Comparison of Heavy and Trace Metals Levels in Soil of Peshawar Basin at Different Time Intervals

[1]SHAHIDA NASREEN ZAKIR, [2]IHSAN IHSANULLAH*, [1]MUHAMMAD TAHIR SHAH, [3]ZAFAR IQBAL AND [2]ANWAR AHMAD

[1]*Center of Excellence in Geology, University of Peshawar, Pakistan.*
[2]*Nuclear Institute for Food & Agriculture, Peshawar, Pakistan.*
[3]*Department of Phamacy, University of Peshawar, Pakistan.*

(Received 15th September 2008, accepted in revised form 22nd November 2008)

Summary: The chemical characteristics of the soils of Peshawar basin have been evaluated in this study. Selected heavy metals *i.e.*, copper (Cu), zinc (Zn), lead (Pb), nickel (Ni), chromium (Cr), and cobalt (Co) have been determined in the soils of horizons A (to a depth of 20 cm) and B (at a depth of 20-40 cm) from the piedmont, floodplain and lacurstrine of Peshawar basin. These samples were collected during the months of January and June of 2003 and 2004. The concentrations of these elements have been estimated to observe the changes against time. High concentrations of Cu, Pb, Ni and Cr have been found in the majority of the Peshawar floodplain soils while Zn is high in the Peshawar piedmont soil. The level of these metals reached to a high toxicity level in the soils of certain areas, which may cause drastic environmental impact on the ecosystem of the region. In addition to rapid industrialization and unplanned urbanization, the high concentration of these elements in the soils of the basin can be attributed to the weathering and erosion of the sulfides, and mafic and ultramafic rocks in the surrounding mountainous regions with greater input from the rocks of the Kohistan island arc in northern regions of the Peshawar basin. This study further suggests that there is no significant change in the concentration of these metals in the soils of the basin with the increase or decrease of the depth and also with the passage of time.

Introduction

Peshawar basin is an *intra*-mountain basin (> 5500 km^2) situated at the southern margin of the Himalayas and northwest of the Indus plain in the North West Frontier Province (NWFP) of Pakistan. Major cities of the basin are Peshawar (capital), Mardan, Charsadda, and Nowshera. The river Kabul flowing from west to east and its tributaries irrigates the basin and joins the Indus at eastern exit [1]. Peshawar basin has a total population of 4.8 millions excluding Afghan refugees [2].

For the last two decades, the high rate of industrialization and unplanned urbanization with heavy load of transportation together with a retarded rate of awareness/education in mainly poor masses have resulted in drastic increase in all sorts of pollution within the Peshawar basin. Heavy and trace metals are one of the environmental toxins released by metal-based industries and the vehicular traffic. These metals cause several carcinogenic impacts and other impairments both in animals and plants [3, 4]. Pakistan is one of the developing countries where the industries and unplanned urbanization are growing at fast rate. It has resulted in high rate of deforestation and expansion of roads, poor sewerage system, and industries without treatment plants in and around the major cities. Both stationary and mobile sources are responsible for the generation and dissemination of pollution. Stationary sources include small and large industrial plants, power generation plants, and construction projects and brick kilns. Mobile sources include cars, trucks, rickshaws and aircrafts [5-7].

The level and distribution of total extractable Cu in the soil profile can be expected to vary with soil types and parent materials. Copper is essential for the normal growth of plants [8, 9]. The Cu concentration for the normal agricultural soil has been reported as 20 ppm [10]. Soils formed from basic rocks are rich in Zn, whereas soils from grainites, gneisses etc are poorer in Zn contents [11]. Zinc is one of the essential nutrients for plants growth. However, about 50 ppm Zn concentration has been reported by Bohn *et al.* [12] for the normal agricultural soil.

Some metals like Pb, Ni and Cr in the agricultural soil have wide ranges, depending on a

*To whom all correspondence should be addressed.

number of factors, such as parent material and anthropogenic input [10]. High levels of Pb in the plants can develop phytotoxicity which usually results in the death or slow growth of the plants. The Pb concentration in the normal agricultural soil has been reported as 10 ppm. Some beneficial effects of Ni on plants growth have been reported. The increasing concentration of Ni from 50 ppm in the soil may produce toxicity in the plants grown on it. Chromium is an essential element in many plant species and hence also for animals and human nutrition. Its concentration in the normal agriculture soil has been reported as 20 ppm [10, 12].

Cobalt has not been demonstrated to be essential for the growth of plants. However, it is constituent of vitamin B_{12} which is essential to most of the animals and possibly in plants. A deficiency of Co is of far greater concern than potential toxic levels in plants [10, 13]. The cobalt content of the normal agricultural soil has been reported as 8 ppm by Bohn *et al.* [12].

This study has therefore, been carried out to monitor the increase or decrease of the heavy metal pollution in the soil of the Peshawar basin with the passage of time.

Results and Discussion

The concentration of Cu, Zn, Pb, Ni, Cr, and Co in the soil samples of horizon A and B collected during the month of January 2003 and 2004 from Peshawar basin has been graphically presented in Figs. 1-5. The concentrations of these elements, reported by Tariq [1] in the soils from the same sites are also given in Figs. 1-5 for comparison.

