Al can be inactivated by some organic acids secreted by plant roots (Ma et al. 2001), and variation in the organic acid exudation among species or genotypes may explain their difference in Al toxicity tolerance (Delhaize et al. 1993; 1995). The identification of the genes related to organic acid exudation provides the direct and strong evidences for the relationship between the exudation and Al toxicity tolerance (Delhaize et al. 2004). However, in some cases, the plants with more organic acid exudation do not show a good growth performance in acid soil, or organic acid exudation is closely associated with acid soil tolerance (Piñeros et al. 2005; Wenzl et al. 2001). Obviously there are other toxic factors which inhibit plant growth. In addition, some plant species, such as oat (*Avena sativa* L.) (Zheng et al. 1998) do not exudate organic acid when exposed to Al stress, implying that the organic acid exudation is not a sole mechanism for Al toxicity tolerance in plants.

Mn toxicity is also an important growth limiting factor, probably only after Al toxicity in acid soils (Foy 1984; Kochian et al. 2004). Like Al, active Mn increases rapidly with the decline of pH in soil, and its toxicity may occur when soil pH is below 5.5 (Foy 1984). Actually there have been a lot of reports on Mn toxicity in acid soils, which is attributed to the existence of high exchangeable Mn (Bortner 1935; Bromfield et al. 1983). While it was found that increasing soil pH to over 5.5 by liming could result in dramatic reduction of exchangeable Mn, thus alleviating or eliminating Mn toxicity (Martini et al. 1974). In comparison with Al toxicity tolerance, little research was done on the species or genotypic difference in Mn toxicity tolerance.

Intensive studies have been performed on Al and Mn toxicity tolerance in plants, but they are almost studied separately as an independent factor. As mentioned above, Al and Mn toxicity often occurs simultaneously in acid soils. Hence, the questions arise if the toxicity of Mn and Al on plant growth is antagonistic or synergistic, and the plants with Al tolerance are also tolerant to Mn toxicity, and vice versa. In our understanding, little study has been done up to date to answer the questions. Therefore, the current study was done to determine the responses of the genotypes with high Al tolerance to Mn toxicity, and possible interaction among Mn and Al in their influence on plant growth and physiological traits.

## Materials and methods

The experiments were conducted in a greenhouse at Zijingang campus, Zhejiang University, Hangzhou, China. Three barley genotypes were used in this study, including one Tibetan annual wild accessions (XZ-16, Al tolerance), and two cultivated varieties (Dayton, Al tolerance; ZU-9, Al sensitivity) (Dai et al. 2013). Healthy seeds were selected and surface sterilized by soaking for 20 min in 3% $H_2O_2$, rinsed in tap water, and then germinated on sterilized moist filter papers. At the second leaf stage (12-day old), uniform seedlings were selected and transplanted into 5 L pots filled with basic nutrient solution containing the following chemicals: 2 mmol/L $NaNO_3$, 0.63 mmol/L $MgSO_4$, 0.18 mmol/L $K_2SO_4$, 0.18 mmol/L $KH_2PO_4$, 0.36 mmol/L $CaCl_2$, 20.9 μmol/L Fe-citrate, 4.5 μmol/L $MnCl_2$, 0.38 μmol/L $ZnSO_4$, 0.16 μmol/L $CuSO_4$, 46.9 μmol/L $H_3BO_3$, and 0.062 μmol/L $H_2MoO_4$. The pH of the solution was adjusted to 5.8 ± 0.1 with NaOH or HCl as required. The plants were grown in the basic nutrition solution up to 3 leaf stage, and then the treatments were applied. The solution pH was adjusted to 4.8 ± 1 daily with HCl or NaOH, as required. There were two Mn levels (no addition as control and 0.2 mM) and two Al levels (0 and 0.1 mM). The experiment was arranged in a completely randomized block design with three replicates. The nutrition solution was aerated continuously with pumps and renewed every 5 days. At the 28 days after treatment, the plants were harvested and separated into shoots and roots for further measurements.

### Determination of growth parameters

For determination of plant growth parameters, including root and shoot length, and biomass, plants were sampled and separated into roots and shoots. Root and shoot length was measured using a scale, and biomass was determined after root and shoot samples were dried in an air circulation oven at 70 °C for 2 days.

