Cadmium Availability from Granulated and Bulk-Blended Phosphate-Potassium Fertilizers

S. H. Chien,* G. Carmona, L. I. Prochnow, and E. R. Austin

Abstract

Recent field experiments have shown that high chloride (Cl) in irrigation waters can increase soil cadmium (Cd) uptake by crops because of the formation of soluble ion-pair complexes of Cd with Cl in soil solution. The present study was aimed at testing a hypothesis that KCl in granulated PK fertilizers may enhance Cd uptake by crops from Cd-containing P fertilizers because of close contact between Cd and Cl in the same granules. Less effect would be expected if the same granular PK fertilizers were bulk-blended because of separation of Cd and Cl in different granules. A single superphosphate (SSP) containing 32 mg Cd kg⁻¹ was granulated by the compaction process with KCl at a P to K ratio = 1:1. Granular KCl was also bulk-blended with granular SSP or Cd-free monocalcium phosphate (MCP) at the same P to K ratio. An acid Ultisol (pH 5.2) was treated with PK fertilizers at 400 mg kg⁻¹ each for P and K. Upland rice (Oryza sativa L.) and soybean [Glycine max (L.) Merr.] were grown to maturity, and signalgrass (Brachiaria decumbens) mixed with 4 kg of soil at 400 mg P kg⁻¹ (McLaughlin et al., 1997; Smolders et al., 1998; Weggler et al., 1998) and the mixture was compacted at 140 MPa on a laboratory-scale, hydraulic-type compactor. The compacted material was soillution and results in an enhanced Cd uptake by plant from solution either through alleviation of a diffusional limitation to Cd transport in the root apoplast or through direct uptake of the CdCl₂⁻⁺ ions (Smolders et al., 2000). These researchers have proposed that Cl forms relatively strong complexes with Cd²⁺ in the CdCl₂⁻⁺ species (CdCl⁺, CdCl⁻) in soil solution and results in an enhanced Cd uptake by plant from solution either through alleviation of a diffusional limitation to Cd transport in the root apoplast or through direct uptake of the CdCl₂⁻⁺ ions (Smolders et al., 1998). Other researchers have also reported that Cd²⁺ and Cl⁻ can form the soluble complexes that result in a decrease of Cd adsorption by soil minerals and an increase of Cd by plants (Garcia-Miragaya and Page, 1976; O’Connor et al., 1984; Hirsch et al., 1989; Sparrow et al., 1994).

One implication from the effect of Cl on Cd availability is that if KCl is granulated with P fertilizers containing high Cd levels, it may result in a higher Cd uptake by crops than that from the same but bulk-blended granular P and K fertilizers. In the granulated PK fertilizers, KCl and Cd-containing P fertilizers are in the same single granule and thus are in close contact, thereby increasing the possibility to form CdCl⁺ and CdCl⁻ complexes. Likewise, it would be less likely that the complexes would form when KCl and Cd-containing P granules are physically separated in bulk-blended PK fertilizers. The objective of this study was to test the hypothesis that granulated KCl and Cd-containing P fertilizers may result in a higher Cd uptake by crops in an acid soil as compared with the same PK fertilizers produced by bulk-blending.

Materials and Methods

A single superphosphate (SSP) was produced from Togo phosphate rock by acidulating with H₂SO₄. The Togo phosphate rock contains a relatively high Cd content (54 mg kg⁻¹). The SSP produced had 92 g kg⁻¹ total P, 87 g kg⁻¹ water-soluble P, 5 g kg⁻¹ citrate-soluble P, 31.5 mg kg⁻¹ total Cd, and 19.7 mg kg⁻¹ DTPA-soluble Cd (Iretskaya et al., 1998). A chemical reagent-grade of monocalcium phosphate (MCP), which is the P compound of SSP, was used as a standard P source for comparison since it contains no Cd.

The granulated PK material was prepared as follows: SSP and MCP were ground separately into powder form (0.15 mm), then predetermined amounts of SSP and KCl were mixed, and the mixture was compacted at 140 MPa on a laboratory-scale, hydraulic-type compactor. The compacted material was then crushed and screened to between 3.35-mm (6-mesh) and 1.18-mm (14-mesh) size. The P to K ratio of the granulated PK material by compaction process was fixed at a 1:1 ratio. Granular SSP, MCP, or KCl alone were also produced by the same compaction process. The bulked-blended PK materials were prepared by simply mixing the granular SSP or MCP with KCl at the same P to K ratio.

