

# **Cadmium Contamination of Agricultural Soils in Catchment of Yamuna Ravine: Response of Sulfur on Yield and Quality of Oat**

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**Continuous use of diammonium and single super phosphates having traces of cadmium (02 to 200 ppm) is contaminating agricultural soils. In order to assess the levels of cadmium contamination of semiarid Indo-gangetic soils in Yamuna ravines and crop quality, a green house study was conducted in oat crop with four levels (mg kg-1 of soil) each of cadmium**  (Cd<sub>o</sub>: 0, Cd<sub>1</sub>: 12.5, Cd<sub>2</sub>: 25.0 and Cd<sub>3</sub>: 50.0) and sulfur (S<sub>o</sub>: 0, S<sub>1</sub>: 12.5, S<sub>2</sub>: 25.0 and S<sub>3</sub>: 50.0) in **factorial randomized block design. Results revealed that increasing Cd doses significantly decreased grain (3.98 g pot-1 in Cd<sup>0</sup> to 2.50 g pot-1 in Cd3) and straw (5.59 g pot-1 in Cd0 to 4.07 g pot-1 in Cd3) yields. Increasing Cd doses significantly enhanced Cd (g pot-1 ) in biological harvest (2.7 in Cd0 to 7.3 in Cd3 in grain and 5.8 in Cd0 to 23.2 in Cd3 in straw) and decreased S (g kg-1 ) in biological harvest in treatment (0.29 in Cd0 to 0.21 in Cd3 in grain and 0.18 in Cd0 to 0.13 in Cd3 in straw) and interactions (0.32 in Cd0 to 0.18 in Cd3 x S0 x S3 in grain and 0.20 in Cd0 x S3 to 0.11 in Cd3 x S0 in straw), over various S doses. Thus, Cd inhibited plant biochemical processes and metabolism and enhanced sink and consumption of reduced sulfur as indicated by lower S in grain and straw. Increasing S enhanced S (mg kg-1 ) in grain (0.21in S0 to 0.28 in S3) and straw (0.14 in S0 to 0.17 in S3) under varying Cd stress confirming mitigation in uptake, accumulation and toxicity of Cd as well as higher S translocation from aerial parts to grain. Cd recovered in biological harvest in Cd0 revealed that semi arid alluvium**  soils are already considerably cadmium polluted. Singnificantly higher productivity (g pot<sup>-1</sup>) **was recorded in Cd0 and S2 for grain and straw i.e. 3.98 and 3.59 and 5.99 and 5.52, respectively. Among interactions, singnificantly higher productivity (g pot-1 ) was recorded in Cd<sup>0</sup> x S<sup>2</sup> for grain (4.34) and straw (6.51). Cd<sup>3</sup> x S<sup>3</sup> produced minimum grain (2.37 g pot-1 ) and straw (4.20 g pot-1 ) yield. Thus, S partially mitigated Cd stress upto 25 mg kg-1 of soil and also maintained higher oat yields.**

**Key words:** Cadmium, Oats, Food chain contamination, Food quality, Heavy metal, Health hazard.

Contamination of agricultural soils with traces of harmful non essential heavy metals and crop quality is a matter of high concern for food and livelihood security of burgeoning population and environment. Cd, a common bio toxic non essential heavy metal (density:  $>5g$  cm<sup>-1</sup>), is readily taken up by plants via the same pathway as for essential heavy metals like Fe, Cu and Zn. Cd produces toxicity and hypertension of kidney in human on consumption. Cd has relatively high mobility in soil-plant system (Clemens 2006), reduces plant growth and chlorophyll and adversely influences enzymes of C, N and S metabolism and guaiacol peroxide activity (Astolfi *et al* 2004). Cd enhanced soybean and maize yield up to 5.0 and 7.5 ppm, respectively but these were upper critical limit in the reference crop (Sakal *et. al.,* 1996). Food chain contamination due to pollution of agricultural soils by traces of Cd (mineral green ockite and Cd linked with zinc) and