Distribution and Spatial Variation

It is clear from the data drawn in Fig. 1 that there is no systematic increase or decrease of Cu with the increase or decrease of depth. However, no significant change has been noticed in the Cu concentration with the passage of time. Cu is ranging from 71 to 631 parts per million (ppm) in the Peshawar piedmont soils, from 67 to 588 ppm in the Peshawar floodplain soils and from 46 to 188 ppm in the Peshawar lacustrine soils. The soils of Peshawar piedmont and Peshawar lacuntrine are relatively highly enriched in copper. The Cu concentration in the soils of certain areas (such as Khairabad, Shabqadar, Mandezai Srikh, Tarangzai and Aman Kot) of Peshawar basin is higher than that of the normal agricultural soil. This increase of the Cu concentration in the soils of Peshawar basin can be attributed to the weathering of sulfides in the surrounding mountainous areas around Peshawar basin. This concentration of Cu in certain areas is reaching to alarming level. The soils of Peshawar lacustrine are highly contaminated with geogenic Cu and this should be evaluated in detail.

The levels of zinc concentration in the soils of Peshawar basin (Fig. 2) clearly show that there is unsystematic increase or decrease of Zn with the increase or decrease in depth. However, no significant change in the concentration of Zn in the soil of Peshawar has been noticed with the passage of time. The Zn concentration in soils of Peshawar basin is highly variable. It is ranging from 88 to 601 ppm in the Peshawar piedmont soil, from 93 to 181 ppm in the Peshawar floodplain soil and from 75 to 240 ppm in the Peshawar lacustrine soil. The Peshawar piedmont soil is relatively enriched in Zn. This high concentration of Zn can be attributed to the weathering of sulfide mineralization in the surrounding rocks of the Peshawar basin. Many fold high concentration of Zn in the soils of certain areas (*i.e.,* Darwazgai, Speen Khak, Khairabad Kafir Dheri, Shabqadar and Mandezai Srikh) of Peshawar basin reaches to toxic level in the plants and hence greater environmental impact in the ecosystem of the region is expected.

It is clear from the data of Pb (Fig. 3) that there is no systematic increase or decrease of Pb with the increase or decrease of depth. No proper change has occurred in the concentration of Pb in these soils with the passage of time. However, the Pb concentration in almost all the soils of the Peshawar basin is high when compared to the levels of normal agricultural soil. This enrichment of Pb in the soil of Peshawar can be attributed to the weathering and leaching of sulfides in the mountainous regions surrounded by Peshawar basin. There could be less anthropogenic input in this regard. The toxicity of Pb in the agricultural lands in certain areas (such as Landiarbab, Shabqadar, Mathra, Mandezai Srikh and Tarangzai) of the basin is imperative and need to be investigated in detail.

