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Arsenic contamination in irrigation water, agricultural soil and maize crop from an abandoned smelter site in Matehuala, Mexico.

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Graphical abstract
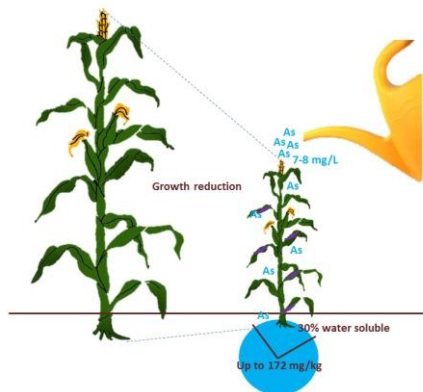
Highlights:

- As contaminates water, soils and maize crops in Matehuala, San Luis Potosi, Mexico.
- High CEC, total N, P, and OM explain lower bioconcentration of As.
- High soil EC explains higher bioconcentration of As.
- Gypsum and calcite play a key and contrasting role on the mobility of As in soils.
- Information on retention mechanisms of As in calcic and gypsic soils is limited.

Abstract

Mobility of Arsenic (As) from metallurgical wastes in Matehuala, Mexico has been accounted for ultra-high concentration of As in water (4.8-158 mg/L) that is used for recreational purposes as well as cultivation of maize. In this study, we (i) measured As concentrations in soils irrigated with this water, (ii) investigated the geochemical controls of available As, and (iii) measured bioaccumulation of As in maize. Water, soil, and maize plant samples were collected from 3 different plots to determine As in environmental matrices as well as water soluble As in soils. Soil mineralogy was determined by X-ray diffraction analysis. Bioaccumulation of As in maize plants was estimated from the bioconcentration and translocation factors. We recorded As built-up in agricultural soils to the extent of 172 mg/kg, and noted that this As is highly soluble in water (30% on average). Maize crops presented high bioaccumulation, up to 2.5 times of bioconcentration and 45% of translocation. Furthermore, we found that water extractable As was higher in soils rich in calcite, while it was lower in soils containing high levels of gypsum, but As

bioconcentration showed opposite trend. Results from this study show that irrigation with As rich water represents a significant risk to the population consuming contaminated crops.

Keywords: *Zea mays* L., arsenic, reduced growth, calcite, gypsum.

1. Introduction

Millions of people worldwide are chronically exposed to high levels of arsenic (As) in food and drinking water with a mortal risk of suffering from various forms of cancer. While drinking water remains the major source of exposure, there has been growing evidence that As in the food chain has a significant contribution to the overall exposure [1,2]. It is also known that irrigation with As rich water causes a gradual and continuous buildup of As in the soil that affects the sustainability of agriculture by degradation of soil, lowering of crop yield, and contamination of the food chain [3–5].

Arsenic concentrations in uncontaminated natural soils are generally below 10 mg/kg and often below 5 mg/kg [6]. Arsenic concentrations in natural topsoils irrigated with As rich water show large variations depending on water and soil characteristics [3,7–12]. In aerated soils, As could be retained by adsorption on iron (III) oxyhydroxides as well as other soil constituents such as organic matter [13,14], clay minerals with surface and edge charges [15], calcite [16–20], and gypsum [21,22]. In calcareous and gypsic soils, As concentration might be controlled by the reactive levels of calcium in soils [17].

Levels of As in soil that are considered safe for agriculture, range from 1 to 20 mg/kg [10,23–27]. Of the total As in soil, plant roots absorb only a very low fraction, which ranges between 0.1 and 1.8% [24,28]. In contaminated, aerobic soils, As(V) enters plants through P-cells channels at the root level and, subsequently, As(V) is reduced to As(III) by the enzyme, arsenate reductase (AR), which is subsequently complexed through phytochelatins, that is stored in cell vacuoles as As(III)–tris glutathione complex in the shoots and As(III)–tris thiolate complex in the roots [29]. A method of measuring the As transference from agricultural soils to crops is the bioaccumulation factor that expresses the relationship between the As concentration in a plant and its respective value in the soil [30]. Symptoms of As toxicity in plants include lower seed germination, reduction in root

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growth, and nutritional deficiencies [31]. Plants surviving at high As concentrations may show chlorosis and reductions in growth [32,33].

This study was carried out in Matehuala, San Luis Potosi, Mexico, where it is a common practice to grow rain-fed maize in small plots owned by subsistence farmers where contaminated water is commonly used to supplement the rainwater during the growing season due to lack of alternative sources. The maize variety grown in this region requires at least 500 mm of water of which circa 50% is available from rainfall during the growing period, May to August, while the remaining 50% is supplemented by gravity-flow of As contaminated water. It is drawn from an As contaminated man-made hydraulic complex that comprises, dug wells, a channel, and a pond between the towns of Matehuala and Cerrito Blanco (Figure 1). Such a complex is only and one concession of water granted to Cerrito Blanco ejido for agriculture and therefore the solitary source of extra water available for agriculture. Previous studies showed that the contamination of water derives from the leaching of As-containing residues from the terrains of an inactive smelter [34]. Such residues resulted from a pyrometallurgical process operating in Matehuala since 1905 until the 1950´s. Total As concentrations in the hydraulic complex range from 4.7 to 19.6 mg/L [34]. This area does not have any other source of irrigation water; as a result, it is estimated that 5000 mg of As are added per square meter of soil during a growing season, assuming that As concentrations in irrigation water account for up to ~20 mg/L [34]. It is therefore expected that, in Matehuala, agricultural soils with a history of irrigation with As contaminated water have increased concentrations of arsenic. Moreover, that As is available and bioaccumulates in maize crops. The objectives of this work are, (i) measuring the concentration of As in irrigation water and agricultural soil from selected sites in Matehuala; (ii) measuring the bioaccumulation of As in maize plants; (iii) assessing the effects of As contamination on total plant weight and height; (iv) investigating the geochemical characteristics of water soluble As; and (v) the soil characteristics that affect As bioaccumulation.

