

## COCLUSIONS

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Environmental pollution associated with burning of fossil fuels has a serious threat on ecosystem and human health. Environmental pollution caused through emissions of smoke, gases, various effluents, and solid wastes from power plants is one of the crucial issues of global concern. Since, there were no comprehensive studies on the mode of occurrence and behavior of trace elements in the soils, fly ash, bottom ash, vegetation and water around Guru Nanak Dev Thermal Power Plant, Bathinda, Punjab; an exploratory study on trace elemental contamination and speciation in the terrestrial environment around the coal fired GNDTPP, Bathinda was carried out. For the purpose of this study, trace elemental analysis on soils, coal ashes (fly ash and bottom ash), vegetation, ground water and surface water was carried out. Three solid matrices viz. soils, fly ash and bottom ash around GNDTPP Bathinda, Punjab were subjected to single as well as two established sequential extraction procedures (i.e. Tessier's SEP and modified-BCR SEP) for trace elemental speciation. The following conclusions can be drawn from this study:

The soils of the study area are alkaline in nature. The electrical conductivity observed in the soils of the study area suggests that most of the soils fall in the non-saline salinity class, except the soils near bottom ash disposal site.

Total organic carbon in surface soils varied between 0.29 to 3.08%. Soils of the study area are calcareous in nature with higher carbonate content ( $11.45 \pm 2.19\%$ ). Particle size analysis following USDA texture triangle classification system shows that the texture of the surface soils varied between sandy loam to sandy clay loam.

Cd, Cr, Cu, Pb, Ni, and Zn contents in surface soils are within safe limits of Indian standards. The sequence of metal concentration in decreasing order was Ni>Zn>Pb>Cr>Cu>Cd for surface soils. Soils in downwind direction have higher trace elemental concentrations than in the soils in upwind direction. Soil metal concentrations in relation to depth suggests that the surface soils have predominantly elevated metal concentrations than the sub surface soils, indicating that the metal content is directly related to the anthropogenic deposition of heavy metals in surface soils. From both of the above observations it can be inferred that Guru Nanak Dev

Thermal Power plant, Bhatinda has contributed towards deposition of heavy metals in the terrestrial environment in its vicinity.

Correlation coefficients and Principal Component Analysis (PCA) used in this study are important statistical tools for better understanding of the source identification and dynamics of pollutants. Statistically significant correlations were found between Cr–Cu ( $r=0.516$ ), Cr–Ni ( $r=0.893$ ), Cr–Zn ( $r=0.621$ ), Cu–Ni ( $r=0.566$ ), Cu–Zn ( $r=0.546$ ) and Ni–Zn ( $r=0.737$ ). Cd and Pb were not significantly correlated with other metals. A strong correlation among elements i.e. Cr, Cu, Ni, and Zn indicates their common origin, which could be especially through the deposition of coal ashes and other emissions from GNDTPP, Bathinda.

Principal Component Analysis was carried out to ascertain the possible contributing factors towards the metal concentrations and thereby determine which metals have a common origin. High loading of Cr, Cu, Ni and Zn in principal component 1 (PC1) clearly indicates their common origin, which is beyond any doubt the technogenic or anthropogenic origin, because soils in the vicinity of Guru Nanak Dev Thermal Power Plant are getting enriched with these elements through deposition of coal ashes and other emissions from it. The second principal component (PC2) has high loadings of Cd and Pb. Pb appears to have mixed origin (natural as well as anthropogenic source) as it has loadings in both PC1 and PC2. Cd appears to be predominantly of natural origin as it has high loadings only in PC2. Also, Cd is not correlated significantly with any other studied element.

Fly ash from GNDTPP is slightly neutral to acidic, whereas bottom ash is alkaline in nature. Fly ash and bottom ash have low soluble salt contents. Both the fly ash and bottom ash have high level of organic carbon and carbonate content.

