

## Quality and Distribution of Lead and Cadmium in Underground Water of Kashmir

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Maintenance of ecosystem based on the biogeochemistry of Kashmir lying at the foothills of Himalayas is not just crucial for its inhabitants but also for down stream Indus river system made up mainly of snowmelt, spring ooze, lake aqua stock of Kashmir. Through an appropriate sampling strategy an area of 13297 Km<sup>2</sup> with a population density of 330 persons/Km<sup>2</sup> was studied. 40 Wells, 20 hand pumps and 30 major springs were selected for measuring 30 *in situ* and laboratory water quality parameters over a period of 4 years providing base line data on underground water source of Kashmir. The study also encompasses seasonal variations over hydrological cycles and effect of anthropogenic activity. The results indicate the presence of major nutrients (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) within WHO thresholds and of trace metal presence of Fe<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> Co<sup>2+</sup>; Cd and Pb show elevated amounts irrespective of seasonal changes or dilution by precipitation. This is a cause of concern endangering the fragile ecosystem of this area. Human activity is also aggravating it. A remedy of this problem could be the recourse to a proper and extended study of the composition of soil and biological interactions per se responsible for releasing these contaminants to the hydro cycle.

**Key Words:** Underground water, Lead & Cadmium levels, Kashmir.

### INTRODUCTION

Ground water quality is coherent with the quantity. Exploitation of ground water has increased greatly and poor quality of water adversely affects the human health and plant growth<sup>1-9</sup>. Adverse conditions increase investment in health and irrigation and decrease agricultural production, that in turn affects economy and retards improvement in the living standard of the people and its upshot is unsustainable development.

The foothills of Himalayas, home to the people of Kashmir, hold unique forest, its allied ecosystems and above all the total water stock of Indus river system. This area has recently been targeted for its water quality,

metal distribution and mobility and other biogeochemical interactions<sup>10-13</sup>. This presentation focuses on the water stock of an area over 1300 Km<sup>2</sup> (longitude 73°-75° and latitude 33°-36°) with a population density of 30 persons/Km<sup>2</sup>, consoled by 40 wells, 20 hand pumps and 30 springs.

**Geochemistry of the area:** Siwalik group of rocks, the accent lines of Kashmir geocharacteristics, consist of granite and crystalline group composed mainly of chlorite, muscovite schists, mica granite, sand stone, magnetite, tourmaline, epidote. An earlier analysis establishes the following order of their presence (based on mean values of samples collected across the area) clay 47.8 ± 10.6, quartz 20.8 ± 10.6, calcite dolomite 18.6 ± 9.07, haematite/limonite 5.2 ± 2.59 others 0.5 - 6.0 %<sup>14,15</sup>.

**Sampling:** Preliminary field survey of the area was undertaken for judgmental sampling of springs, wells and hand pumps in terms of their location, water stock/discharge, forest cover, soil complexion and land use. The springs were sampled laterally at the extremes, in the middle and vertically at varying depths of these points of the stream. The wells were sampled by drawing water straightway through Teflon pails. Hand pump samples were just sucked at by lowering of arms of the pump. First few pails of the water were discarded prior to sampling. The frequency of sampling was scheduled according to Nyquist principle<sup>16</sup>.

## EXPERIMENTAL

The study involves preliminary survey, monitoring of water resources and testing of water to ascertain the physico-chemical parameters. The objective of the field survey was to locate and select the wells, hand pumps and springs for the study. The wells, hand pumps and springs can be considered as the representative of underground water<sup>17</sup>. 40 Wells, 20 hand pumps and 30 major springs were selected for the study. The samples were collected three times during the months of June, October and February 2004-2005. Measurements of each parameter were obtained through field and laboratory analysis of grab samples. Well mixed sample was transferred to a clean 2.5 L plastic bottle after rinsing several times with the sample. The temperature of water and air 1 m above the surface of water was noted. The dissolved oxygen (DO) in the samples was determined by Wrinkler method<sup>18</sup>. Chemical oxygen demand (COD) was estimated by micro-dichromate oxidation method<sup>19</sup>. Hardness, chloride and alkalinity were determined by titration with standard EDTA, silver nitrate and hydrochloric acid. Conductivity, salinity and total dissolved solids (TDS) were evaluated with Orion 115 conductivity meter. The pH was recorded with Orion 420 A pH meter. Kjeldahl nitrogen was determined by using standard procedure<sup>19</sup>. Orthophosphate, nitrate and nitrite were determined by spectrophotometry. Orthophosphate was determined by reducing phosphomolybdic acid formed