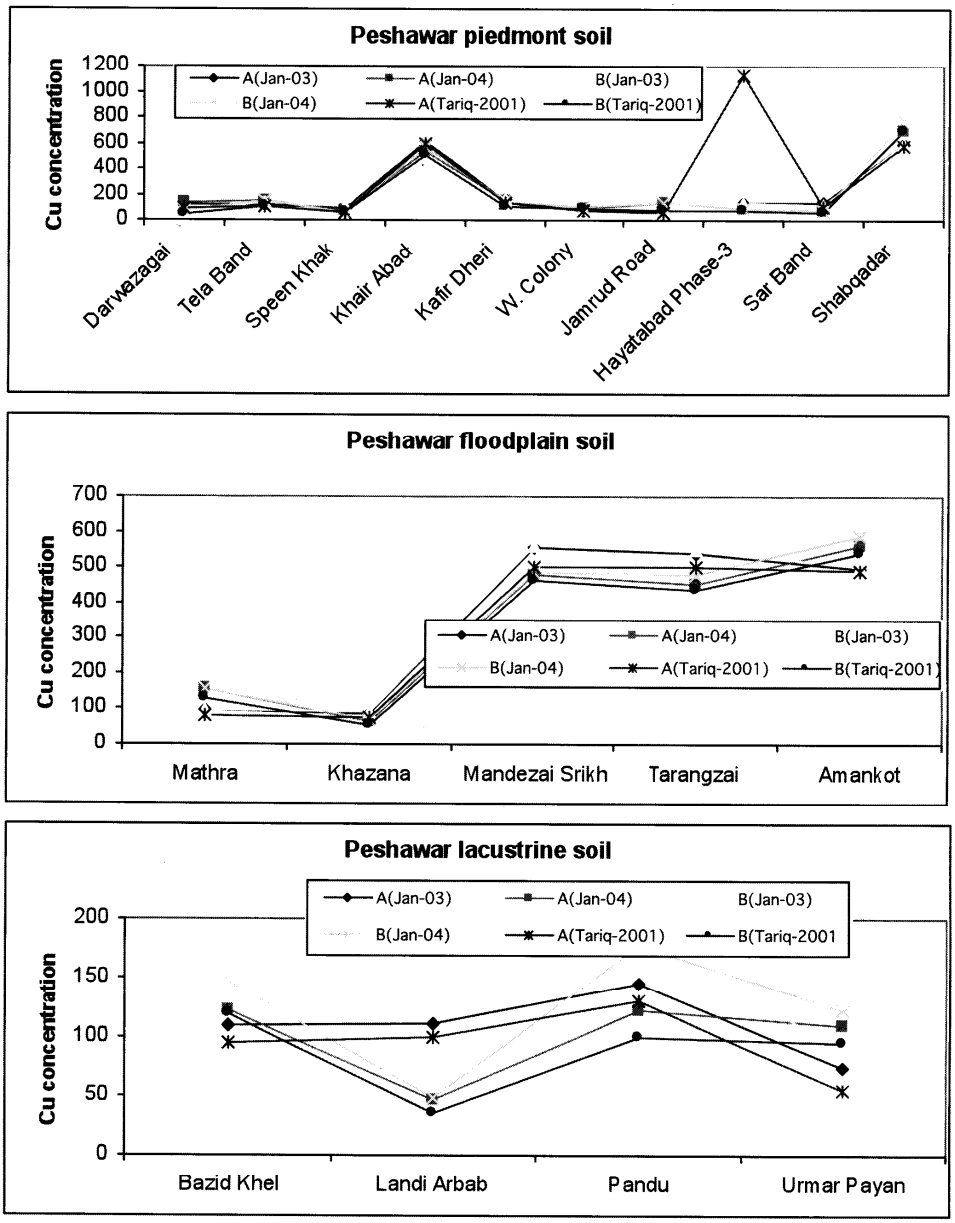

Fig. 1: Variation in concentration of Cu (ppm) in the soils of Peshawar basin during different times.

It is evident from Fig. 4 that no correlation of Ni concentration is present with the increase or decrease of depth. However, it is clear from the data that no significant change has been observed in the Ni concentration with the passage of time. The Ni is highly variable in the soils of Peshawar basin. It is ranging from < 0.5 to 378 ppm in the Peshawar piedmont soil, from 7 to 206 ppm in the Peshawar floodplain soil and < 0.5 to 232 ppm in the Peshawar lacustrine soil. The Ni concentration in the Speen Khak and Hayatabad Phase-3 of the Peshawar piedmont, in the Amon Kot and Khazana of

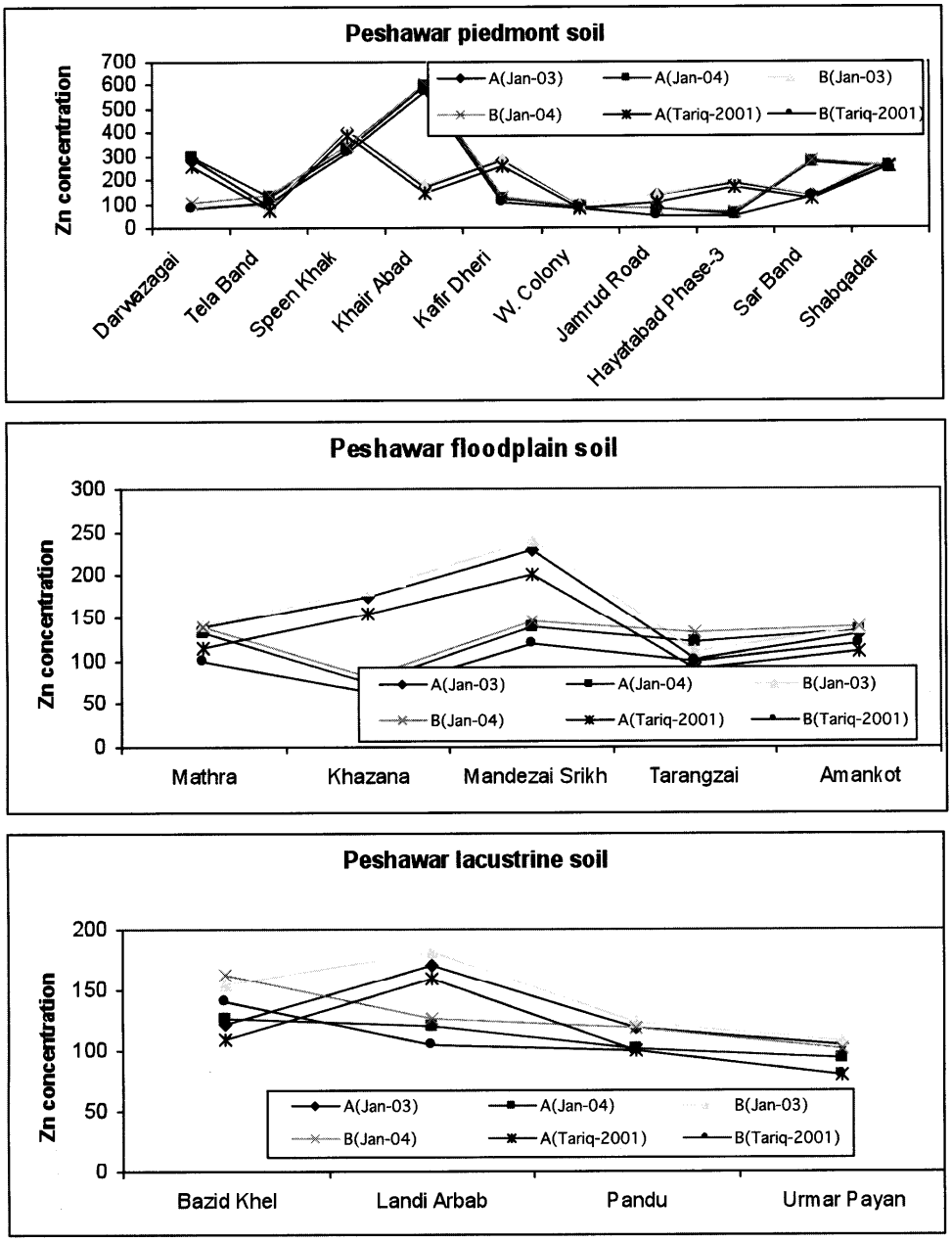

Fig. 2: Variation in concentration of Zn (ppm) in the soils of Peshawar basin during different times.