### Determination of Mn and Al concentration and accumulation

Roots and shoots of all plant samples were dried in an oven for 3 h at 105 °C and then for another 24 h at 80 °C, and weighted. Approximately 0.1 g of the dried samples was digested in 5 ml $HNO_3$ at 120 °C for 2 h and then at 80 °C for another 2 h using a microwave digester (ANTOON PAAR, MICROWAVE 3000). Then the digested solution was diluted to 20 ml with Milli-Q water, and Al and Mn concentrations were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 8000DV, PerkinElmer, USA). Accumulation of Al and Mn (mg/plant) was calculated based on dry weight of plants and Al or Mn concentration.

### Gas exchange parameters

At the 28 day after treatment, gas exchange parameters including net photosynthetic rate ($P_n$), stomatal conductance ($g_s$) and transpiration rate ($T_r$) were measured on the 2nd topmost fully expanded leaf using an infra-red gas analyzer (LI-COR 6400, Lincoln, NE, USA). The measurement was done during 9.00–12.00 am on the same day.

### Statistical analysis

All data were presented as the mean values of each treatment. Two-way analysis of variance (ANOVA) was carried out between barley genotypes and different treatments, and followed by the LSD (least significant difference) test ($P < 0.05$), using DPS9.50 (Data Processing System).

## Results

### Plant growth

Plant seedlings showed different response to the treatments among genotypes. Sole Mn treatment (0.2 mM) led to the development of Mn toxicity symptoms, such as yellowing of shoot and browning of root in the seedlings of ZU9 and Dayton. Al toxicity symptom was only obvious in the seedlings of ZU9. Combined treatment of Al and Mn showed less toxicity on plant growth in comparison with Al or Mn treatment alone. On the other hand, no toxicity symptom was detected in the seedling of genotype XZ16 exposed to all treatments (Fig. 1).

There was a significant interaction of genotype and treatment in their influence on root and shoot length and weight (Table 1). High Mn or Al treatment resulted in the dramatic growth inhibition, with root growth being more inhibited than shoot growth, and ZU9 and ZX16 being relatively more inhibited than Dayton. It is interestingly found that the combination of Al and Mn treatment did not cause more inhibition of root and shoot growth in comparison with Al or Mn treatment alone. On contrast, the combined treatment could alleviate the growth inhibition caused by Al or Mn treatment, in particular for shoot length and weight.

### Al and Mn concentrations in plant tissues

The effect of the different treatments on aluminum and manganese concentrations in roots and shoots of three barley genotypes was presented in Table 2. Under control, there was a marked difference among three genotypes in tissue Al and Mn concentrations, with Dayton having the highest Mn concentration, and ZU9 having the highest Al concentration both in roots and shoots. As expected, high Mn or Al treatment resulted in the significant increase of Mn or Al concentration in plant tissues for all genotypes. However, the increased extent varied with genotype and plant tissue. Hence, XZ16 had relatively less increase in root Mn concentration than other two genotypes, and similarly Dayton had the least increase in root Al concentration among three genotypes. Interestingly, Dayton and XZ16 had much lower Al concentration than ZU9 in both roots and shoots for all treatments, being completely consistent with the previous results. As expected, in the combined treatment of Al and Mn, there was no increase in the concentration of Al and Mn as compared to Al or Mn treatment alone. On contrast, the combined treatment caused significant reduction of Mn concentration both in roots and shoots of three genotypes.