heavy use of phosphoric fertilizers (2 to 200 ppm Cd), needs to be prevented. Detoxification of Cd in soils through nutrient interactions in soil and plant systems using appropriate nutrient schedules may be a practically feasible and economically viable option to growers, users and environmentalists. S, a ubiquitous essential element, acts as a catalyst in plant metabolism and biochemical and physiological processes. S is a structural component of amino acids (cysteine and methionine), iron sulfur clusters, polysaccharides, lipids, vitamins (thiamine and biotine), peptides (glutathione and phytochelatins), cofactors (Co A, S-adenosyl-Met) and secondary products (allyl Cys sulfoxides and glucosinolates). Cellular roles of S extend to regulation of enzyme activity (eg. proteolytic and nitrogenase), redox cycle, xenobiotic detoxifications etc. Sulfhydryl group (-SH) confers many thiols having ability to react with a broad spectrum of agents i.e. free radicals to heavy metals

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(Rabenstein, 1989). Main source of S for plants is sulfate iron and limitation of soil sulfate drastically influences plant growth and productivity. S request of plants is demand driven in accordance with the environments that plants experience during their growth. Plant S request suddenly enhances under both abiotic and biotic stresses. Crop demand for S is almost identical to phosphorus but use of S is manyfold lower than phosphorus in Indian agriculture characterized by maximum acerage under cereals. Factors associated with low S use in India are unawareness of growers about optimum S schedules in different Crop in various agro-climates, subsistent agriculture and poor socio-economic status, non responsive S varieties, incidental S returns to soil through farm yard manure and use of S conventional and S containing fertilizers (eg. single super phosphate and diammonium sulphate). Soil S mining by Crop has rapidly raised during post green revolution in India and widespread soil S deficiency is being encountered. The situation is further aggravated by decreasing use of manures and organic fertilizers. Until S mining is not balanced, optimum gains from intensive use of N, P and K fertilizers and other investments in Indian agriculture, can not be realized, particularly on light textured soils having low organic matter and being highly prone to S deficiency. S influences uptake of P and N but had no or meager residual effect. S favorably influences yield of S containing essential amino acids and proteins and enhances productivity of cereals and grasses. S response on Indo-gangetic alluvium soils was oilseeds> pulses> cereals (Ramkala and Gupta, 1999). S responded more in oat than wheat and barley (66 kg forage kg-

 $1$  of soil S application) while response of S (20 to 60 kg ha<sup>-1</sup>) in cereals was 638 to 813 kg grain ha<sup>-1</sup>. Cereals have S uptake equivalent to 3 to 4 kg ton-1 of biomass (Tripathy and Hazra, 1992). Plant nutrition not only depends on soil nutrient supplying potential but also on nutrients absorption rate, mobility in plant and distribution to functional sites. Each one of these processes is influenced by interactions between micro and macro nutrients in soil and plant systems which modify plant nutrition and determine ultimate productivity. However, information on interaction of Cd and S in Crop raised on deep alluvium soils in semi arid India is extremely meager; therefore, a green house study was conducted to assess the effect of different levels of S and Cd on yield and quality of oat.

## **Materials and Methods**

This study was carried out as pot experiment during 2004-05 in a fully equipped green house at Raja Balwant Singh College, Bichpuri, Agra in Uttar Pradesh, India located at a latitute of 27.2 <sup>0</sup>N and longitude of  $77.9$   $^0$ E at 163.4 m from msl. The study site had semi-arid sub tropical climate (average annual rainfall: 650 mm). Soil (upper 0-20 cm depth) from a cultivated field of Research Farm of the

