Conclusions
Conclusions

Man’s activities have increased the quantity and distribution of heavy metals in the atmosphere, on the land and in rivers, lakes and seas. The extent of this widespread but generally diffuse contamination has caused concern about its possible effects on plants, animals and human beings. Little is known about the mode of occurrence and behavior of heavy metals (the main metallic contaminants) in the soils of the region. The present study pertains to the geo-chemical characterization of the different solid matrices viz. mine tailings (New and Old), mining wastes, medieval metallurgical slags and soils. In addition to contamination by the main ore metals (Zn, Pb), the environmental hazard resulting from the associated toxic trace metal (Cd) was investigated. However, the intimate association between the toxic trace metal and the main ore-forming minerals is more important in terms of occurrence and speciation. The following conclusions can be drawn from this study:

The soils as well as mine tailings are alkaline in nature, with the mean pH 7.622 ± 0.590 in the surface soils. The organic matter content of soils was usually low with a median value of 2.49%.

The EC was high for both types of tailings than the soil samples, indicating the presence of soluble salts such as sulphates in mine tailings. The mean carbonate content of surface (0-10cm) new tailings (78.00 ± 6.097%) and old tailings (78.33 ± 6.77%) was quite high, indicating calcareous nature of these tailings.

Mineralogical analysis by using XRD indicates the presence of Dolomite, Quartz, Ankerite and other sulphide minerals in New and Old tailings, and mining wastes. Not many crystalline phases were observed in old smelting slags.

All the solid matrices showed elevated heavy metal contents. The values are mostly within the usual range observed for similar kind of
Conclusions

environmental settings. The frequency distribution for all the physicochemical parameters and total metal concentrations (viz. Cd, Pb, Zn and Mn) is skewed.

In surface soils from all the locations (n=95), Zn concentrations were closely correlated with Cd ($r=0.8662$) and Mn ($r=0.7135$), while Pb showed a more variable pattern ($r=0.4602$ b/n Pb and Zn, $r=0.4970$ b/n Pb and Cd; $r=0.4402$ b/n Pb and Mn). No significant correlations were observed between physico-chemical parameters and total metal concentrations.

The depth-wise distribution of metals in new tailings indicates a decrease in Pb levels with depth upto 20cm and an increase in Cd and Zn levels after 20cm, and no differences were observed for Mn levels with depth. The contrasting trend noted for Pb could be explained by the formation of highly insoluble anglesite (PbSO$_4$) in the surface layer as conformed by XRD analysis of surface samples.

The amount of Cd, Pb and Zn extracted by EDTA and their total concentrations show a linear positive correlation for soils as well as wastes, which are statistically significant ($r$ values for Cd, Pb and Zn being 0.8359, 0.9692 and 0.8096 respectively for soils, and $P$ values being <0.001; and $r$ values for other wastes being 0.8669, 0.9437 and 0.5033 respectively for Cd, Pb and Zn with $P$ values <0.001). These results can appear to justify the use of ‘total’ metal contents as a useful preliminary indicator of areas where the risks of metal excess or deficiency are greatest.

EDTA extractability followed the sequence Pb > Cd > Zn. Results of single extraction indicate that tailings are the most and smelting slags are the least hazardous materials from metal mobility point of view.

Regardless of the solid matrix type carbonates dominate in the binding of cadmium, except the soils near old workings.
Conclusions

Fe-Mn oxide bound is the most abundant Pb fraction in soils from the 4 locations, old Zawar Village, smelting slags and from the soils near old workings. In new tailings, old tailings and mining wastes acid soluble (B1) is the predominant metal fraction. It can be concluded that the Pb associations are dependent on the matrix type.

Single as well as sequential extraction experiments show that tailings have the highest potential of toxic metal release into the environment. Apparently, the medieval slags present the lowest contamination hazard. Their heavy metal contents are relatively low and they are generally bound to residual (silicate) phases, which are relatively resistant to alteration.

In all kind of matrices, out of the three elements fractionated, highest percentage of Zn was incorporated into the residual fractions, indicating the least mobility of this metal in comparison to Cd and Pb.

Irrespective of solid matrix type, cadmium was predominantly associated with acid soluble fraction. The metal associated with this fraction is considered to be the most mobile. Of the elements that were studied, Cd seems to be of particular concern because of the high mobility exhibited even in neutral and slightly alkaline soils. Further studies are needed to investigate human exposure and to assess the environmental risk posed to local inhabitants, in particular by dietary ingestion of Cd. It should be borne in mind that the availability of metals can increase when the soil pH falls.