Peshawar floodplain and in the Baszid Khel and Urmar Payan of Peshawar lacustrine of the Peshawar basin is very high. The soils of these areas have alarming concentration of Ni as far as the toxicity of Ni on the plants and animals are concerned. The Ni enrichment in the soils of Peshawar basin can be attributed to the weathering and erosion of ultramafic and mafic rocks exposed in the north west and north of the Peshawar basin, especially those of Dargai mafic and ultramafic complex [14]. The toxicity of Ni in the soils of the Dargai and surrounding areas has also been reported by Kafayatullah *et al.* [15].

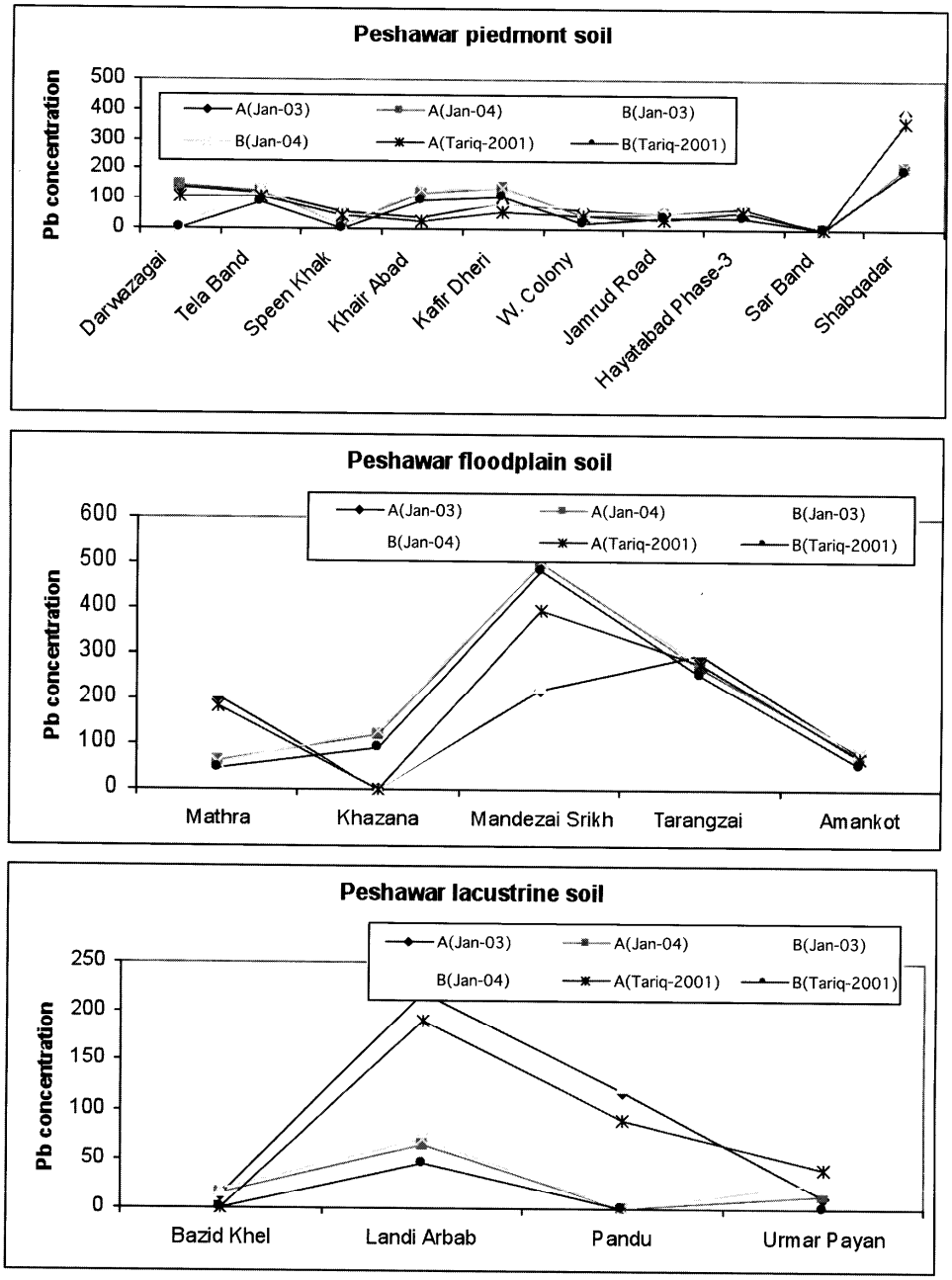

Fig. 3: Variation in concentration of Pb (ppm) in the soils of Peshawar basin during different times

Chromium contents of the soils samples are shown in Fig. 5 for comparison. It is clear from the data that the Cr concentration exhibits no correlation with the increase or decrease of depth. The amount of Cr in both the horizons of soils of the Peshawar basin is highly variable. There is no significant change in the Nickel contents of these soils with the passage of time. Chromium is ranging from < 0.5 to 602 ppm in