The heavy metal contents in both fly ash and bottom ash decreased in the order: Zn>Ni>Pb>Cr>Cu>>>Cd. Also, Cd, Cr, Cu, Pb, Ni, and Zn contents were found to be higher in fly ash than in bottom ash.

In the present study the accumulation and distribution pattern of metals viz. Cd, Cr, Cu, Pb, Ni and Zn in different parts of mustard and wheat crop is observed as roots > stem > leaves > seed for all the samples. Results indicate that the concentration of all the studied trace elements viz. Cd, Cr, Cu, Pb, Ni, and Zn are higher in mustard crop than wheat crop. The bioconcentration factor (BCF) and translocation factors (TF) for both

crops are less than unity, indicating that these crops are not hyper-accumulating trace elements. Alkaline and calcareous nature of soils of the area appears to be an important plausible reason for immobilizing the metals in soils and limiting the soil to root transfer of trace elements, and hence lower BCF for both the crops.

Assessment of water samples indicated that groundwater in study area is chemically not suitable for drinking purpose on the basis of high levels of  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{F}^-$  and TDS than the acceptable limits prescribed by WHO (2017) as well as BIS (2012) for drinking purpose. The concentration of some heavy metals viz. Cd, and Pb were exceeding the WHO (2017) and BIS (2012) prescribed limits for water. Cu, Ni and Zn were within permissible limits of WHO standards.

Trace elemental concentrations in the water, vegetation, soil, fly ash and bottom ash can be a useful parameter for characterization of contamination potential of thermal power plant. As a result, trace elements have accumulated to the extent that their distributions in water, vegetation, soil, fly ash, and bottom ash are capable of causing adverse health effects through the food chain to the human beings and animals.

To assess the potential mobility of Cd, Cr, Cu, Ni, Pb and Zn in soil and coal ashes, single extraction scheme using 0.05M EDTA (pH 7.0) was adopted. The EDTA extractability is highest for Cr followed by Cd, Ni, Zn, Pb, and Cu in the soils. Statistically significant and positive correlations were found between EDTA extractable Cd and total Cd ( $r=0.498$ ) and EDTA extractable Cr and total Cr ( $r=0.595$ ) in soils. EDTA extractability is highest for Cd followed by Cu, Pb, Zn, Ni, and Cr in the both fly ash and bottom ash.

The metal partitioning by sequential extraction schemes allowed us to elucidate metal associations with different operationally defined fractions and hence the potential mobility of these six elements in all three contaminated solid matrices.

In modified-BCR SEP, B1 fraction (exchangeable and carbonate bound) is the least abundant fraction for Cd, Cu, Pb, Ni and Zn in surface soils.

Reducible fraction (B2) is the third most abundant fraction for Pb, Cd, and Cu in soils. Organic bound (B3) fraction is the second most abundant fraction for the metals Cd, Cu, Pb, Ni, Zn and least abundant for Cr in soils.

B1 is least abundant fraction for Cr, Cu, Pb, Ni, and Zn and second most abundant for Cd in fly ash and bottom ash. This indicates that Cd has the highest mobility in comparison to other metals studied.

Reducible fraction (B2) is the third most abundant fraction for all six metals in fly ash and bottom ash. B3 fraction is the second most abundant fraction for 5 metals viz. Cr, Cu, Pb, Ni, and Zn and least abundant for Cd in both fly ash and bottom ash.

In all the three matrices speciation data indicates that all the six metals viz. Cd, Cr, Cu, Ni, Pb and Zn, are incorporated into residual fraction (B4) of modified-BCR scheme, which indicates the least mobility of these metals. The uniform fractionation pattern is observed for copper, lead, nickel, and zinc in all the three matrices i.e. soils, fly ash and bottom ash, by modified-BCR scheme.

By Tessier's scheme exchangeable fraction (T1) is the fifth most abundant fraction for Cd, Cu, Ni, Pb and Zn, and fourth most abundant fraction for Cr in soils. Present findings indicate the low mobility of these metals in soils.