2. Materials and Methods

2.1. Location and sampling characteristics

Soil, irrigation water, and maize samples were collected from three fields in Cerrito Blanco, Matehuala. Location of the different fields and sampling points are given in Table 1S (*Supplemental Information*). Figure 1 shows each of the collection points along the Matehuala-Cerrito Blanco channel and the Cerrito Blanco pond. Sampled agricultural areas are located in the Sierra Madre Oriental of Mexico. These areas have predominantly a dry semiarid and temperate dry climate [35]. The soil types in this region are Calcisol and Gypsisol while precipitation is scarce in the area, which ranges from 300 to 500 mm/yr [35], so that surface water from the Matehuala-Cerrito Blanco hydrahulic complex is used for irrigation during the single growing season to supplement rainwater. The three agricultural areas were labeled M1, M2, and M3 and had crops of 8 and 20 weeks old. A rectangular systematic sampling was performed in each field, which involved the collection of soil and maize plant samples from four points (A, B, C, and D), except for M2 where a fifth sample, E, was collected. A total of 13 soil as well as 13 plant samples were collected for analysis. Additionally, a composite surface irrigation water sample was collected for each sampling field. A total of three water samples were collected from irrigation channels. As mentioned above, no groundwater wells are available in the study area for agricultural use and therefore surface water from the hydraulic complex is the only extra source of water for irrigation during the growing season. Distance between sampling points varied, from 20 to 50 m, according to the size of each cultivated plot. Sampled areas accounted for 50x50 m^2 for sampling plot M1, 50x40 m^2 for sampling plot M2, and 30x20 m^2 for sampling plot M3. At each sampling point, maize root, shoot, and leaves were taken from a single maize plant. In addition to1 kg of soil from a 0 to 30 cm depth, from directly under the sampled plant, close to the root crop (<20 cm). Immediately after collection, height and total weight of plant samples were recorded in the laboratory to assess any effect of As on plant growth by comparing the recorded data with literature data for the particular variety of maize grown in this area (H-430 *Zea mays*). Literature data shows that adult plants of the species H-430 may vary from 1.97 to 2.30 m in height and from 430 to 480 g in wet-weight [36].

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2.2. Sample preparation

The soil samples were dried at room temperature and then sieved to obtain the fraction less than 2 mm. The plant samples were thoroughly rinsed with running tap water, followed by three rinses with deionized water. All plant samples were carefully disaggregated into roots, stem, and leaves. They were oven dried at 65ºC for 72 h, crushed, sieved (<325 µm), homogenized, and weighed. Irrigation water samples were filtered (<0.45 µm) and acidified to pH < 2 using HNO_3. The samples were hermetically sealed and stored at 4ºC until analyses.

2.3. Digestion of samples

Samples of agricultural soil and maize plant were digested according to the slightly modified ISO 11466:1995 method. A 1.0 g soil sample was placed in a beaker and then 10 mL of aqua regia (HNO_3:HCl, 3:1) were added. This procedure is considered adequate for analyzing total-recoverable heavy metals in soils and is used to estimate the maximum availability to plants [37]. Residual elements that are not released by aqua regia digestion are mostly bound to silicate minerals and are considered unimportant for estimating the mobility and behavior of elements of environmental interest [38]. In this study, the As recovered by aqua regia digestion is called total As. For maize plants, 1 g of plant tissue was placed in a beaker and then 10 mL of concentrated HNO_3 and $HClO_4$ were added in 8:2 ratio. The beakers were heated at near boiling temperature (≈85ºC) until the digests were evaporated to near dryness. Residues were re-dissolved in 10 mL of acid, allowed to cool, transferred to volumetric flasks, brought to a final volume of 50 mL with 0.5 M nitric acid, filtered (through a Watman filter paper No 40), and stored at 4ºC for analysis.

2.4. Characterization of irrigation water and agricultural soil

For each field, parameters such as temperature, pH, electrical conductivity, total dissolved solids, oxidation-reduction potential, and dissolved oxygen were analyzed in situ in the irrigation water using a WE50050 multi meter from YSI. Additionally, soil pH (potentiometric method), electrical conductivity (saturation extract method), organic matter (Walkley and Black method), total nitrogen (Kjeldahl method), P (Olson method), cation exchange capacity (ammonium acetate method), $CaCO_3$ amount (HCl titration method),

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and soil texture (Bouyoucos hydrometer method) were determined for agricultural soils. Additionally, water extractable As in soil samples was determined by mixing 1g of soil with 40 mL of deionized water in an orbital shaker at 300 rpm, for 16 h, at room temperature [39]. After equilibration, suspensions were centrifuged at 3000 rpm for 20 minutes. Supernatants were filtered through a 0.45 μm membrane, acidified at pH<2 using HNO_3, and stored at 4ºC for subsequent analysis of As, calcium, and sulfate. In this study, water extractable As represents the As that is soluble in slightly acidified water, meant to represent a risk to the environment according to Mexican regulations [39]. This chemical extraction is expected to extract the fraction of As associated with gypsum and the calcite that dissolves at pH 5.5.

Bulk mineralogy was determined by X-ray diffraction (XRD) of soil samples using a Bruker D8 ADVANCE X-ray diffractometer fitted with a Cu Kα source. Soil samples for X-ray powder diffraction were ground using an agate mortar and pestle, compacted into a glass holder, and analyzed from 5º to 90º 2Ө. Phase identification was made by matching the experimental diffractogram with data from the PDF-4 of the ICDD (International Center for Diffraction Data). Semi-quantification of the mineral phases was done by the Reference Intensity Ratio (RIR) method embedded in PANalytical-High Score Plus software. The RIR method is based on scaling all diffraction data to the diffraction of the standard reference material to estimate concentration of mineral.

2.4. Arsenic, calcium and sulfate determination

Arsenic was determined in irrigation water, agricultural soil maize plant parts; and water soluble As extracts were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-EOS) [40]. The calibration curve was in the range of 0.05 to 20 mg/L and showed good linearity (r=0.999, n=6). The detection limit was 0.10 mg/kg. The validation of the total As determination was verified using certified reference materials (NIST SRM 2711 for soils and 1547 for plants). There were no significant differences (P=0.05) between the measured and the certified values for the total As content in the analyzed materials. Calcium in water extracts was determined by ICP-EOS [40] while

sulfate was determined by a turbidimetric method using barium chloride as a precipitating agent [41].

2.5. Bioaccumulation of As

Bioaccumulation of As in maize plants was estimated using the bioconcentration and translocation factors. Bioconcentration factors were calculated by dividing the concentration of As in the roots over the concentration of either total or water extractable As in soil, namely total bioconcentration factor and water extractable bioconcentration factor, respectively. Translocation factors of As in maize plants were calculated by dividing the concentration of As in shoots (stem and leaves) over the concentration of As in roots times 100 [42].