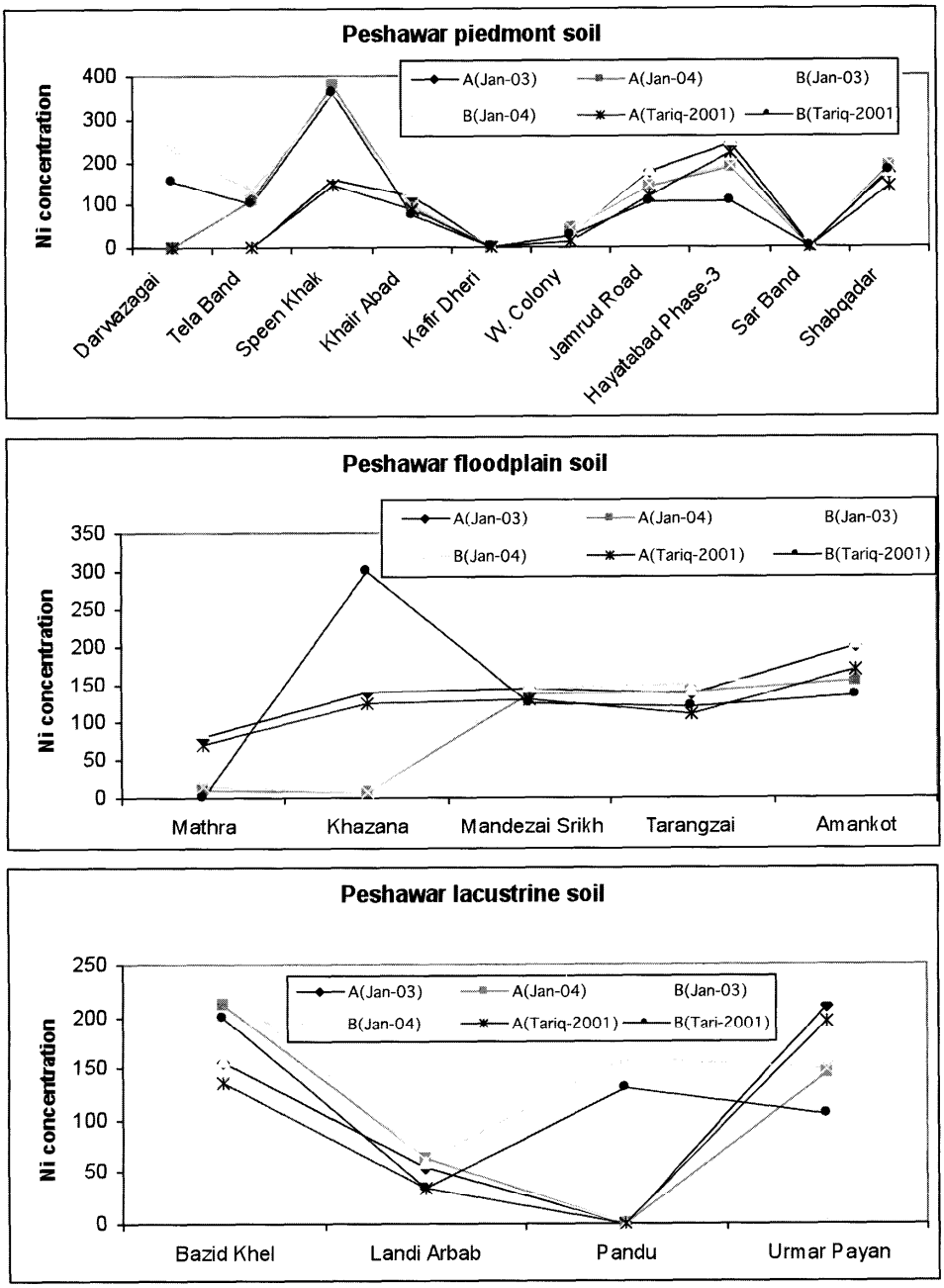

Fig. 4: Variation in concentration of Ni (ppm) in the soils of Peshawar basin during different times.

the Peshawar piedmont soils, from < 0.5 to 651 ppm in the Peshawar floodplain soils and from < 0.5 to 165 ppm in the Peshawar lacustrine soils. Majority of the soils of the Peshawar basin are having multifold high concentration of Cr as compared to that of normal agricultural soils. Some of the soils (*i.e.*, Khairabad and Shabqadar of Peshawar piedmont and Mandezai Srikh, Tarangzai and Amankot of