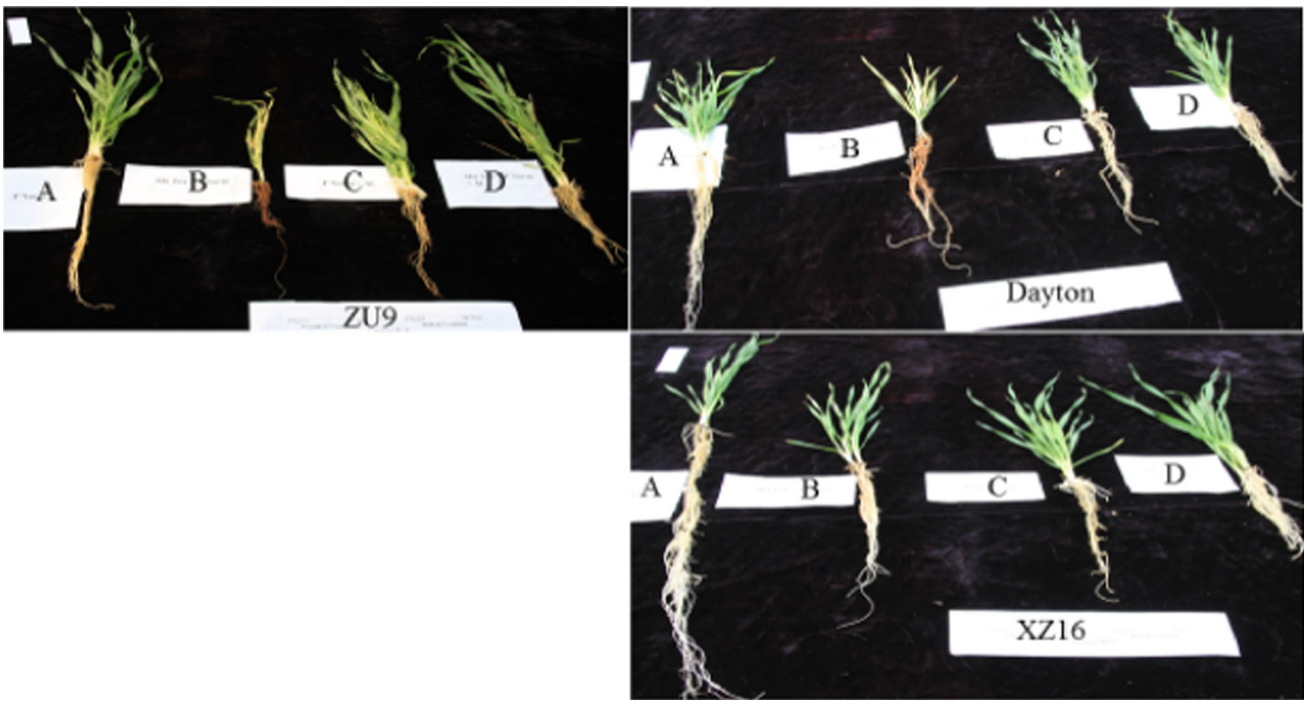


**Fig. 1** Toxicity symptoms of Al and Mn on roots and shoots in three barley genotypes under different treatments. *A* Seedling subjected to complete nutrient solution (control), *B* seedling subjected to 0.2 mM Mn. *C* Seedling subjected to control + 0.1 mM Al, *D* seedling subjected to high 0.2 mM Mn + 0.1 mM Al

**Table 1** The effect of aluminum and manganese concentration on root and shoot length (cm/plant) and root and shoot dry weight (g/plant) in three barley genotypes

| Genotype | Treatment | Root length | Shoot length | Dry weight root | Dry weight shoot |
|---|---|---|---|---|---|
| Dayton | Control | 38.66 a | 23.66 ab | 0.09 a | 0.20 b |
| | High Mn | 27.33 b | 22.00 b | 0.10 a | 0.14 c |
| | Control + Al | 25.33 b | 24.00 ab | 0.11 a | 0.29 a |
| | High Mn + Al | 22.66 b | 25.33 a | 0.11 a | 0.32 a |
| ZU-9 | Control | 41.33 a | 37.00 a | 0.23 a | 0.50 a |
| | High Mn | 24.00 b | 26.00 b | 0.09 b | 0.17 c |
| | Control + Al | 20.67 b | 33.33 a | 0.10 b | 0.40 ab |
| | High Mn + Al | 19.33 b | 35.66 a | 0.08 b | 0.40 ab |
| XZ-16 | Control | 50.33 a | 36.33 ab | 0.19 a | 0.41 a |
| | High Mn | 33.66 b | 34.67 b | 0.14 ab | 0.32 b |
| | Control + Al | 31.00 b | 35.67 ab | 0.10 b | 0.37 ab |
| | High Mn + Al | 25.67 b | 37.00 a | 0.11 b | 0.36 ab |
| Interaction G × T | | ns | ** | ** | ** |

The same letters within a column indicates no significant difference at 95% probability