college was used to carry out pot experiment. Soil had sandy texture (61.56 % sand, 20.65 % silt and 17.79 % clay), pH: 8.0, electrical conductivity: 0.19 dSm<sup>-1</sup>, CaCO<sub>3</sub>: 5.0 g kg<sup>-1</sup>, organic carbon: 3.9 g kg<sup>-</sup> <sup>1</sup>, available nitrogen: 78.0 mg kg<sup>-1</sup>, available phosphorus: 4.8 mg kg-1 , available potassium: 105 mg kg-1 , available S: 8.5 mg kg-1 and available Cd: 0.06 mg kg<sup>-1</sup>. pH, electrical conductivity, CaCO<sub>3</sub>, organic carbon, available N, available phophorus, available potassium, available S and available Cd were determined following standard procedures. Plant samples were carefully washed with deionised water, rinsed twice with distilled water, oven dried at 65-70 °C, ground well with pestle and mortar and stored in wide mouth glass stoppered bottles with proper labeling. The ground material was subjected to chemical analysis. Treatment comprising of four levels of Cd (Cdo: 0, Cd1: 12.5, Cd<sub>2</sub>: 25.0 and Cd<sub>3</sub>: 50 mg  $kg<sup>-1</sup>$ of soil) and four levels of S  $(S_0: 0, S_1: 12.5, S_2: 25.0 \text{ and } S_3: 50.0 \text{)}$ mg kg-1of soil) were tested in factorial randomized block design with three replications. Polythene lined earthen pots having holes at the bottom for proper aeration were filled with five kilograms of well pulverized soil. Recommended dose of nitrogenous, phosphoric and potassic fertilizers were applied to each pot before sowing. Ten seeds of oat pot<sup>-1</sup> was sown on 25 December 2004. Nitrogen, phosphorus and potassium were applied as urea, diammonuim phosphate and murate of potash, respectively. S was applied as elemental S while Cd as cadmium chloride at the time of sowing. Deionized water was uniformely applied for irrigating oat plants in accordance with recommended irrigation schedule for the region. Grain and straw samples were collected for chemical analysis at harvest on 7 April 2005. Data obtained were statistically analyzed using standard schedule of factorial randomized block design.

## **Results and Discussion**

## *Grain and straw yield of oat*

Increasing Cd doses significantly decreased both grain and straw yields at each increment over different S levels (Table 1) showing toxic effect of Cd on biochemical processes, metabolism and physiology of oat plants. Minimum grain (2.50 g pot<sup>-1</sup>) and straw  $(4.07 \text{ g} \text{ pot}^{-1})$  yield was recorded at the highest Cd level (Cd3) which may be attributed due to biological Cd accumulation and associated toxic effects (chlorosis, wilting and growth reduction due to cell death). Cd interferes carbohydrate metabolism (Sanita di Toppi and Gabrielli 1999), nitrate absorption and reduction (Hernandez *et. al.,* 1996), enzyme catalysts (Van Assche and Clijsters

1990), water balance (Perfus-Barbeoch *et. al.,* 2002) and photosynthesis (Pietrini *et. al.,* 2003). Oat grain yield (g pot<sup>-1</sup>) ranged between 2.50 in  $Cd<sub>3</sub>$  to 3.98 in Cd<sub>o</sub> (59.2 % reduction at 50 mg Cd kg<sup>-1</sup> of soil than control) which showed enhanced Cd toxicity and



**Table 1. Effect of different levels of cadmium and sulfur on grain and straw yield of oat in semi arid India**

ionic imbalances at higher heavy metal stress (Sarkunan *et. .al.,* 1998). Oat productivity significantly declined even at lowest level  $(Cd_1)$  which may be again attributed to extreme capability of Cd to bind sulfhydryl group of proteins leading to enzyme deactivation and oxidative stress induced by formation of superoxide anion and hydrogen peroxide (Romero-Puertas *et. al.,* 2004). S significantly enhanced both grain and straw yield upto 25 mg kg<sup>-1</sup> of soil i.e. each incremental dose of S significantly enhanced grain and straw yield of oat plants over different Cd stress. This may be attributed due to diverse role of S in plant physiology including protein and chlorophyll synthesis and formation of a stable high molecular weight S-Cd complex that is essential for maximum Cd detoxification. Results on S response in this study (S2> S1> S3> S0) can be supported by Sarkunan *et. al.* (1998) who recorded deterioration in crop productivity at higher S level.  $Cd_3 \times S_3$  produced maximum and significant decline in oat grain yield which showed that enhanced Cd stress at Cd3 was not fully mitigated by S use even at S<sub>3</sub> level. However, variations produced by Cd x S interactions in straw yield of oat were not significant. Thus, strength of sink for S request by oat plants at the highest level of Cd stress did not exceed 25 mg