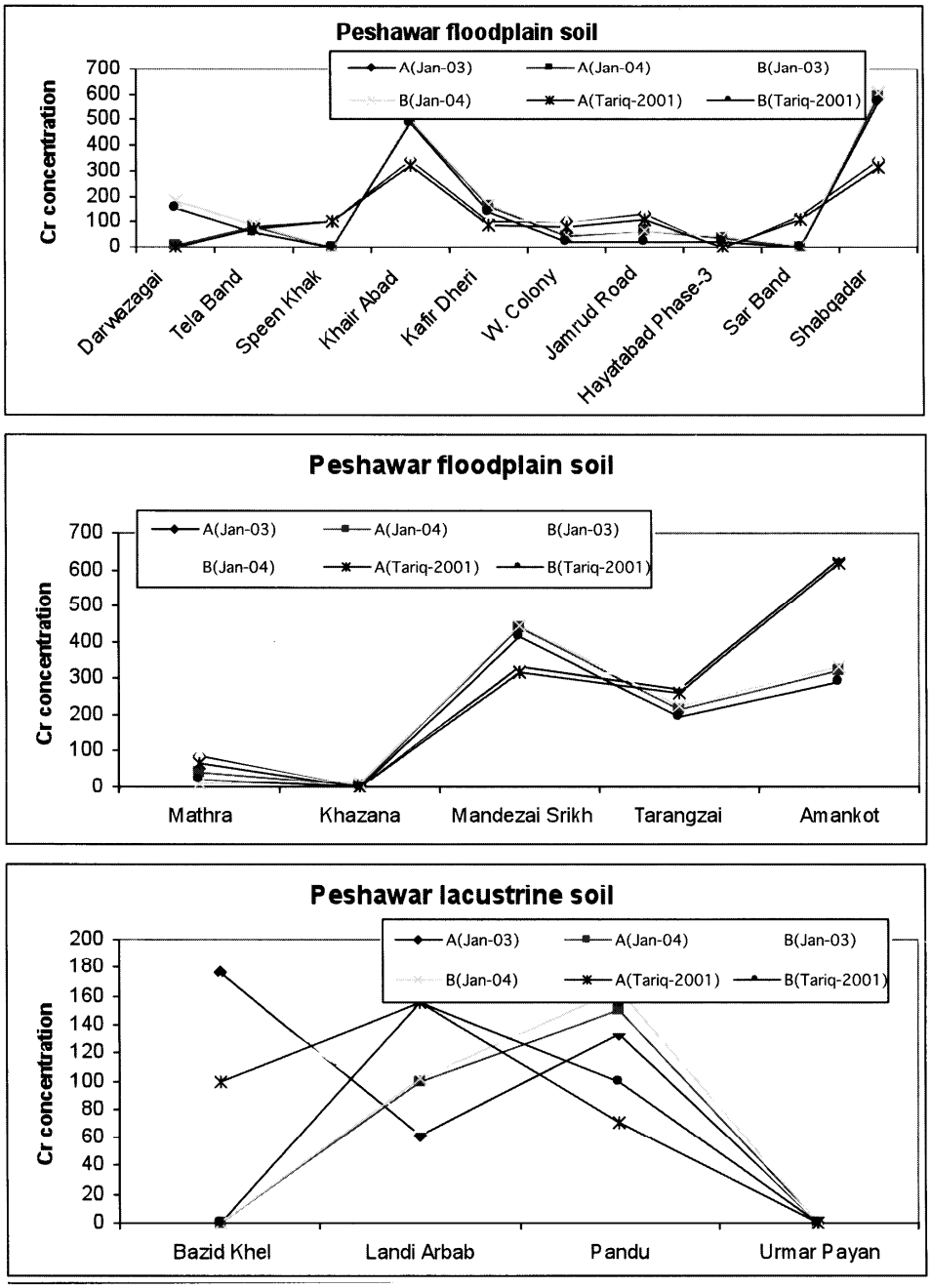

Fig. 5: Variation in concentration of Cr (ppm) in the soils of Peshawar basin during different times.

Peshawar flood plain) of the Peshawar basin have Cr to an alarming level and may cause highly toxic effects on the plants and other living organisms of the area. This Cr enrichment can also be attributed to the weathering and erosion of the mafic and ultramafic rocks occurring in the north and north west of the basin, especially from the Dargai ultramafic complex (Ahmad 1971). The toxicity of Cr in the soil of

Dargai and surrounding areas has also been reported by Kafayatullah *et al.* [15].

Various types of soils of the Peshawar basin had Co contents less than 1 ppb. Tariq [1] has also reported that Co concentration in the soils of the basin from the same sites is below the detection limit (< 1ppb). This suggest that there is a greater deficiency of Co in the soils of Peshawar basin which can have drastic effects on the plants and also on the human beings as these soils have no capability of enhancing the important component of vitamin B12, therefore, such soils should be further investigated.

Possible Sources and Contamination

It is a hard fact that the Indus River has played a major role in the deposition of quaternary sediments in the Peshawar basin but the role played by the Kabul and Swat rivers and their tributaries in the deposition of quaternary sediments in the basin can not be ruled out. The major input in the quaternary deposits from the Kohistan Island arc covering most of the mountainous region of the northern parts Pakistan is important. The multiple episodic flooding in the Indus river has deposited rhythmite sequences in the basin. Therefore, these sediments have very thick single large confined aquifer with the Paleozoic rocks at the base and the clay on the top acting as an aquiclude [1, 16]. Various semi-confined aquifers, above this major confined aquifer in the middle part of the basin, have been defined in the Nowshera, Mardan and Peshawar areas. These aquifers are generally recharged by the Kabul and Swat rivers and their tributaries. These semi-confined aquifers generally known as piedmont, lacustrine and floodplain type aquifers depending on the nature of the sediments hosting these aquifers. The lacustrine and floodplain aquifers make small local aquifers of breached and artesian type [1, 17]. The lacustrine and flood plain aquifers at Jalala, Kheshki, Jehangira, Spin Khak and Swabi are composed of sand, silt, clay in the middle of the basin while the piedmont aquifers at Warsak, Ziarat Kaka Sahib and Piran are generally consisting of clast supported conglomerates mainly in the marginal parts of the basin. These piedmont sediments in the surrounding of the Peshawar basin are considered as the major catchment areas of rain water for the aquifer. In many parts of these catchment areas no industry is present; except in the western and southern portion of the Peshawar city. Therefore, there are less chances of anthropogenic contamination in the aquifer system of the basin. The middle part of the basin is having thick clay and silt which also plays a major role in protecting the aquifer system of the basin from contamination to greater extent through anthropogenic sources. However, the contamination through banks of the rivers Kabul and Swat where the river beds cut deep through the aquifer can not be ruled out.