Carbonate bound fraction (T2) is the fourth most abundant fraction for Cu, Pb, Ni and Zn and third most abundant for Cd, and fifth least abundant for Cr in soils.

Reducible fraction (T3) is the second most abundant fraction for Zn, third most abundant fraction for Pb, Cr and Ni, whilst the fourth most abundant fraction for Cd in soils. However, Fe-Mn bound fraction (T3) is the most abundant fraction for Cu.

In surface soils organic bound fraction (T4) is the second most abundant fraction for Cd, Cr, Pb, Ni, and Zn, while third most abundant for Cu. This indicates that these elements are present in the forms of stable organic complexes and metal sulfides.

Residual fraction (T5) is the most abundant fraction for Cd, Cr, Pb, Ni, and Zn, whilst second most abundant for Cu in soil.

Exchangeable fraction (T1) is found to be the fifth most abundant fraction for Cu, Pb and Ni in both type of ashes. T1 fraction had lowest extractabilities for Cu (<1%) in both ashes and highest for Cd in fly ash as well as in bottom ash in this fraction.

Carbonate bound fraction (T2) is second most abundant for Cd and Zn and least abundant for Cr in both type of ashes, whilst fourth most abundant for Cu, Pb and Ni in both type of ashes.

Reducible fraction (T3) is the third most abundant fraction for Cr, Pb, and Ni in bottom ash and Cd, Pb and Ni in fly ash. T3 is also second most abundant for Cr and Cu in fly ash and Cu in bottom ash.

Organic bound fraction (T4) is the second most abundant fraction for Pb, Ni and Cr in bottom ash and only for Pb and Ni in fly ash. Also, this fraction is fifth most abundant for Cd in both type of ashes and third most abundant for Cr and Cu in flyash and Cu in bottom ash. Zn is equally fractionated in T3 and T4, which are fourth most abundant Zn containing fractions in both types of ashes.

Residual fraction (T5) is the most abundant fraction for all the six studied metals in both types of ashes, which represents the metals are difficult to separate from this fraction and have lowest mobility and bioavailability and hence safe for environment.

Speciation data indicates that in all three solid matrices i.e. soils, fly ash and bottom ash, all six metals viz. Cd, Cr, Cu, Ni, Pb and Zn are found to have greatest overall affinity in the residual fraction by both schemes, which indicates that these metals are strongly bound to minerals and resistant components.

By using modified-BCR and Tessier's sequential extraction procedure satisfactory agreement is found between the gross metal concentration obtained by total digestion and the cumulative total obtained by adding metal content of all the fractions of SEPs in all the three solid matrices.

The distribution of metals among four equivalent fractions was compared for the two sequential extraction procedures in soil and coal ashes (flyash and bottom ash). Generally in acid soluble fraction Tessier's scheme tends to extract relatively higher metal content than the modified-BCR scheme irrespective of the matrix type and metal extracted, indicating  $\text{MgCl}_2$  and NaOAC to show superior selectivity and greater efficiency in extracting these metals from carbonate phases, as compared to the acetic acid used in modified-BCR scheme.

In reducible fraction the Tessier's scheme extracted higher levels of Cu, Pb and Cr in both type of coal ashes, whereas more of Cu and Zn in soils. Although, similar reagents are used for extraction in this fraction in both schemes but experimental conditions are different. This indicates that stronger experimental conditions are maintained in Tessier's scheme in this fraction.

In organic/ sulfide bound fraction more Cd, Cr, Cu and Ni are extracted by Tessier's scheme in soils. Whereas, higher quantities of Cu, Pb, Ni and Zn are extracted from both type of ashes in this fraction by modified-BCR scheme. So, the extractability of metals depends not only on the reagent used in the scheme, but also on the solid phase/matrix type from which the metals are extracted.