with ascorbic acid to molybdenum blue. Total phosphate was estimated by persulphate acid hydrolysis, followed by determination as for orthophosphate. Nitrate was determined after derivatization with brucine sulphate. Nitrite was estimated using N-naphthyl ethylenediamine as derivatizing reagent as reported<sup>19</sup>. Sulphate was determined by turbidimetry as BaSO<sub>4</sub> using Hitachi 220 spectrophotometer. The metal ions Na, K, Ca, Mg, Fe, Pb, Cu, Zn, Ni, Cd and Co were determined with Varian Spectr AA-20 atomic absorption spectrometer with standard burner head and air acetylene flame at the conditions recommended by the manufacturer. The analysis was carried out in triplicate with integration time 3 s and delay time 3 s. Na, K, Ca and Mg were determined after appropriate dilution. Sample (250 mL) containing nitric acid (1 mL) was heated gently at 90-95 °C and was concentrated to about 15-20 mL. The solution was transferred to volumetric flask and final volume was adjusted to 25 mL. The solution was analyzed for the contents of Fe, Pb, Cu, Zn, Ni, Cd and Co by air acetylene flame atomic absorption spectrometer.

## RESULTS AND DISCUSSION

Spring water over a hydrological cycle for major cations follows the order  $Ca > Mg > Na > K = HCO_3 > Cl > SO_4 > NO_3 > CO_3$ . Alkali earth exceeds alkalis and weak acids predominate strong acids. Thus the overall category of spring water is Ca-Mg-HCO<sub>3</sub> and Ca-Na-Mg-Cl. Mass charge balance is also sustained through seasons and hydro cycles, but due to soil-water interface absorptions and metal mobility: Ca substitutes for Na and Mg replaces K.

Well water for some variables also follows the similar order. In case of hand pumps, Na takes the place of Mg by following the overall order Ca-Na-HCO<sub>3</sub> and Ca-Na-Mg-Cl, other distribution patterns being same. Mass charge balance in ground water is also sustained through seasons and hydro cycles except soil-water interface absorptions and mobility: Ca substituting for Na and Mg for K<sup>12,13</sup>.

Seven metals were assayed for minor presence and their distribution: springs  $Zn > Cd > Pb > Fe > Co > Ni > Cu$ ; wells  $Co > Pb > Zn > Fe > Cd > Cu > Ni$ ; hand pumps  $Pb > Cd > Co > Zn > Fe > Cu > Ni$ .

The availability of all minor metals in water other than lead and cadmium fall within WHO thresholds. In springs and wells Pb predominates Cd and hand pumps it's the other way round (Figs. 1-3). An inter-category correlation of Pb is indicated in Figs. 4 and 5 showing an order Pb wells > Pb springs > Pb hand pumps. Pb presence is depth dependent and order for Cd is Cd hand pumps > Cd springs > Cd wells (Figs. 4 and 5).

The overall dynamics of metals mobility and their availability in water stocks (springs, wells, lakes, hand pumps) varies with the level of their