2.6. Principal component and cluster analyses

The correlation between the chemical changes of the rhizosphere and the accumulated As in maize roots was determined using principal component analysis (PCA) with the soil characterization data and the bioaccumulation factor. PCA was carried out in OriginPro2016. The similarity in the agricultural soil samples was evaluated by the cluster analysis (CA) using the nearest neighbor clustering and the Euclidean distance.

3. Results and discussion

3.1. Characterization of soil and irrigation water

Characteristics of the water used for irrigation of maize at the three sampling sites and soils were determined. Tables 2 and 3 show the characterization of the irrigation water and the soil as well as the As content from each sampling site. Arsenic concentrations in irrigation water were 7.748 mg/L in sampling plot M1, 7.815 mg/L in sampling plot M2, and 8.684 mg/L in sampling plot M3 (Table 2). It was observed that As concentrations exceeded the guideline value in irrigation water in Mexico, which is 0.1 to 0.4 mg/L [43,44], highlighting a potential contamination risk for soil and maize crop.

Soil samples from M1, M2, and M3 were silt loam, clay loam, and silt loam, respectively, according to textural analyses (Table 3). The soils were mostly rich in total N and electrical conductivity was high, from 3.3 to 5.9 dS/m, according to Mexican

guidelines [45]. The latter likely due to the calcic and gypsic nature of the soil samples [35]. A high concentration of salt can cause the decrement of crop biomass and would cause negative effects on the growth and physiology of the plants [46]. As the salinity increases, growth decreases until the plant becomes chlorotic and dies [46]. High salt levels can affect the stress conditions and alter nutrient absorption by crops. Soil samples in this study were classified as saline (4-8 mS/cm), except for samples M2B and M2D that were classified as moderately saline (2-4 mS/cm), according to Mexican guidelines [45]. Although soils showed saline levels, these agricultural sites are high in macronutrients, such as phosphate and nitrogen, which should increase salt tolerance [47,48]. Cation exchange capacity was low (5-15 cmol(+)/kg) in samples from plot M1, high (25-40 cmol(+)/kg) in samples from plot M2, and low to medium (15-25 cmol(+)/kg) in samples from plot M3, according to the Mexican guidelines [45]. Additionally, soil organic matter ranged from moderate (1.6-3.5%) to very high (>6%), according to the Mexican guidelines [45]. Different to salinity, soil organic matter should enhance plant growth.

Arsenic concentrations in the soil samples ranged from 6 to 172 mg/kg (Table 3); range of individual samples at M1 ranges from 32 to 172 mg/kg, the soil sampling plot M2 ranging from 100 to 160 mg/kg while those from M3 ranged from 6 to 43 mg/kg (Table 3). Arsenic concentrations in our samples were up to five times higher than the regional background levels, ranging from 4 to 35 mg/kg, for non-impacted and/or mineralized areas, while many were also higher than the local background levels, ranging from 35 to 80 mg/kg, associated with diffused mineralization, fluvial dispersion of eroded material from areas of higher As concentrations, diffuse impact from historic human activities or a mixture of all [49]. Due to the fact that all of our soil samples were higher than local background levels in terms of As (except M3D), we attribute As enrichment in our samples to soil irrigation with As contaminated water. Eleven out of 13 samples exceeded the Mexican guideline value of 22 mg/kg for As in agricultural soil [23] supporting then a potential contamination risk for maize crop.

Figure 2a shows the concentrations of water extractable As as a function of total As. Water soluble As reached up to 50 mg/L with the highest concentrations of water extractable As being released from the most polluted soils. On average, water extractable

As accounted for 30% of total As (Figure 2a). In this study, such a percentage represents the fraction of the total As content in soil that might be dissolved in the water pore soil solution and may be chemically and physically readily available for root uptake; that is, the concentration of As that depends on soil (i.e. pH, texture, cation exchange capacity, and organic matter, among others) and As properties (i.e. solubility and speciation). Nevertheless, the plant-available As fraction might be greater as plants are able to locally reduce soil pH, by proton excretion or by releasing chelating agents, in order to acquire nutrients like phosphorous, which might mobilize further As from the soil [50–54]. The biological availability of As in soils is controlled by species-specific parameters (roots organic complexes exudates, pH changes) and As toxicity (internal allocation mechanisms controlled by organism specific parameters) [55]. Commonly, As available percentages for plants range from 0.1 to 1.8% [24,28].

Water extractable As concentrations were higher than those of Rosas-Castor et al. [56], who reported water extractable As concentrations below 1.9 mg/kg in a sampling plot common to our study area with total As concentrations up to 10.05 mg/kg yet the data are in good agreement with previous experiments that showed a solubility of up to 60 mg/L of As in contaminated soils in Matehuala. Widely varying concentrations of total and water soluble As in soils may result from the amount and frequency of irrigation [28]. In our study area, the concentration of As in irrigation water is fairly uniform ranging from 7.748 to 8.684 mg/L, but irrigation rates might vary highly as they depend on individual farmers, who probably use different quantities of water for unit area of land. However, no records exist to document irrigation practices by local farmers at Cerrito Blanco. While the unknown and varying irrigation rates with homogenously contaminated water might explain the contrasting results on total As concentrations in soils in this and other studies, soil mineralogy might explain the contrasting results found for As solubility.

In this study, the mineralogical composition of soils is shown in Table 4. Soils are largely dominated by either calcite or gypsum, followed by quartz, except for sample M2B that contains 9% muscovite (Table 4). This soil mineralogy is consistent with other studies and explained by the geological settings [34,57,58]. The study area is located inside the physiographic province of the Eastern Sierra Madre Range, composed primarily of

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sedimentary marine rocks. The stratigraphic column consists of some PreOxfordian, Upper Jurassic and Cretaceous carbonate sequences including Tertiary volcanic rocks that cover a small part of the region and Quaternary alluvial deposits that floor the Matehuala valley [34,49].