 $S$  kg<sup>-1</sup> of soil in this study. Enhanced sulfate assimilation, glutathione biosynthesis and Cd detoxification are common response of plants that constitute glutathione consuming activities but plant S request depends on strength of Cd induced additional sink for thiol compounds (Nocito *et. al.,* 2006). Thus, not only adequate soil S supply but also other associated processes in Cd detoxification need to be investigated to fully mitigate higher Cd

stress. Modulation of S flux along the whole plant is needed for Cd detoxification (Herbette *et. al.,* 2006) as greater production of glutathione provided higher Cd tolerance and detoxification (Zhu *et.al.,*

# of soil) also need to be further investigated. *Cadmium content in grain and straw of oat*

Cd content in grain and straw of oat plants significantly enhanced on increase in Cd stress  $(Cd_3>Cd_2>Cd_1>Cd_0)$  (Table 2). This may be attributed due to quicker uptake of Cd at each incremental Cd dose. The results obtained on Cd uptake and assimilation are supported by Hirschi *et. al.* (2000) who reported 1.6 to 2.1 fold more Cd

1999a and 1999b). Thus, factors inhibiting S flux along whole plant at higher Cd stress (50 mg kg-1

**Table 2. Effect of different levels of cadmium and sulfur on cadmium content in grain and straw of oat in semi arid India**

| Cadmium level                                   |             |      |        | Sulfur level |               |  |  |  |  |
|---|-------------|------|--------|--------------|---------------|--|--|--|--|
|   | $(mg kg-1)$ |      |        | $(mg kg-1)$  |               |  |  |  |  |
|   | 0.0         | 12.5 | 25.0   | 50.0         | Mean          |  |  |  |  |
| Cadmium content in grain (mg kg <sup>-1</sup> ) |             |      |        |              |               |  |  |  |  |
| 0.0   | 3.5         | 2.7  | 2.5    | 1.9          | 2.7           |  |  |  |  |
| 12.5  | 5.2         | 3.9  | 3.0    | 2.7          | 3.7           |  |  |  |  |
| 25.0  | 6.7         | 6.1  | 5.8    | 5.1          | 5.9           |  |  |  |  |
| 50.0  | 9.5         | 7.4  | 6.5    | 5.7          | 7.3           |  |  |  |  |
| Mean  | 6.2         | 5.0  | 4.5    | 3.9          |               |  |  |  |  |
|   | Cadmium     |      | Sulfur |              | $Cd \times S$ |  |  |  |  |
| SE (P=0.05)                                     | 0.1         |      | 0.1    |              | 0.2           |  |  |  |  |
| Cadmium   | 0.2         |      | 0.2    |              | 0.4           |  |  |  |  |
| Cadmium content in straw (mg kg <sup>-1</sup> ) |             |      |        |              |               |  |  |  |  |
| 0.0   | 6.8         | 6.0  | 5.6    | 4.7          | 5.8           |  |  |  |  |
| 12.5  | 13.6        | 11.0 | 10.0   | 9.2          | 11.0          |  |  |  |  |
| 25.0  | 17.0        | 14.9 | 14.0   | 12.5         | 14.6          |  |  |  |  |
| 50.0  | 31.7        | 24.0 | 19.5   | 17.5         | 23.2          |  |  |  |  |
| Mean  | 17.3        | 14.0 | 12.3   | 11.0         |               |  |  |  |  |
|   | Cadmium     |      | Sulfur |              | $Cd \times S$ |  |  |  |  |
| SE (P=0.05)                                     | 0.2         |      | 0.2    |              | 0.4           |  |  |  |  |
| Cadmium   | 0.4         |      | 0.4    |              | 0.9           |  |  |  |  |