** Highly significant and ns shows non-significant interaction between treatment and genotype at $P \leq 0.05$ level

**Table 2** The effect of aluminum and manganese concentration on root and shoot uptake of aluminum and manganese (mg/g) in three barley genotypes

| Genotype | Treatment | Mn in root | Mn in Shoot | Al in root | Al in Shoot |
|---|---|---|---|---|---|
| Dayton | Control | 2.93 b | 0.37 c | 0.44 c | 0.078 b |
| | High Mn | 20.13 a | 0.91 a | 0.34 c | 0.085 b |
| | Control + Al | 0.33 c | 0.07 d | 1.22 a | 0.117 a |
| | High Mn + Al | 1.01 c | 0.49 b | 1.03 b | 0.076 b |
| ZU-9 | Control | 2.64 b | 0.23 c | 0.79 c | 0.33 a |
| | High Mn | 22.90 a | 1.17 a | 0.45 d | 0.22 a |
| | Control + Al | 0.27 b | 0.07 d | 2.68 a | 0.37 a |
| | High Mn + Al | 1.40 b | 0.51 b | 1.95 b | 0.36 a |
| XZ-16 | Control | 2.25 b | 0.18 c | 0.38 c | 0.034 c |
| | High Mn | 9.81 a | 1.31 a | 0.49 c | 0.054 bc |
| | Control + Al | 0.51 d | 0.07 d | 2.15 a | 0.091 a |
| | High Mn + Al | 1.44 c | 0.65 b | 1.78 b | 0.068 ab |
| Interaction G × T | | ** | ** | ** | ** |

The same letters within a column indicates no significant difference at 95% probability

** Highly significant interaction between treatment and genotype at $P \leq 0.05$ level

### Al and Mn accumulation in plant tissues

Table 3 shows the effect of different treatments on Al and Mn accumulation in roots and shoots of three barely genotypes. For control, the significant difference could be found in accumulation of Mn and Al in roots and shoots among barely genotypes, with Dayton and ZU9 having the least and largest Al and Mn accumulation in both roots and shoots. As expected, Al or Mn treatment dramatically increased Mn accumulation in both roots and shoots for all genotypes. However, the increased extent differed greatly among three genotypes, with XZ16 having the least and most accumulation in roots and shoots, respectively. Moreover, addition of Al caused the marked reduction of Mn accumulation in roots, although no significant difference was found between Mn treatment and Mn + Al treatment in shoot Mn accumulation. The influence of all treatments on Al accumulation differed greatly among the three barley genotypes. No significant difference was found for Dayton among all treatments, while Al treatment had significantly higher Al accumulation than other treatments for ZU9 and XZ16. Moreover, in comparison with Al alone, the combination of Mn and Al treatment, on the whole, had less Al accumulation, although the difference between Al alone and the combination Mn and Al was not significant for XZ16.

**Table 3** Effect of aluminum and manganese concentration on the accumulation of Al and Mn (mg/plant) in three barley genotypes

| Genotype | Treatment | Mn in root | Mn in Shoot | Al in root | Al in Shoot |
|---|---|---|---|---|---|
| Dayton | Control | 0.29 b | 0.07 c | 0.04 a | 0.02 a |
| | High Mn | 2.04 a | 0.15 b | 0.04 a | 0.01 b |
| | Control + Al | 0.13 b | 0.02 d | 0.45 a | 0.02 a |
| | High Mn + Al | 0.11 b | 0.16 a | 0.11 a | 0.02 a |
| ZU-9 | Control | 0.62 b | 0.12 b | 0.18 b | 0.040 ab |
| | High Mn | 2.12 a | 0.20 a | 0.04 c | 0.014 c |
| | Control + Al | 0.03 c | 0.03 c | 0.28 a | 0.047 a |
| | High Mn + Al | 0.12 c | 0.20 a | 0.16 b | 0.030 b |
| XZ-16 | Control | 0.43 b | 0.08 c | 0.07 b | 0.014 b |
| | High Mn | 1.41 a | 0.43 a | 0.07 b | 0.018 b |
| | Control + Al | 0.05 c | 0.02 d | 0.21 a | 0.034 a |
| | High Mn + Al | 0.16 bc | 0.24 b | 0.20 a | 0.026 ab |
| Interaction G × T | | ** | * | ** | ** |

The same letters within a column indicates no significant difference at 95% probability