Although As is known to incorporate in calcite and gypsum by surface adsorption and/or (co)precipitation [17–22,59–61], very little is known on the retention and the solubility of As in actual calcic and gypsic soils contaminated with As [34,62]. In this study, we observed that the water extractable As was higher in the soils containing more calcite (Figure 2b) and lower in the soils containing more gypsum (Figure 2c). Additionally, Figure 2d shows the concentrations of calcium as a linear function of the concentration of sulfate while water extractable As was found to decrease with increasing calcium (Figure 2e). These results suggest that the more gypsum is in soil, the lower is the solubility of As. In contrast, higher calcite in soils resulted in higher dissolution of As, regardless of its capacity to adsorb and/or incorporate As in its structure [16–20,60,61]. Questions remain on whether gypsum would be more beneficial than calcite for As immobilization as As in maize roots increased linearly with total As in gypsic soils (see below). No clear effects on the solubility of As were observed within the (narrow) soil pH observed in this study (Figure 2f).

3.2. Arsenic concentrations in maize crops

Total As concentrations in roots, stems, and leaves are shown in Table 5. Total As concentrations in roots ranged from 10.19 to 217.67 mg/kg, while total As concentrations in stems reached up to 28.43 mg/kg (Table 5). Total As concentrations in leaves varied from 0.10 to 13.36 mg/kg (Table 5). In agreement with other studies, As was higher in roots followed by stems and then leaves [56,63–67].

Figure 3a shows the concentrations of As in roots as a function of total As in soils with higher As in roots in the most contaminated soils (Figure 3a). In fact, an increasing relationship between total As in roots and total As in soils was found in sampling plots M1 and M3 (Figure 3a). A similar observation could be drawn from the data of Rosas-Castor

et al. [56] who reported relatively high concentrations of As in maize roots in the same study area (see Figure 3a). In contrast, sampling plot M2 showed no clear relationship between total As in roots and total As in soils (Figure 3a). Interestingly, increasing relationships were observed in the soils richer in gypsum while an inverse relationship was found in the soils richer in calcite (Figure 3a and Table 4). Therefore, As bioconcentration was higher in gypsic soils than calcic soils, despite showing a higher solubility in soils richer in calcite. On the other hand, in contrast to the studies that conclude that total As in soil is not an appropriate indicator of plant available As [28], in the gypsic soils studied here, the total As in soil samples was well correlated to those in maize plants (Figure 3a). Although these results seem to contrast with those in Figure 2c, showing less water extractable As in gypsic soils, it is possible that, besides gypsum dissolution, more complex processes took place during the experiments of dissolution of As, leading to apparent higher immobilization of As in the gypsic soils. Among such processes could be the precipitation of As as gypsum supplied calcium to the solution for the precipitation of calcium arsenates [34] and/or to the precipitation of calcite with As adsorbed and/or incorporated within its structure [16–20,60,61]. Calcium arsenate salts, such as pharmacolite, haindingerite, and guerinite have been found in the study area as a result of cycles of dissolution and precipitation of As in the environment [57]. Additionally, more recent studies show the presence of pharmacolite, haindingerite, guerinite, pharmacosiderite, clinoclase and bukovskyite in As contaminated soil samples in Matehuala. From these minerals, the precipitation and dissolution of pharmacolite and haindingerite might account for the solubility and bioaccumulation of As in soils and maize plants. The competitive effects of calcite and gypsum in the retention and availability of As in agricultural soils have not yet been investigated but overall effects might result from adsorption and precipitation processes influenced by their kinetics and solubility.

In our study, maize roots adsorbed a very large fraction of the total As in soils (up to 250%), which contrast studies that suggest that the proportion of As in roots, as compared to total As in soils, ranges between 0.01 and 2.1% [66] due to strong adsorption capacity of As in clays and iron oxyhydroxides [24,28]. In calcium rich soils, where the

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commonly reported mechanism of adsorption to iron (III) oxyhydroxides is not the dominant process, plant roots can adsorb considerable quantities of As according to our findings.

Figure 3b shows the concentration of As in roots as a function of the concentration of water extractable soil As. Arsenic in roots proves to be a function of both the total and the water extractable As, as the latter resembles the former (Figures 3a and b). Figure 3c shows the bioconcentration of As in maize, as determined by the ratio of As in roots over the total As in soil. In this study, As bioconcentration ranged from 0.37 to 2.46 (Table 5 and Figure 3c). These values were lower than those of Rosas-Castor et al. [56], who reported values between 4.73 and 8.01 (Figure 3c). In their study, Rosas-Castor et al. [56] attributed high bioaccumulation to low soil adsorption capacity, which might hold for calcareous and/or gypsic soils (where the immobilization of As through sorption on iron oxyhydroxides is not majorly operating) but their high bioconcentration is also the result of the relatively low levels of As in the denominator.

Regarding translocation, As translocation reached up to ~45% but vary greatly depending on the agricultural plot (Table 5). Although tissue as the stem is not directly eaten by humans, corn silage, made from stems, can be used by livestock and represents risk through the food chain. In this study, As concentrations in stems were, in some cases, higher than the maximum tolerable concentrations of As in silage in countries like Switzerland which accounts for 4 mg/kg [63].

Figure 4 shows height as a function of total plant weight. According to Hernández Alatorre [36], 8 weeks old maize plant should be 147 to 172 cm tall and weigh between 215 and 240 g wet-weight, while at 22 weeks, it should be 197 to 230 cm tall and weigh between 430 and 480 g wet-weight. In this study, plant specimens were generally lighter and, in all cases, shorter than normal values (Figure 4). This observation suggests that As accumulation in the plants inhibits their normal growth; several authors have also observed these symptoms in other studies [56,63,66,67,69,70]. Eight week-old specimens weighed only between 3.3 and 385.0 g and reached only from 31.5 to 118.0 cm while older

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specimens weighed only between 115 and 410 g and reached only from 126 to 175 cm (Figure 4). Figure 5a shows a panoramic view of M2 sampling plot showing plant specimens exhibiting shorter heights, arguably due to As toxicity. Chlorosis and metabolic damage were also observed in the study area (Figure 5b). Chlorosis and reduced growth are symptoms of As toxicity [63,66,69,71,72].