Recommendations

In order to minimize the future environmental problems regarding soils of the Peshawar basin following measures are recommended on priority basis:

- Environmental laws already formulated for disposal of domestic waste and industrial effluents should be forcefully implemented.
- Industrialists should encourage ISO certification and the industrial effluents should be subjected to pre treatment before being disposed to any segment of the environment.
- The soil samples must be monitored regularly to check for the trace elements.
- As the soils of certain areas of Peshawar basin are rich in certain heavy metals, the impact of these metals is needed to be studied in plants and animals on urgent basis.
- The inhabitants of these areas should be educated regarding the soil pollution and their impacts on the ecosystem of the region.

Experimental

Collection of Soil Samples

Representative samples of soil were collected from the selected locations (Fig. 6) during the months of January and June of 2003 and 2004. The samples have been divided into two horizons "A" and "B". Horizon "A" represents the core sample surface to a depth of 20 cm and horizon "B" represents a core sample from a depth of 20-40 cm. The collected samples were properly labeled and transferred to polythene bags that were further placed into canvas bags. The color, texture and loose fragments of these samples were noted at the site.

Crushing of Soil Samples

Various types of soils collected during field visit from the study area were air dried and selected

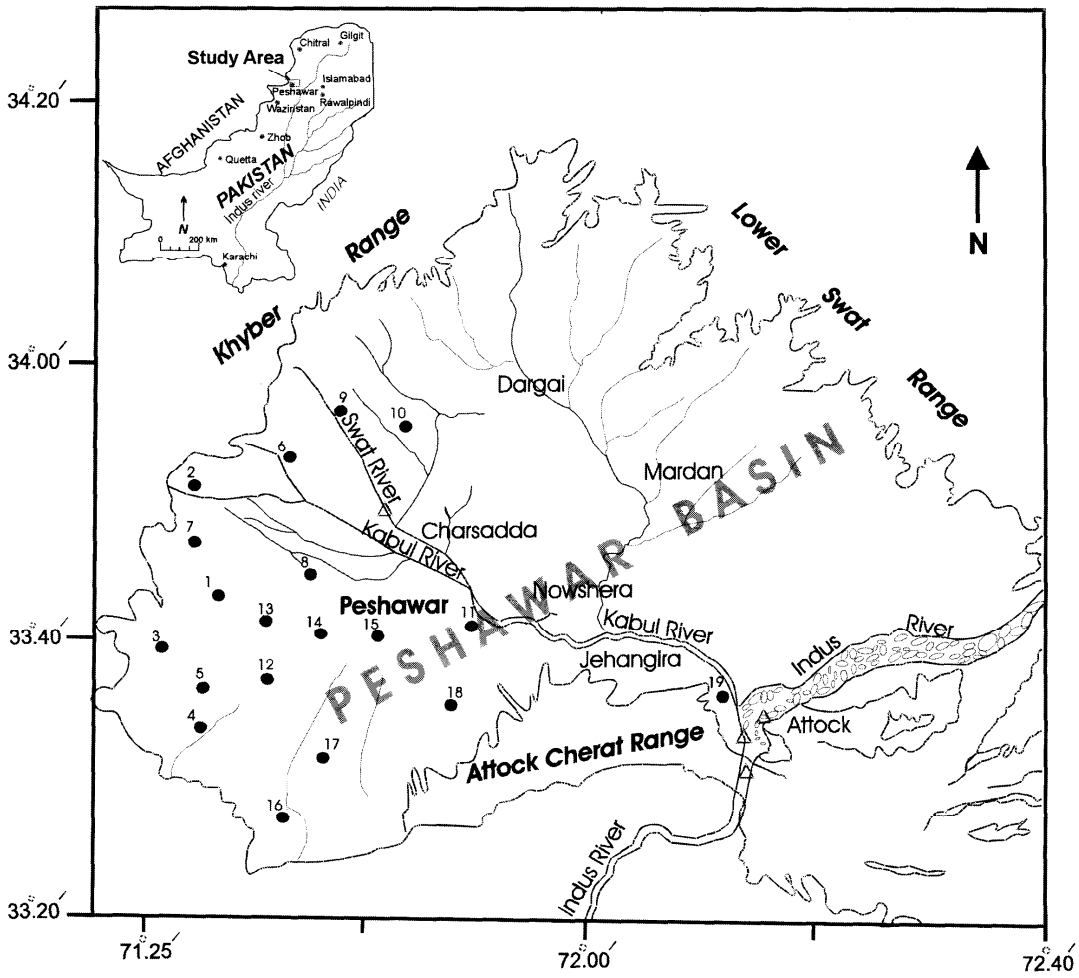

Fig. 6: Location map of the soil samples of the Peshawar basin (modified after Tariq, 2001).

portion of the soil samples were pulverized in a tungsten carbide ball mill to 200 mesh size. A portion of individual sample was collected after proper quartering and coning. During this whole process greater care was practiced to avoid contamination. The powdered samples were stored in the air tight glass bottles. These bottles, after removing the lids, were kept in the oven at 110 °C for two hours in order to remove the moisture.

Determinations of Trace & Heavy Metals in Soils

Preparation of Stock Solution

The moisture free powders of the soil samples as well as the world known rock standards were converted in to stock solutions of known volume by standard methods. This stock solution was used for the determination trace and heavy elements by instrumental method.