* Significant interaction between treatment and genotype

** Highly significant interaction between treatment and genotype at $P \leq 0.05$ level

## SPAD value and photosynthetic parameters

The effect of different treatments on SPAD value and photosynthetic parameters ($P_n$, $g_s$, $T_r$, SPAD values) is shown in Table 4. In comparison with control, Al treatment had little effect on SPAD value, while Mn treatment caused the significant reduction of SPAD value for all genotypes. The combination of Al and Mn treatment dramatically alleviated the reduction of SPAD value by Mn treatment alone. High Mn treatment resulted in a dramatic reduction of all three photosynthetic parameters ($P_n$, $g_s$, and $T_r$), and the reduced extent differed obviously among three genotypes, with ZU9 and Dayton being more affected than XZ16. Similarly, Al treatment also caused the reduction of all photosynthetic parameters relative to control, but the difference between Al treatment and control was not significant for all genotypes. The combined treatment of Al and Mn had higher values of $P_n$, $g_s$, and $T_r$ than Al or Mn treatment alone, again indicating the antagonistic interaction between Al and Mn in their influence on photosynthetic parameters.

**Table 4** Effect of aluminum and manganese concentration on photosynthetic rate ($P_n$) and SPAD value in three barley genotypes

| Genotype | Treatment | $P_n$ (μmol $CO_2/m^2s$) | $g_s$ (mol $H_2O/m^2s$) | $T_r$ (m mol $H_2O/m^2s$) | SPAD value |
|---|---|---|---|---|---|
| Dayton | Control | 5.58 a | 0.18 a | 2.48 a | 31.83 b |
| | High Mn | 2.04 b | 0.05 d | 1.04 b | 12.2 c |
| | Control + Al | 4.87 a | 0.10 c | 2.22 a | 39.40 a |
| | High Mn + Al | 5.48 a | 0.15 b | 2.53 a | 39.07 a |
| ZU-9 | Control | 7.93 a | 0.19 a | 3.24 a | 39.50 a |
| | High Mn | 0.87 c | 0.05 b | 0.97 d | 10.96 b |
| | Control + Al | 5.27 b | 0.10 ab | 2.47 ab | 33.83 a |
| | High Mn + Al | 6.53 ab | 0.14 ab | 2.45 abc | 38.63 a |
| XZ-16 | Control | 6.02 ab | 0.15 a | 2.54 a | 39.98 a |
| | High Mn | 4.49 b | 0.08 a | 1.46 b | 33.40 a |
| | Control + Al | 6.34 a | 0.15 a | 2.29 a | 43.93 a |
| | High Mn + Al | 6.12 ab | 0.15 a | 2.45 a | 36.87 a |
| Interaction G × T | | ** | ns | ns | ** |

The same letters within a column indicates no significant difference at 95% probability

*ns* non-significant interaction between treatment and genotype

** Highly significant interaction between treatment and genotype at $P \leq 0.05$ level

## Discussion

Among cereal crops, barley is relatively sensitive to acid soil, e.g., both to Al and Mn toxicity (Vlamis and Williams 1964). Al concentration in the acidic soil solution of southern China was very high (Shen et al. 2006). Total and exchangeable Mn concentration was reported as 763 soil and 19.6 mg $kg^{-1}$ soil, respectively, in the above-mentioned acidic soil (Chinese National Soil Survey Office 1998), but the amount of exchangeable Mn varies greatly, depending on the total Mn content in soil and the extent of waterlogging. Accordingly, we used 0.1 mM Al and 0.2 mM Mn to investigate their interaction in this study. The current results showed that there was a significant difference among treatments and among three barley genotypes in the responses of root, shoot length and biomass to Mn and Al stress (Table 1). The treatment with Al addition adversely affected plant growth, as reflected by reduced root and shoot length, and biomass, being consistent with the previous findings (Delhaize and Ryan 1995; Zheng et al. 1998; You et al. 2005). However, the inhibition of plant growth by Al toxicity differed greatly among the three genotypes, with Dayton and XZ16 being less affected than ZU9, proving the previous findings (Dai et al. 2013). Similarly, addition of 0.2 mM Mn in the culture solution caused severe reduction in shoot length and biomass, due to toxic effect on barley seedlings, including leaf necrosis, chlorosis, and yellowing (Fig. 1). The results confirmed the previous report in canola (Moroni et al. 2003), clover (Rosas et al. 2007) and ryegrass (de la Luz Mora et al. 2009). Although Mn caused detrimental effect, there was a large diversity among barely genotypes, with XZ16 showing higher tolerance, without any toxic symptom in the seedlings. As we understand, it is the first report on genotypic difference in Mn toxicity tolerance.