3.3. The chemical effect of the rhizosphere in As accumulation by maize

The relationship between the chemical parameters in the rhizosphere (Table 3) and the bioaccumulation of As (Table 4) was determined using PCA. PCA was able to extract three principal components (criterion: eigenvalues greater than 1) that contribute to 80% of the total variance: PC1 (46%) by CEC, total N, EqCaCO3, OM, water extractable As (Aswe), and total As (Astot), while PC2 (18%) will explain bioconcentration, electrical conductivity (EC) and phosphorous (P) and PC3 (16%) was loaded with height, age, total dry weight and pH. The combined plot of scores and loadings of PC1 and PC2 shown in Figure 6a shows that PC1 accounts for the characteristics of soil samples and classifies soils with similar characteristics in two different groups at opposite extremes. Within the first group, samples from M1 and M3 are included. Their common characteristics are concerned with low levels of carbonates, and therefore higher ECs and gypsum content, and their location along the hydraulic complex, nearer to the pollution source. The other group, containing the samples from M2, is further from the pollution source, being the CEC, macronutrients, carbonates, and OM the main variables contributing to PC1. These samples showed the highest growth of maize plants and the lowest bioaccumulation of As, likely due to their higher content of macronutrients and cation exchange capacity and lower salinity as compared to samples from M1 and M3, soil properties that seemed to control As solubility and therefore the availability of As to plants, even at high As

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concentrations in soil samples. Results from the dendogram in Figure 6b confirms the observation of two characteristic groups of soil samples that allocate samples with a high content of gypsum and electrical conductivity in one group (M1 and M3) and samples with a high content of carbonates in group two (M2). Results from this analysis suggest that As is less soluble in gypsic soils but bioconcentrates most in this type of soils as compared to calcic in the study area.

4. Conclusions

Current practice of irrigating farm land in Matehuala, Mexico with As contaminated water for maize cultivation has increased As concentration in soil and caused As bioaccumulation in maize, plant toxicity, and As translocation within maize plant. While surface adsorption and/or (co)precipitation of As in calcite and/or gypsum may retain As, their dissolution would allow for their transport and translocation of As to agricultural soils and maize crops, highlighting the importance of understanding better As disposal in calcareous and gypsic soils and environments.

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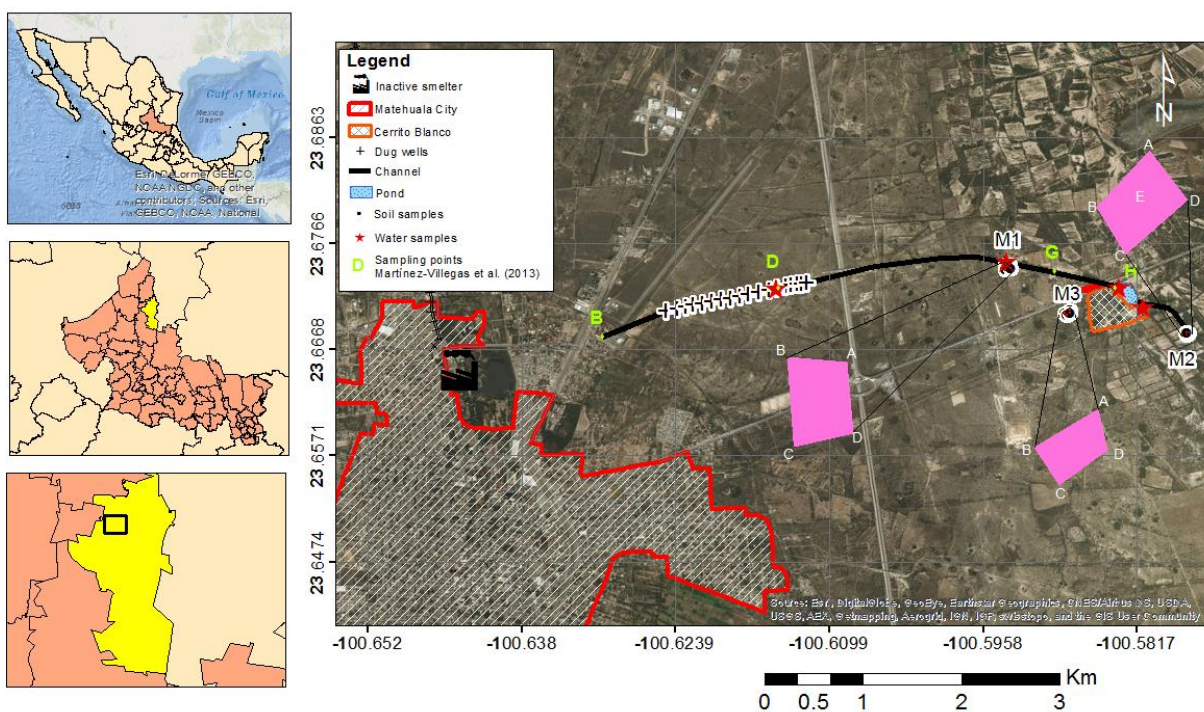
Figure 1. *Schematic of Matehuala, San Luis Potosi, Mexico showing the inactive smelter where calcium arsenate dissolution occurs and contaminates water running from Matehuala city to Cerrito Blanco through a hydraulic complex (running from B to H) comprising dug wells, a channel, and an artificial pond called Cerrito Blanco pond. M1, M2 and M3 indicate the three positions where plant and soil samples were collected. The red stars indicate the position where water samples were collected while purple polygons represent the rectangular sampling system used at each sampling field.*
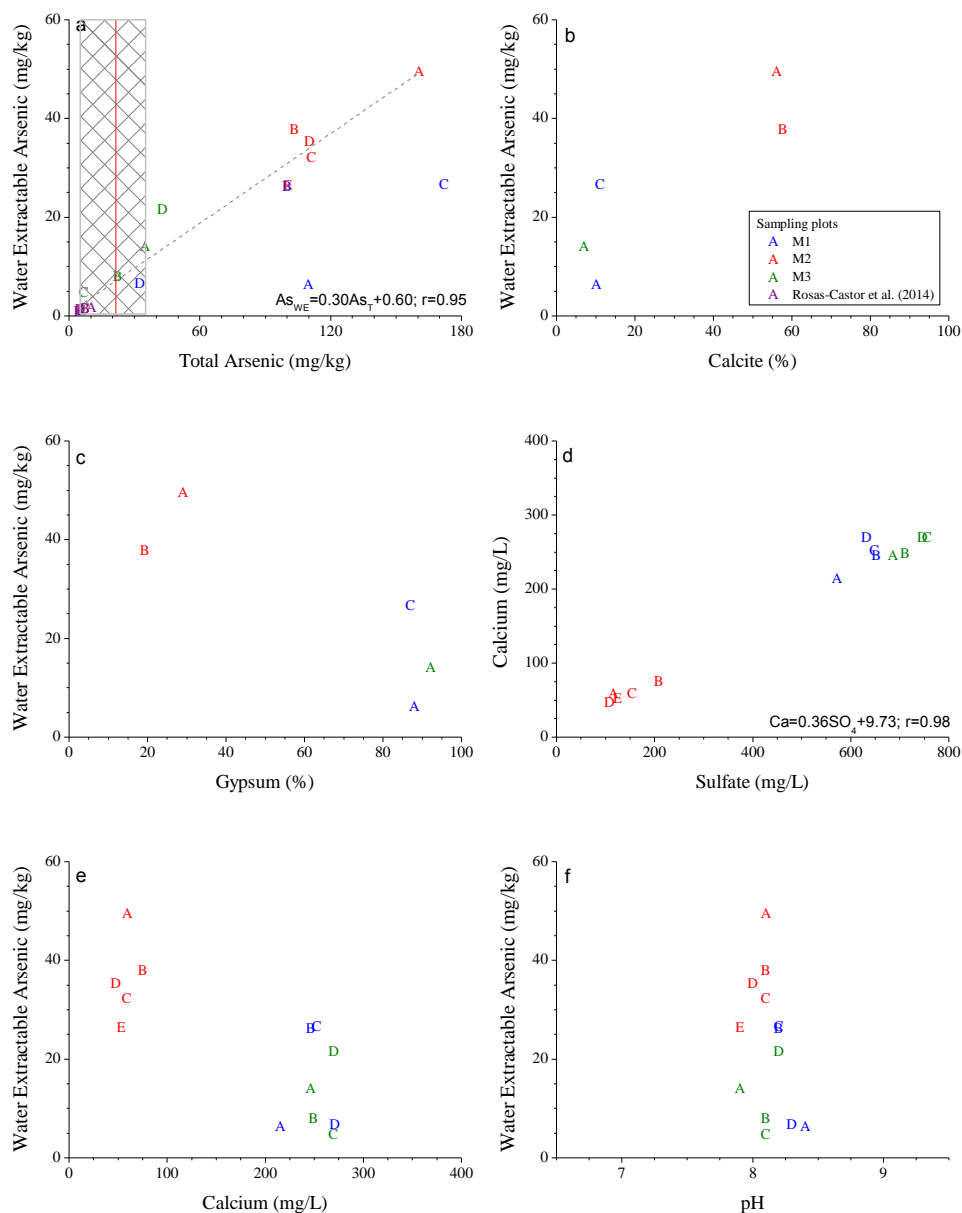
Figure 2. *Water extractable and total As in agricultural soils and their mineralogical controls. (a) Water extractable As as a function of total As showing soluble As amounts 30% average of the total As in soil samples, as determined by the slope of the data. Sampling points M1A and M1C were not taken into account for the regression analysis. The gray box indicates As regional background levels (Chiprés et al., 2009) while the red line indicates the federal environmental reference value for soil restauration [23]. (b) Water extractable As as a function of calcite showing water extractable As was higher in soils richer in calcite. (c) Water extractable As as a function of gypsum showing the higher*