than control in transgenic tobacco plants. Cd content (mg  $kg^{-1}$ ) in oat grain ranged between 2.7 in Cdo to 7.3 in Cd3 while in straw Cd ranged between 5.8 in  $Cd<sub>0</sub>$  to 23.2 in  $Cd<sub>3</sub>$ . Thus, Cd uptake enhanced 2.7 fold in grain and 4.0 fold in straw at 50 mg Cd  $kg^{-1}$  of soil than control. Higher Cd in straw than grain shows that source to sink flow of Cd (translocation from aerial parts to grain) was inhibited which may be attributed due to enhanced glutathione consumption. Even at Cd<sub>0</sub>, appreciable Cd traces were recovered in grain and straw indicating that alluvium soils of semi arid India have considerably been polluted by Cd due to continuous use of single super and diammonium phosphates. Sarkunan *et. al.* (1998) have also reported higher Cd in grain and straw at increasing Cd levels. S significantly decreased Cd (mg kg<sup>-1</sup>) in grain  $(6.2 \text{ in } S_0 \text{ to } 3.9 \text{ in } S_3)$  and straw  $(17.3 \text{ in } S_0 \text{ to } 11.0 \text{ in } S_0)$ S<sub>3</sub>) revealing detoxification of Cd (58.97 % in grain and 57.27 % in

| Cadmium level<br>$(mq kq^{-1})$         |         | Sulfur level (mg $kg^{-1}$ ) |        |      |               |  |  |  |  |
|---|---------|------------------------------|--------|------|---------------|--|--|--|--|
|   | 0       | 12.5                         | 25     | 50   | Mean          |  |  |  |  |
| Sulfur content in grain (mg $kg^{-1}$ ) |         |                              |        |      |               |  |  |  |  |
| 0.0                                     | 0.25    | 0.27                         | 0.30   | 0.32 | 0.29          |  |  |  |  |
| 12.5                                    | 0.23    | 0.25                         | 0.27   | 0.29 | 0.26          |  |  |  |  |
| 25.0                                    | 0.19    | 0.23                         | 0.27   | 0.27 | 0.24          |  |  |  |  |
| 50.0                                    | 0.18    | 0.20                         | 0.23   | 0.24 | 0.21          |  |  |  |  |
| Mean                                    | 0.21    | 0.24                         | 0.27   | 0.28 |               |  |  |  |  |
|   | Cadmium |                              | Sulfur |      | $Cd \times S$ |  |  |  |  |
| SE (P=0.05)                             | 0.01    |                              | 0.01   |      | 0.01          |  |  |  |  |
| Cadmium                                 | 0.01    |                              | 0.01   |      | NS            |  |  |  |  |
| Sulfur content in straw (mg $kg^{-1}$ ) |         |                              |        |      |               |  |  |  |  |
| 0.0                                     | 0.16    | 0.18                         | 0.19   | 0.20 | 0.18          |  |  |  |  |
| 12.5                                    | 0.14    | 0.15                         | 0.17   | 0.18 | 0.16          |  |  |  |  |
| 25.0                                    | 0.13    | 0.14                         | 0.15   | 0.16 | 0.15          |  |  |  |  |
| 50.0                                    | 0.11    | 0.12                         | 0.14   | 0.15 | 0.13          |  |  |  |  |
| Mean                                    | 0.14    | 0.15                         | 0.16   | 0.17 |               |  |  |  |  |
|   | Cadmium |                              | Sulfur |      | $Cd \times S$ |  |  |  |  |
| SE (P=0.05) 0.01                        |         |                              | 0.01   |      | 0.01          |  |  |  |  |
| Cadmium                                 | 0.01    |                              | 0.01   |      | NS            |  |  |  |  |

**Table 3. Effect of different levels of cadmium and sulfur on S content in grain and straw of oat in semi arid India**

straw). The results obtained on detoxification of Cd by S are supported by Herbette *et. al.* (2006) and Nocito *et. al*. (2006). Also, formation of insoluble cadmium-sulphide complexes in soil restricts mobilization and transport of Cd. Such restriction may lower Cd uptake and assimilation in grain and straw of oat plants at higher S levels. Interactive effect of Cd x S on Cd content in grain and straw of oat was significant at all levels of S. Contrary to this, increasing S doses significantly decreased Cd levels in grain which endorse enhancement in reduced sulfur uptake on increasing Cd stress by oat plants. Maximum Cd in grain and straw of oat plants were recorded in  $S_0$  x  $Cd_3$  when no S was applied. This indicates that S inhibited Cd uptake by oat plants while increasing Cd doses enhanced Cd content in grain and straw even up to a maximum dose of 50 mg Cd kg-1 of soil revealing that increased Cd doses significantly enhanced Cd uptake by oat plants. Thus, it is well evident from the data that addition of S in soil partly mitigated Cd stress (uptake and toxicity) of oat plants on alluvium soils of semi arid India.