Lead and zinc were mainly associated with acid soluble (B1) fraction in new tailings, old tailings and mining wastes, while in all kind of soils and slags these were associated with Fe-Mn oxide bound fraction (B2).

In case of mine tailings, all the three metals were extracted in the acid soluble fraction (B1), indicating the effect of matrix type on metal binding. Co-precipitation with carbonate may be an important elimination mechanism for metals such as Zn, Pb and Cd when other substrates, particularly hydrous Fe oxides and organic substances are less abundant.
Conclusions

(Forstner and Whitmann, 1979). This phase contains metals which are moderately available for release, which are greatly effected by pH.

Based on the speciation results, it appears that relative proportion of Zn as well as Cd, as compared to Pb in B3 (organic/sulphide) fraction significantly decreased in old tailings as compared to new tailings. The metal extracted in this fraction might be due to dissolution of metal sulphides in new tailings, and with time such phases would have weathered old tailings, leading to low extractability in B3 fraction. Such a pattern was not observed for Pb, this may be due to low soluble secondary minerals formed by the oxidation of sulphides, which could not be extracted in this fraction. A particular problem of the sequential extraction schemes is their inability to distinguish between associations with organic matter and sulphides, a distinction which, although not made here, would appear to be highly desirable from an environmental point of view.

The metal partitioning by sequential extraction schemes in these contaminated samples allowed us to elucidate metal associations with different operationally defined fractions and hence the potential mobility of these elements in different kind of solid matrices. Speciation data indicates that Cd has the greatest affinity in the acid soluble fraction, Pb is associated with reducible fraction and Zn is incorporated into the residual fraction (crystalline silicate matrices) irrespective of the solid matrix type. The metal associations in oxidizable fraction appear to be matrix specific i.e., Zn dominates this fraction in new tailings, and soils from Balaria, Mochia, Baroi, Zawarmala and near the old workings; Pb in old tailings and Old Zawar village soils and Cd in mining wastes and old smelting slags.

The estimated comparative metal mobility indicated that Cd is the most mobile and Zn is the least mobile heavy metal in all kinds of solid matrices, except the slags where Pb is the most mobile, and old tailings where Pb is least mobile metal. Cd is more easily mobilized than Zn and Pb.

Systematic variations in the “reducible” fraction i.e. the content of metal in reducible fraction obtained using Tessier’s procedure, in general, higher
that those obtained with BCR scheme, probably because of stronger conditions used in Tessier's scheme to extract this fraction, reflect that the fractions are only empirically (operationally) defined and are not totally exclusive to the specified mineral phase.

The present study highlights a range of uncertainties in the interpretation of partitioning data acquired through the use of two individual schemes. There is therefore a felt need for more chemical and mineralogical investigations into the application of operationally-defined selective leach schemes for uncommon matrices such as tailings etc. An effort to be more definitive as to the nature and extent of phases thus analyzed is emphasized.

The total content of polluted elements in the soil can be a useful parameter for characterization of contamination potential. However, 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 three studied metals in the various fractions confirms their differences in mobility.

Characterization of the study locations together with the historical information gathered strongly suggest that soils in Zawar area have received large quantities of trace metals either naturally or by direct deposition of different types of waste materials (tailings, mining wastes, smelting slags etc.) generated over the years by different types of ore beneficiation activities. As a result, trace metals have accumulated to the extent that their distributions in soils are capable of causing adverse health effects in grazing livestock or through the food chain to human.

A management plan to limit the transfer of metals into other compartments of the ecosystem is needed in order to alleviate the probable impacts. This can only be accomplished by reducing the solubility and concentrations of these metals in the soils. Removal of contaminated soils or coverage with layers of unpolluted soils is impractical due to extensive contamination throughout the area. Unfortunately, only a few options remain to reduce the hazards of trace metals to soil-plant-animal systems. Metal concentrations in soils could be reduced by leaching with acids or chelates; however this tactic could send a hazardous pulse of soluble metals into groundwater with high potential for bioaccumulation.
Conclusions

Changes in environmental conditions such as redox, pH etc. may release heavy metals bound to different fractions, so monitoring of environmental conditions would appear to be a priority, particularly since such conditions in a mining environment are in a state of constant flux. This raises management implications. It is therefore unlikely that the "multicomponent, multiphase" environment described here can ever be satisfactorily modeled. The remediation of such degraded environments also remains a challenging task.