the content of gypsum the lower the water extractable As. (d) Linear relationship between calcium and sulfate in the water extracts as a result of gypsum dissolution during the experiments, suggesting gypsum controls calcium. (e) Water extractable As as function of calcium showing the former was lower in the extracts containing more calcium. (f) Water extractable As and soil pH.
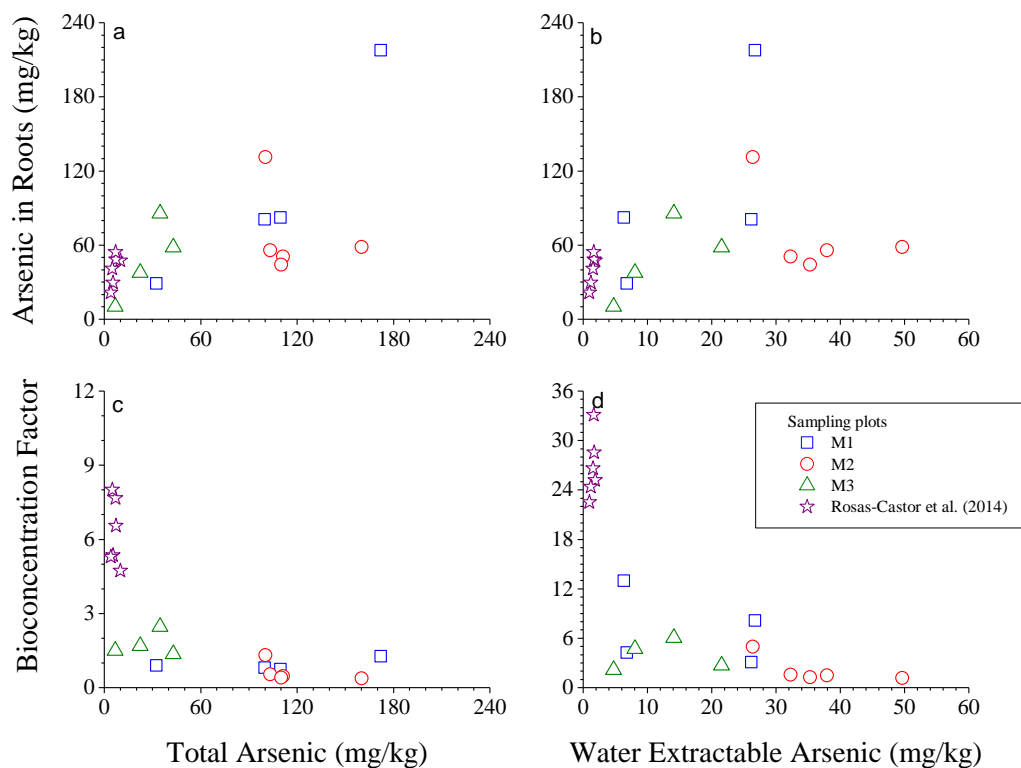
Figure 3. Bioconcentration of As in maize plants. (a) As in roots as a function of total As in soils, (b) As in roots as a function of the water extractable As in soils, (c) total bioconcentration factor as a function of total As in soil samples, and (d) water extractable bioconcentration factor as a function of water extractable As in soil samples. Arsenic in roots, total As and water extractable As data in this figure are mean values presented in Table 5.
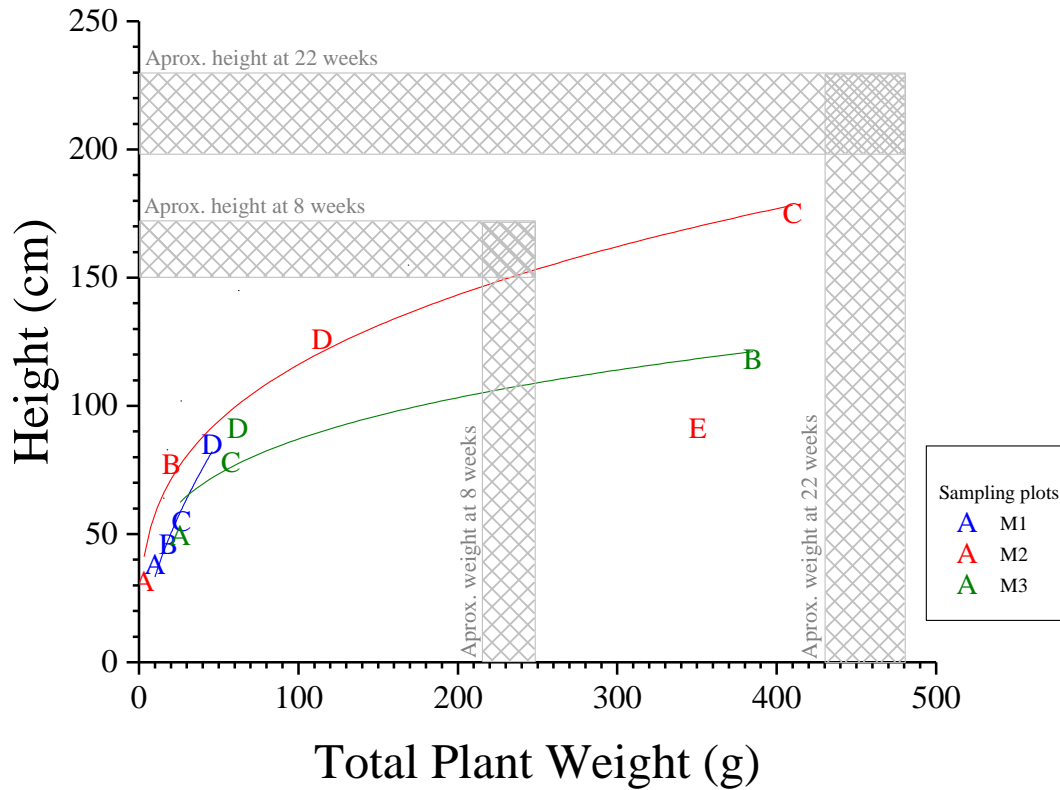
Figure 4. *Height and total plant weight of maize plant specimens sampled at Matehuala showing, in general, lighter weights and shorter heights than average values (gray boxes) [36] for the maize species grown in the study area (H-430 Zea Mays). Specimens from M1, M2, and M3 sampling plots were 8 weeks-old, except for M2C and M2D which were 20 weeks-old when collected.*
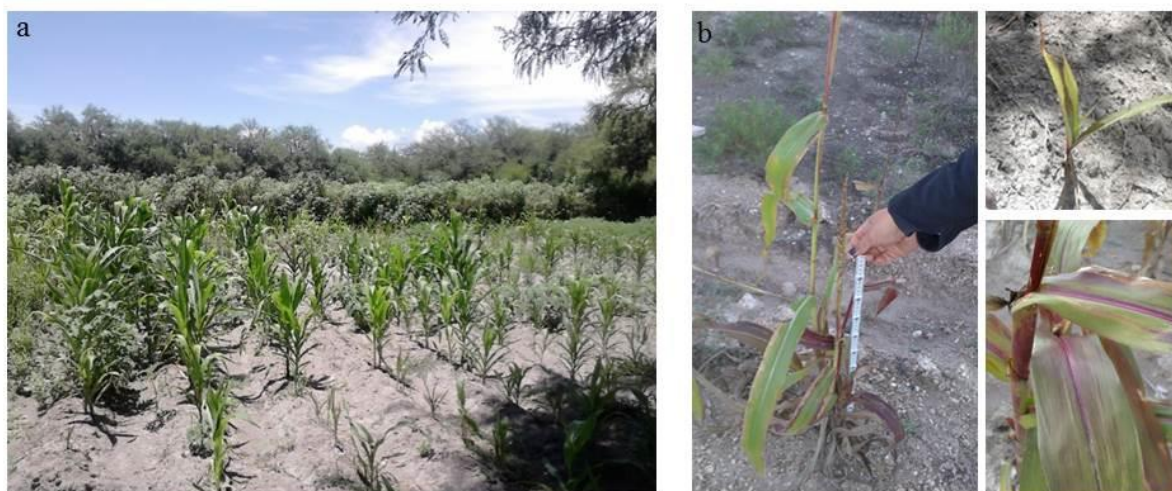
Figure 5. Panoramic view of M2 sampling plot showing symptoms of As toxicity such as a) reduced height and b) chlorosis.