### *Sulfur content in grain and straw of oat*

Increasing Cd doses significantly decreased S levels in grain and straw of oat than control (Table 3). This may be attributed due to more glutathion consumption and deactivation in physiology of oat plants due to inhibition in chlorophyll synthesis, enzyme activation and other toxic effects of Cd. S (mg  $kg^{-1}$ ) in oat grain decreased from 0.29 in Cd<sub>0</sub> to 0.21 in Cd3 (33.33 %) while corresponding decrease in oat straw was 0.18 to 0.13 (21.43 %). Thus, either S ion uptake and assimilation in oat plants was

adversely affected at higher Cd stress that inhibited plant metabolism, biochemical processes and activeness of plant cells or more Cd stress led to higher biosynthesis and consumption of glutathione for Cd detoxification that reduced S levels in oat plant. S content (mg kg-1 ) in oat grain and straw increased with increase in S dose (0.21 in  $S_0$  to 0.28 in  $S_3$  in grain and  $0.14$  in S<sub>0</sub> to  $0.17$  in S<sub>3</sub>). Higher S content in grain and straw reveals enhanced translocation of S from aerial parts of oat plants to grain. This may be attributed due to enhancement in S content in plant biomass to plant responses to biotic and abiotic stresses. Cd stress enhanced reduced S request of plants for enhanced biosynthesis of glutathione due to induced S metabolism (Herbette *et. al*., 2006 and Nocito *et. al.,* 2006). To sustain Cd detoxification, total S request of plant is enhanced in this study too. More application of S in soil led to more S uptake by oat plants as revealed by S assimilation in grain and straw. Results on enhanced S assimilation in plants are supported by Sarkunan *et. al.,* (1998). However, interaction effect of Cd x S on S in grain and straw of oat plants was non-significant. Maximum S in grain and straw were recorded under  $Cd_0$  x  $S_3$ . This showed that any Cd addition in soil inhibited sulphate ion uptake and assimilation in oat plants. Application of S significantly decreased Cd levels in grain and straw which may be attributed due to lower uptake of Cd at higher levels of S. Plant S metabolism is deeply affected by Cd stress due to wide range of adoptive responses mainly glutathione which acts as direct or indirect antioxidant in mitigating Cd. This ultimately induces oxidative stress as rise in Cd levels depletes cell glutathione level which enhances plant demand for reduced S compounds (Fabio *et. al.,* 2007). Use of S mitigated Cd stress in oat plants due to lower Cd uptake and/ or detoxification of assimilated Cd.

### **Conclusion**

Application of chemicals in Indian agriculture mainly continuous use of substantive quantities of single super and diammonium phosphates have built considerable Cd levels in alluvium soils of semi arid India. Heavy metal pollution of Indian soils through non essential heavy metals like Cd has wide and long lasting implications (endanger to sustainable crop productivity, contamination of food stuffs and future food, human and cattle health security). Cd not only declined the oat productivity but also contaminated grain and straw and apart from decreasing the S levels in biological parts of plants at higher Cd stress. Cd recovered in oat plants (3.5 mg  $kg^{-1}$  in grain and 6.8 mg kg $^{-1}$  in straw) at Cd<sub>0</sub> was just only reduced by 1.6 mg  $kg^{-1}$  in grain and 2.1 mg  $kg^{-1}$  in straw using 25 mg S kg<sup>-1</sup> of soil. This showed that though the use of S inhibited plant uptake of Cd and/ or led to Cd detoxification, even then considerable Cd traces were yet available in soil and recovered in oat plants. This attracts the

attention of researchers to achieve a decline in the Cd to negligible levels in soil and crop biomass and warns planners, environmentalists, fertilizer and chemical industries and growers for holistic solution of the problem of heavy metal contamination of agricultural soils in semi arid India and other parts round the globe.

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