Stock Solution

Hydrofluoric acid (HF) + aqua regia digestion method: Accurately weighed 1.0 g of finely powdered soil sample was taken in a 100 ml teflon beaker. 5 mL of HF was added to it and was kept on hot plate at a temperature of approximately 75 °C. After 10 minutes, about 15 mL of aqua regia (HCl/HNO_3) was added and the heating was continued until complete dryness. 2N HCl was added to the residue and was heated until the maximum dissolution

of residue. The residue was filtered by using 2N HCl and the final volume was made to 25 mL and was stored in polythene bottle. This solution was then used for trace elements determination using Perkin Elmer Atomic Absorption Spectrophotometer. These are established facts and need not be mentioned at this level.

All these analysis were carried out at the Geochemistry Laboratory, National Centre of Excellence (NCE) in Geology, University of Peshawar and cross checked in PCSIR laboratories Peshawar and Department of Environmental Sciences, University of Peshawar.

Conclusion

The trace and heavy metals data of the soils of the Peshawar basin suggest that there is variable concentration of these metals in the horizon A and B and also in the soils of different localities. However, no significant change in the concentration of these metals occurs with the passage of time, from 2001 to 2004, in the studied soils. By comparing the three types of soils of the basin among each other and also with the normal agricultural soils elsewhere in the world, it has been noted that the Peshawar floodplain soils have relatively high concentration of Cu, Pb, Ni and Cr, while Zn is relatively high in the Peshawar piedmont soil. The data further suggest that almost all the studied heavy and trace elements, except Co, exceed that of normal agricultural soil. The agricultural lands of Shabqadar, Khairabad, Mandzai, Sirk, Taranzai, Amankot, Kafir Dheri, Darwazgai, Speen Khak, Khazana and Basid Khel areas of the Peshawar basin have toxic level concentration of the studied heavy and trace metals and need further detailed investigation for their environmental impact on the ecosystem of the region. The high concentration of these elements in the soils of the basin can be attributed to the weathering and erosion of the sulfides, and mafic and ultramafic rocks in the surrounding mountainous regions with greater input from the northern regions of the Peshawar basin.

On the basis of varying lithologies, the quaternary sediments, covered soils and hosting aquifers of the Peshawar basin are classified as Peshawar piedmont, Peshawar flood plain and Peshawar lacustrine sediments, soils and aquifers. High rate of industrialization and transportation have contributed to the high levels of pollution in the soils of Peshawar basin. In fact the pollution level has increased with passage of time and it is the time to aware the communities, government and non-government organizations about the pollution.

References

1. S. Tariq, *Environmental Geochemistry of Surface and Subsurface Water and Soil in Peshawar Basin*, N.W.F.P., Pakistan, Ph.D. thesis, University of Peshawar (2001).
2. Technical Report on "*Hydrogeology and Groundwater of the North West Frontier Province, Pakistan*", Hydrogeology Directorate, Pakistan and TNO-DGV Institute of Applied Geoscience, the Netherlands (1994).
3. IARC, *Monograph on the Evolution of Carcinogenic Risk of Chemicals to Man.* International Agency for Research on Cancer, *Lyon,* **2,** 329 (1976).
4. Baranowska, *Journal of the Environmental Studies*, **2,** 5 (1993).
5. S. Hamidullah, M. S. Khan and M. T Shah, Comparison of the heavy metals pollution of the eastern and western part of Peshawar metropolis, NWFP, *Pakistan, Geology Bulletin, University of Peshawar, Special Issue* **31,** 75 (1997a).
6. S. Hamidullah, M. Saifullah and M. T. Shah, *Heavy Metal Pollution in the Eastern Part of Peshawar Metropolis, North Pakistan,* Spec. Publ. Third National Symposium on Modern Trends in contemporary chemistry, PINSTECH, Feb. 24-26, 1997, Islamabad Pakistan, p. 65 (1997b).
7. S. Hamidullah, S. Tariq and M. T. Shah, *Heavy Metals in Surface and Underground Water of Peshawar Basin, Pakistan Terra Nostra-Schriften der Alfred-Wegener-Stiftung* 99/2, 14th Himalaya Karakoram Tibet workshop, Kloster Etal, Gemany, p. 67 (1999).
8. P. Bleeker and M. P. Austin, *Australian Journal of Soil Research*, **8,** 133 (1970).
9. J. Kubota and W. H. Allaway, In: J. J. Mortvedt, P. M. Giordano and W. L. Lindsay, Eds. *Micronutrients in Agriculture, Soil Science Society of America,* Inc. Madison, WI. p. 525 (1972).
10. D. C. Adriano, *Trade Elements in the Terrestrial Environment,* Springer-Verlag New York (1986).
11. A. P. Vinogradov, *The geochemistry of rare and*

dispersed chemical elements in soils, Consultants Bureau Inc. New York (1959).
12. H. L. Bohn, B. L. McNeal and G. A. O' Connor, *Soil Chemistry*, 3rd Ed. John Wiley & Sons, New York (2001).
13. D. C. Adriano, *Trace Elements in Terrestrial Environments*; Biogeochemistry, Bioavailability and risk of Metals. 2nd Ed. Springer-Verlag, New York (2001).
14. Z. Ahmad, *Economic Geology*, **79,** 1334 (1971).
15. Q. Kafayatullah, M. T. Shah and M. Arfan, *Geology*, **40**, 1482 (2001).
16. K. Cornwell, *Geological Society America, Abstract. Prog.*, **26**, 304 (1992).
17. A. Hussain, R. S. Yeats and K. R. Pogue, *Geological Map of the Attock-Cherat Range and Adjoining Area*, NWFP and Punjab, Pakistan. Geology Survey of Pakistan (1991).