Figure 6. (a) Combined plot of scores and loadings for the bioconcentration of As in agricultural soils. (b) Dendogram obtained by cluster analysis of the physicochemical characteristics of agricultural soils and bioconcentration factors.

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Table 2. *Physicochemical characterization of the irrigation water.*
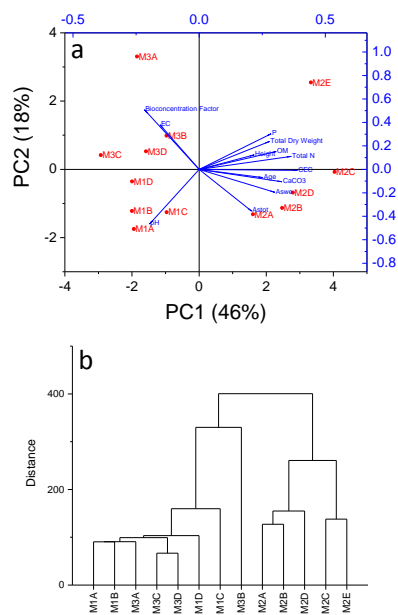
Sampling plot	T (°C)	pH	EC (mS/cm)	TDS (g/L)	ORP (mV)	DO (mg/L)	As (mg/L)
M1	26.10±0.18	8.15±0.25	2.95±0.21	1.87±0.28	127.90±4.02	12.70±0.20	7.75±0.40
M2	26.60±0.32	9.30±0.09	3.09±0.11	1.95±0.08	83.50±2.54	8.64±0.19	7.82±0.15
M3	28.50±0.28	8.76±0.29	3.15±0.14	1.93±0.07	58.60±3.17	10.03±0.06	8.68±0.11

T: Temperature; EC: Electrical conductivity; TDS: Total dissolved solids; ORP: Oxidation-reduction potential; DO: Dissolved oxygen. Mean values and standard deviations for field parameters are the result of three different lectures. Mean As concentrations and standard deviations are the result of triplicate analysis.