Metals extracted in residual fraction are generally higher in modified-BCR scheme than the Tessier's scheme, irrespective of metal type and matrix type. Systematic variations in the "residual" fraction i.e. the content of metal in residual fraction obtained using modified - BCR scheme, in general, higher than those obtained with Tessier's scheme, were probably because of relatively lesser efficiency of reagents used in first three steps of modified-BCR scheme to extract these fractions, reflect that the fractions are only empirically (operationally) defined and are not totally exclusive to the specified mineral phase.

It is assumed that the first two fractions of Tessier's scheme and the first fraction of modified-BCR scheme represent the forms of the metals that are more available than the metals in the later fractions. Results of relative metal affinities in operationally defined solid phase fractions shows that Cd in all three matrices by Tessier's scheme and Ni in soils and Cd in both type of ashes by modified-BCR scheme have the highest overall affinity in acid soluble fraction. So, Cd appears to be potentially most mobile heavy metal in all the three matrices studied.

In all three type of matrices, Cu by Tessier's scheme and Ni by modified-BCR scheme are shown to have highest affinity with reducible fraction. In comparison to other metals, higher percentages of Ni are associated with OS bound fraction by Tessier scheme in all three type of matrices, while by modified-BCR scheme Zn in soil and Ni in both type of ashes is associated with organic/sulfide bound fraction. In the residual fraction Cr shows greatest affinity by modified-BCR scheme in all three matrices whereas Zn by Tessier scheme in fly ash and bottom ash. So, Cr appears to be the least potentially mobile heavy metal in all the three matrices in comparison to Cd, Cu, Pb, Ni and Zn.

Sequential extraction procedures are not fully specific in extracting the element bound to a given solid fraction; they may provide comparative information on trace-metal mobility in changing environmental conditions, such as pH or redox potential. Alkaline

nature of soils and high carbonate content of all the three matrices i.e. soils, fly ash and bottom ash have a positive influence on immobilization of trace elements.

There are also considerable differences in trace elemental fractionation obtained by using two sequential extraction procedures i.e. Tessier's and modified-BCR procedure. In spite of some differences being found at different extraction steps, there is good agreement between present work and other similar studies cited in literature. The variability of the results of two sequential extraction schemes depends on various factors and thus could be explained by:

- The origin of the material
- Types of reagents utilized and the operational conditions to extract each fraction
- The matrix from which the metal is to be extracted, and
- Variation in the inorganic and organometallic chemistry i.e nature of each metal.

Elemental concentrations in soil and coal ashes show that Guru Nanak Dev Thermal Power Plants have the potential of toxic metal release into the environment. The speciation of heavy metals with selective extracting agents gives additional information about the fundamental reactions governing the behavior of the metals in soils. The distribution of the six studied metals in the various fractions confirms their differences in mobility. Apparently trace metals are bound to residual (silicate) phases, which are relatively resistant to alteration.

A range of uncertainties in the interpretation of partitioning data acquired through the use of two individual schemes is being highlighted in the present study. Therefore, further chemical and mineralogical investigations are recommended into the application of operationally defined selective leach schemes for soil and coal ashes.

The present research work provides information about the levels, potential mobility, and bioavailability of heavy metals in fly ash and soils in the vicinity of thermal power plant. This work also provides information about geochemistry and partitioning of metals in various phases of the solid matrices and also helps in assessing the current status of the levels of metals and potential mobility of heavy metals in environment.

A management plan to limit the transfer of trace elements into other compartments of the ecosystem is needed in order to alleviate the probable impacts. This can only be

done by reducing the solubilities and concentrations of these metals in the different type of matrices around thermal power plant. An effort to be more definitive as to the nature and extent of phases thus analyzed is emphasized. Therefore, it is essential to monitor the evolution of soil quality in the area influenced by the thermal power plants, as well as to avoid the loss of the soil functions and possible cross contamination of underground water and vegetation by introduction of various contaminants, such as heavy metals, without any irreversible negative consequences.