An acid Hartsells soil (fine-loamy, siliceous, subactive, thermic Typic Hapludult) was used in the greenhouse experiments. Pertinent soil properties were: pH (1:1 soil and water), 5.2; organic matter, 17 g kg⁻¹; effective cation exchange capacity (1 M KCl), 5.1 cmol kg⁻¹; DTPA-extractable Cd, 0.02 mg kg⁻¹; Bray I, 2.0 mg P kg⁻¹; and clay content, 196 g kg⁻¹. Granulated and bulk-blended PK fertilizers were thoroughly mixed with 4 kg of soil at 400 mg P kg⁻¹ and 400 mg K kg⁻¹.

Abbreviations: MCP, monocalcium phosphate; SSP, single superphosphate.
The corresponding rates of Cd added were 0 from MCP and 0.55 mg Cd kg\(^{-1}\) from SSP. A check of soil without P and K was also included in the treatments. Other nutrients were also added to all the treatments at the rates of 1.74 g N urea, 200 mg MgSO\(_4\), 7H\(_2\)O, 50 mg CuSO\(_4\), 5H\(_2\)O, 20 mg ZnSO\(_4\), 7H\(_2\)O, and 20 mg Na\(_2\)B\(_4\)O\(_7\)·10H\(_2\)O per pot. The pots were placed in a randomized complete block design with three replicates for each treatment. Upland rice, soybean, and signalgrass were planted. Soil moisture was maintained at approximately 80% of field capacity by watering daily. The average daylength time was 10 to 12 h and temperature was 32 to 36°C during the plant growth. Both upland rice and soybean were grown to maturity. For signalgrass, four cuts were made with the PK treatments, whereas only one cut was made with the check.

For upland rice, grain and straw were collected at harvesting. For soybean, grain, leaf, stem, and pod were separately collected. After harvesting of aboveground soybean plant parts, the soil in pots was carefully washed with water on a screen to obtain soil-free soybean root samples. The plant samples of upland rice, soybean, and signalgrass were dried in a forced-air cabinet at 65°C for 10 d followed by grinding. For soybean, the ground samples of leaf, stem, and pod were combined (hereafter called soybean “straw”). To determine Cd concentrations in plant samples, the ground plant samples were ashed in the furnace at 400°C. The samples were then dissolved with 5 M HNO\(_3\) at 90°C, and concentrations of Cd in the solutions were then determined by an inductively coupled plasma (ICP) spectrometer. The detection limit for Cd was 0.002 to 0.004 mg Cd L\(^{-1}\) in solution corresponding to 0.008 to 0.015 mg Cd kg\(^{-1}\) of plant tissue. Data of different parts of plant tissue weights and Cd concentrations were analyzed statistically by analysis of variance using the Statistical Analysis System (SAS) computer package (SAS Institute, 1985). The least significant difference (LSD) test was then used to make comparisons among the means of treatments at the 0.05 level of significance.

**Results and Discussion**

It is well known that, unlike Cd from industrial wastes and biosolids that generally contain very high Cd content and are applied at very high rates (Mg ha\(^{-1}\)), Cd accumulation in soil and Cd uptake from annually applied P fertilizers at normal rates (kg ha\(^{-1}\)) could be an environmental issue only after long-term applications of P fertilizers (Mortvedt, 1987; Mulla et al., 1980; Rothbaum et al., 1986; Loganthan et al., 1995). Short-term P application should not result in a serious Cd accumulation in soils and its subsequent Cd uptake by crops, unless P fertilizers contain unusually high Cd content. Since it is difficult to conduct a long-term greenhouse experiment on Cd from annual P applications at normal rates, we tried to shorten the time frame by one-time application of a high PK rate at 400 mg kg\(^{-1}\) based on the following assumptions:

- The strong complexes of (CdCl\(_2\))^\(-\) and (CdCl\(_2\))\(^0\) could form and accumulate in soils from long-term annual applications of granulated PK fertilizers. If so, the amount of Cd–Cl complexes formed from one-time PK application at a high rate might be proportional to that from long-term annual applications of PK fertilizer at normal rates.
- There would be no P and Cd interaction in soils from the granulated PK fertilizers applied by long-term annual applications at normal rates or one-time application at a high rate. Mortvedt (1982) suggested that the chemical form of Cd contained in water-soluble P fertilizers is Cd(H\(_2\)PO\(_4\))\(_2\), CdHPO\(_4\), or a mixture of these salts, which would be predicted to form during the manufacture of these P fertilizers. Thus, it could be assumed that Cd would not react further with P in soil solution from the applied P fertilizers.
- Mortvedt (1982) found that crop response to P sources containing various Cd concentrations was similar for the forage harvest and the mature harvest. He suggested that early crop response to P fertilizers can be used to predict results in the mature crop. Therefore, he concluded that greenhouse evaluation based on results harvesting immature forage crops may be valid in predicting crop response throughout the entire season. On similar assumption, we could also predict Cd uptake by crops for long-term annual applications of PK fertilizers at normal rates from the results obtained by one-time application at a high rate in greenhouse experiments.
- Since Cd availability in soils decreases with time (Bidwell and Dowdy, 1987), a short-term one-time application of PK fertilizers at a high rate would not overestimate potential Cd availability from the long-term annual applications at normal rates (Chien and Menon, 1994a).

The results of the upland rice experiment are shown in Table 1. All the PK fertilizers, whether granulated or bulk-blended, were equally effective in increasing grain yield of upland rice. Since KCl, SSP, and MCP were all water soluble and the granule size of granulated and bulk-blended PK fertilizers was the same, their P and K availabilities would be expected to be the same. Rice grain yield increased from 1.2 g pot\(^{-1}\) with the check (no P and K) to the average value of 23.6 g pot\(^{-1}\) with PK fertilizers, indicating a strong PK effect on rice grain yield.

It should be pointed out that potential Cd toxicity to human health from Cd-contaminated food crops is based on Cd concentrations in edible parts of crops rather than total Cd uptake by crops. For example, the maximum permissible Cd concentrations in cereal grains generally adopted by European countries are 0.10 to 0.15 mg Cd kg\(^{-1}\) (deBoo, 1990). A low Cd concentration associated with application of Cd-containing P fertilizers could be an environmental issue only after long-term applications of granulated PK fertilizers. If so, the amount of Cd–Cl complexes formed from one-time PK application at a high rate might be proportional to that from long-term annual applications of PK fertilizer at normal rates.

**Table 1. Grain yield of upland rice and Cd concentrations in rice, grain, and straw.**

<table>
<thead>
<tr>
<th>PK source†</th>
<th>Grain yield‡</th>
<th>Grain concentration</th>
<th>Straw concentration</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>g pot(^{-1})</td>
<td>mg kg(^{-1})</td>
</tr>
<tr>
<td>Granulated (SSP + KCl)</td>
<td>22.6A§</td>
<td>0.13A</td>
<td>1.53A</td>
</tr>
<tr>
<td>Bulk-blended (SSP) + (KCl)</td>
<td>23.1A</td>
<td>0.12A</td>
<td>1.18B</td>
</tr>
<tr>
<td>Bulk-blended (MCP) + (KCl)</td>
<td>25.1A</td>
<td>0.01B</td>
<td>0.20C</td>
</tr>
</tbody>
</table>

† MCP, monocalcium phosphate; SSP, single superphosphate.
‡ Grain yield of check (no P and K = 1.2 g pot\(^{-1}\)).
§ Values followed by the same letter within column are not significantly different (P < 0.05).
tilizer, however, does not necessarily indicate a low total Cd uptake because of a possible dilution effect. If a soil is deficient in available P, application of P to the soil will increase the plant’s growth and produce higher yield, which frequently decreases plant Cd concentration (Mortvedt, 1987, Chien and Menon, 1994b). Therefore, to compare plant Cd concentrations associated with different treatments, we should also consider their plant yields. In the present study, all of the P treatments produced about the same crop yield, and thus a direct comparison of Cd concentration in plants can be made. In other words, Cd uptake and Cd concentration are equally related to Cd availability from the P sources in the soil.