In acid soil, Mn and Al toxicity coexists, both being detrimental for plant growth and development (Foy 1984; Kochian et al. 2004; Marschner 1995). It is commonly considered that active Mn and Al in acid soil should be additional in their detrimental effect on plant growth. However, in the current study, the combined treatment of Mn and Al alleviated the toxicity in the seedlings of all barley genotypes as compared to sole Mn or Al treatment (Fig. 1; Table 1), indicating that both metals are antagonistic rather than synergistic in the interaction on plant growth, and the similar findings was once reported earlier in soyabean (Yang et al. 2009).

In this study, concentration and accumulation of both metals in plant tissues increased by many folds for the sole treatment of Al or Mn. However, there was a large difference among the genotypes in Al and Mn concentration and accumulation, with ZU9 having higher root and shoot Al concentrations than other two genotypes, and XZ16 having the lowest shoot Mn concentration among the three genotypes. Obviously, both responses of barley to Al or Mn toxicity are closely related to their concentrations in plant tissues. The high tolerant genotypes, such as Dayton and XZ16 for Al tolerance and XZ16 for Mn tolerance, tended to have lower Al or Mn concentration, respectively. It suggests that the tolerance is closely associated with less uptake of the toxic element, and the similar findings were reported previously (Khan and McNeilly 1998; Culvenor 1985; Taylor et al. 1998; Blair and Taylor 1997). In the present study, the unexpected results were obtained in the combined treatment of Al and Mn, which had lower Al and Mn concentrations, in comparison with Al or Mn treatment alone, explaining less inhibition of plant growth (Fig. 1; Table 1) in the combined treatment of Al and Mn. Up to date, only in soybean was antagonistic interaction of Al and Mn detected (Yang et al. 2009). The mechanism underlying the antagonism of the two elements is still unknown.

Mn is an essential micro-nutrient for plants. However, excessive Mn in growth medium is toxic to plants. In the present study, 0.2 mM Mn in the culture solution caused the dramatic reduction in SPAD value (chlorophyll content) and photosynthetic parameters, including net photosynthetic rate ($P_n$), transpiration rate ($T_r$), and stomatal conductance ($g_s$) for all barley genotypes. The similar results were found in rice (Lidon et al. 2004; Lidon and Teixeira 2000) and tobacco (Nable et al. 1988). The current results showed that the excessive Mn is highly detrimental for photosynthesis, confirming the earlier findings (Führs et al. 2008, 2010). But the responses of these photosynthetic parameters to Mn toxicity also differed among the three barley genotypes, with XZ16 being less affected than other two genotypes. It may be assumed that the high Mn tolerance in terms of photosynthetic parameters could be associated with lower Mn concentration in plant tissues. Similarly, Al toxicity also caused the reduction of $P_n$, $g_s$, and $T_r$ values for the three barley genotypes, although SPAD value was little changed. As expected, the two Al tolerant genotypes, Dayton and XZ16, had less reduction in comparison with ZU9. Again the combined treatment of Al and Mn showed less reduction of all photosynthetic parameters than Al or Mn treatment alone, indicating the antagonistic interaction between Al and Mn in their influence on photosynthesis.

## Conclusions

In conclusion, the current results showed that Al and Mn are antagonistic in their effect on uptake and accumulation of each element in plants, and consequently the coexistence of both elements in soil may cause less toxicity on plants than existence of Al and Mn alone. In addition, the mechanisms of Al and Mn tolerance should be different, as Dayton is highly

tolerant to Al toxicity and sensitive to Mn. From these results, we surmise that there may be two possible mechanisms which explain how Al and Mn interact antagonistically: one is that the competition may exist between $Al^{3+}$ and $Mn^{2+}$ on the binding sites in plasma membrane or cell wall. Therefore, the negative charges in cell wall and plasma membrane can attract and bind strongly with $Al^{3+}$ due to trivalent as compared to divalent $Mn^{2+}$, thus Mn binding competitively inhibited to root which greatly reduced Mn toxicity. The possible explanation of other is that may be $Al^{3+}$ disturb and alter the physiology of root cells that reduced $Mn^{2+}$ uptake. However, further research required for clear explanation of Al and Mn interaction mechanism.

**Author contribution statement** NM, SC, and GZ conceived the study. NM, SC, and JMS conducted the experiment. NM, SC, and GZ analyzed the data. NM and GZ wrote the manuscript. All authors read and approved the final version.

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