Table 3. *Textural classification and physicochemical characterization of the agricultural soils.*

Sampling plot	Sampling point	Sand (%)	Silt (%)	Clay (%)	Texture	EC (dS/m)	Total N (%)	P (mg/kg)	CEC (cmol/kg)	OM (%)	pH	EqCaCO$_3$ (%)	Org C (%)	As (mg/kg)
M1	A	20	70	10	Silt loam	4.2±0.4	0.2±0.04	12.5±0.3	13.5±0.3	3.5±0.13	8.4±0.1	1.3±0.06	2.0±0.1	109.7±2.0
	B	18	72	10	Silt loam	4.4±0.4	0.1±0.03	13.7±0.7	12.1±0.2	2.6±0.09	8.2±0.1	1.1±0.07	1.5±0.1	99.9±0.2
	C	16	74	10	Silt loam	4.2±0.6	0.2±0.04	13.4±0.2	14.1±0.2	3.9±0.06	8.2±0.1	1.3±0.06	2.3±0.1	172.0±1.9
	D	28	64	8	Silt loam	5.2±0.1	0.2±0.07	3.5±0.2	13.8±0.2	3.5±0.16	8.3±0.2	1.6±0.17	2.0±0.1	32.4±0.3
M2	A	36	36	28	Clay loam	4.8±0.4	0.3±0.09	25.9±0.2	31.0±0.7	5.5±0.11	8.1±0.2	1.9±0.19	3.2±0.2	160.3±12.6
	B	30	34	36	Clay loam	3.3±0.3	0.3±0.11	22.4±0.6	42.4±1.0	8.9±0.84	8.1±0.2	2.0±0.19	5.2±0.4	103.2±0.9
	C	32	34	34	Clay loam	4.3±0.2	0.3±0.03	27.6±2.0	35.4±2.5	5.2±0.31	8.1±0.3	2.5±0.22	3.0±0.1	111.2±0.2
	D	26	44	30	Clay loam	3.5±0.1	0.3±0.02	27.9±1.5	31.3±1.1	4.7±0.25	8.0±0.3	1.7±0.13	2.7±0.1	110.2±0.4
	E	38	36	26	Loam	4.8±0.3	0.4±0.13	39.5±0.4	38.2±0.9	11.4±0.44	7.9±0.5	1.6±0.09	6.6±0.3	100.3±0.5
M3	A	26	64	10	Silt loam	5.9±0.2	0.2±0.05	36.6±0.8	13.5±0.6	3.5±0.28	7.9±0.5	1.1±0.12	2.0±0.3	34.7±0.3
	B	24	66	10	Silt loam	4.3±0.3	0.2±0.08	11.6±0.3	16.4±0.1	3.9±0.05	8.1±0.1	1.8±0.15	2.3±0.2	22.4±0.2
	C	24	68	8	Silt loam	4.1±0.2	0.1±0.02	2.1±0.14	10.9±0.3	2.8±0.16	8.1±0.1	1.0±0.10	1.6±0.1	6.8±0.2
	D	30	62	8	Silt loam	5.5±0.4	0.2±0.07	11.1±0.5	15.4±0.5	3.5±0.25	8.2±0.1	1.4±0.07	2.0±0.1	43.0±0.7

EC: Electrical conductivity; CEC: Cation exchange capacity; OM: Organic matter. Mean and standard deviations are the result of triplicate analyses.

Table 4. *Mineralogical composition of agricultural soils as determined by XRD analysis.*

Mineral name	Formula	M1A	M1C	M2A	M2B	M3A
		Soil sample				
		Mineral semiquantification (%)				
Calcite	$CaCO_3$	10	11	56	43	7
Gypsum	$CaSO_4 \cdot 2H_2O$	88	87	29	13	92
Quartz	SiO_2	2	2	15	35	1
Muscovite	$KAl3Si_3O_{10}(OH)_2$	-	-	-	9	-
	Sum	100	100	100	100	100

Table 5. *Arsenic concentrations in plant tissue and bioconcentration and translocation factors. Concentrations equal to 0.10 mg/kg were less than the detection limit of 0.01 mg/L during ICP—OES determinations. Mean and standard deviations are the result of triplicate analyses.*

Sampling plot	Sampling point	Arsenic (mg/kg)			Bioconcentration factor		Translocation factor (%)
		Roots	Stem	Leaves	Total As	Water Extractable As	
M1	A	82.27±0.40	28.43±0.83	8.53±1.04	0.75	12.96	44.92
	B	80.70±1.21	26.99±0.66	8.17±0.14	0.81	3.09	43.56
	C	217.67±4.69	6.62±0.32	8.76±0.68	1.27	8.13	7.06
	D	28.90±0.50	0.10±0.00	0.10±0.00	0.89	4.26	-
M2	A	58.58±1.36	10.99±0.33	11.06±0.46	0.37	1.18	37.64
	B	55.82±1.83	3.93±0.43	4.70±0.66	0.54	1.47	15.46
	C	50.69±0.68	0.10±0.00	1.54±0.34	0.46	1.57	3.03
	D	44.17±0.74	0.10±0.00	13.36±1.18	0.40	1.25	30.24
	E	131.19±3.96	0.10±0.00	0.10±0.00	1.31	4.97	-
M3	A	85.48±2.34	0.10±0.00	0.10±0.00	2.46	6.05	-
	B	37.63±2.56	0.10±0.00	0.10±0.00	1.68	4.69	-
	C	10.19±2.01	0.10±0.00	0.10±0.00	1.50	2.15	-
	D	58.24±0.89	0.10±0.00	0.10±0.00	1.35	2.71	-

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