Concentrations of Cd in rice grain and straw were much higher with granulated (SSP + KCl) or bulk-blended (SSP) + (KCl) than Cd concentrations with bulk-blended (MCP) + (KCl) (Table 1). There was no significant difference in Cd concentration in rice grain between granulated and bulk-blended (SSP) + (KCl). However, Cd concentration in rice straw was significantly higher with granulated (SSP + KCl) than that with bulk-blended (SSP) + (KCl). The results thus tended to support the hypothesis that Cl– probably complexed with Cd2+ to form soluble complexes in soil solution from granulated (SSP + KCl), thereby increasing Cd concentration in rice straw as compared with bulk-blended (SSP) + (KCl). The lack of Cl effect on Cd concentration in rice grain between granulated (SSP + KCl) and bulk-blended (SSP) + (KCl) was probably due to a low Cd uptake by rice grain as compared with that by rice straw. Data in Table 1 show that Cd concentrations in rice straw were about 10 times that in rice grain. Iretskaya et al. (1998) also observed that Cd concentration in upland rice straw was much higher than that in rice grain.

The results of the soybean and signalgrass experiments are shown in Tables 2 and 3. Application of PK fertilizers greatly increased the grain yield of soybean and dry-matter yield of signalgrass and there were no significant differences between granulated and bulk-blended PK fertilizers. Concentrations of Cd in different parts of plant tissue followed the order of granulated (SSP + KCl) > bulk-blended (SSP) + (KCl) > bulk-blended (MCP) + (KCl), suggesting possible formation of soluble ion-pair complexes of Cd2+ and Cl– when granulated (SSP + KCl) dissolved in soil solution. Similar to upland rice (Table 1), concentrations of Cd of soybean straw and root were much higher than Cd concentrations of soybean grain (Table 2).

The results obtained in this preliminary study suggest that if a P fertilizer contains a high Cd content, granulation of this P fertilizer with KCl may result in a higher Cd uptake by crops compared with the same but bulk-blended PK fertilizer. Because of the simplicity of the bulk-blending process and its relatively low investment and operating cost, bulk blending has become popular worldwide (Shultz, 1988). The present study suggests that bulk blending of PK fertilizers may have another beneficial effect, that is, less Cd uptake by crops from Cd-containing P fertilizers as compared with the process of PK granulation. However, more agronomic research work with different crops is needed to confirm this possibility, especially under field conditions. Also, different P to K ratios and N fertilizers such as urea were not granulated with PK fertilizers in the present study. Therefore, there is a need to study the effect of P to K ratio and N source in granulated and bulk-blended NPK fertilizers on Cd availability to crops from Cd-containing P fertilizers.

### Table 3. Dry-matter yield and Cd concentration of signalgrass.

| PK source† | Dry-matter yield‡ | Cd concentration
<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
<td>g pot⁻¹</td>
<td>mg kg⁻¹</td>
</tr>
<tr>
<td>Granulated (SSP + KCl)</td>
<td>43.9A§</td>
<td>0.24A</td>
</tr>
<tr>
<td>Bulk-blended (SSP) + (KCl)</td>
<td>42.8A§</td>
<td>0.21B</td>
</tr>
<tr>
<td>Bulk-blended (MCP) + (KCl)</td>
<td>41.5A§</td>
<td>0.08C</td>
</tr>
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</table>

† MCP, monocalcium phosphate; SSP, single superphosphate.
‡ Dry-matter yield of check (no P and K) = 4.1 g pot⁻¹.
§ Values followed by the same letter within the columns are not significantly different (P < 0.05).

### References


### Table 2. Grain yield of soybean and Cd concentrations in soybean, grain, straw, and root.

| PK source† | Grain yield‡ | Cd concentration
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g pot⁻¹</td>
<td>mg kg⁻¹</td>
</tr>
<tr>
<td>Granulated (SSP + KCl)</td>
<td>27.1A§</td>
<td>0.54A 1.66A 1.34A</td>
</tr>
<tr>
<td>Bulk-blended (SSP) + (KCl)</td>
<td>29.5A§</td>
<td>0.35B 0.88B 0.99B</td>
</tr>
<tr>
<td>Bulk-blended (MCP) + (KCl)</td>
<td>23.8A§</td>
<td>0.06C 0.26C 0.27C</td>
</tr>
</tbody>
</table>

† MCP, monocalcium phosphate; SSP, single superphosphate.
‡ Grain yield of check (no P and K) = 1.4 g pot⁻¹.
§ Combined leaf, stem, and pod samples.
¶ Values followed by the same letter within the columns are not significantly different (P < 0.05).