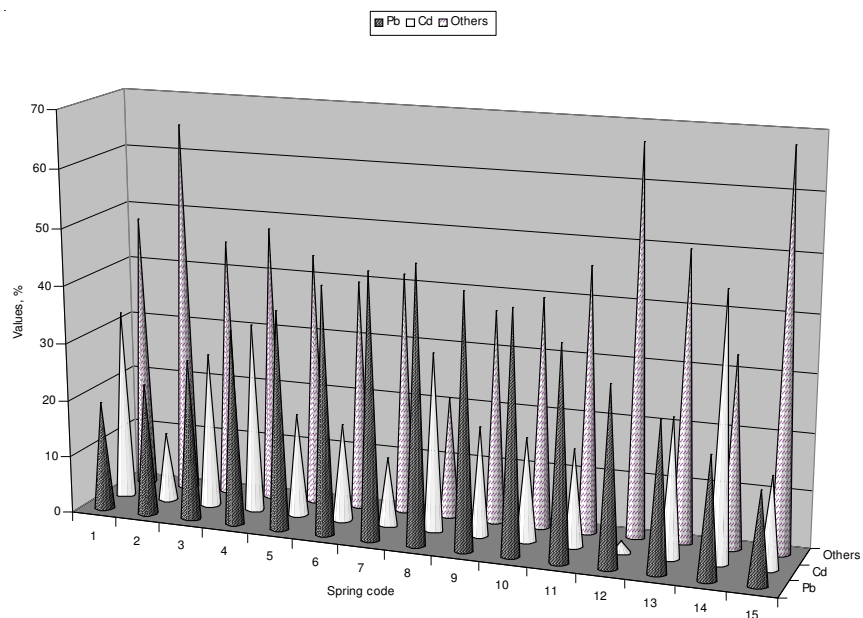


Fig. 1. Distribution of Pb and Cd in representative springs

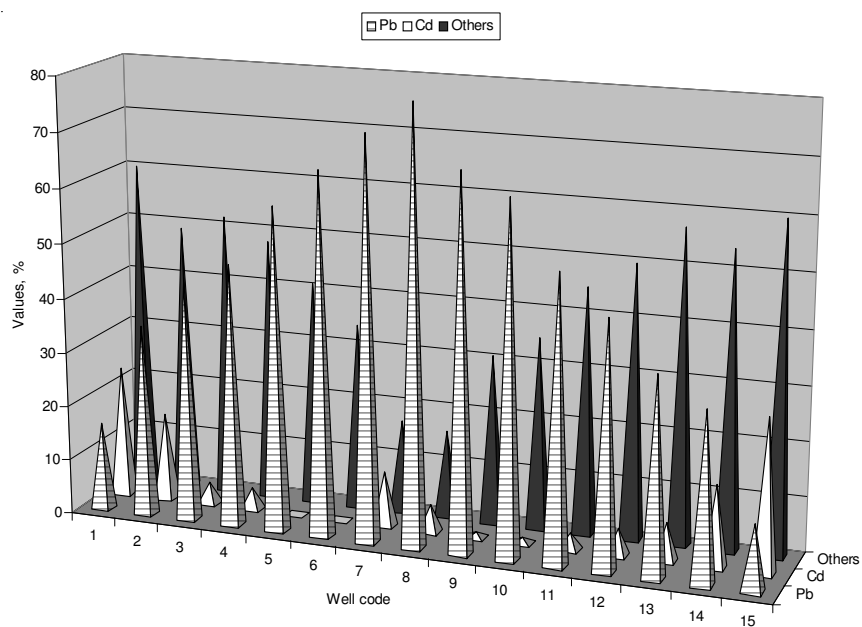


Fig. 2. Distribution of Pb and Cd in representative wells

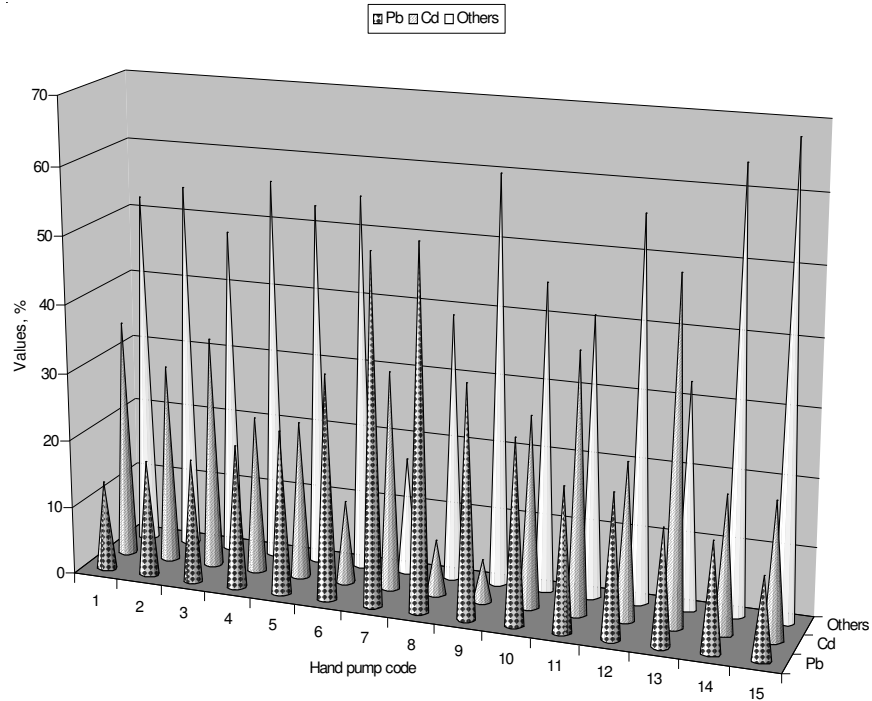


Fig. 3. Distribution of Pb and Cd in representative hand pumps

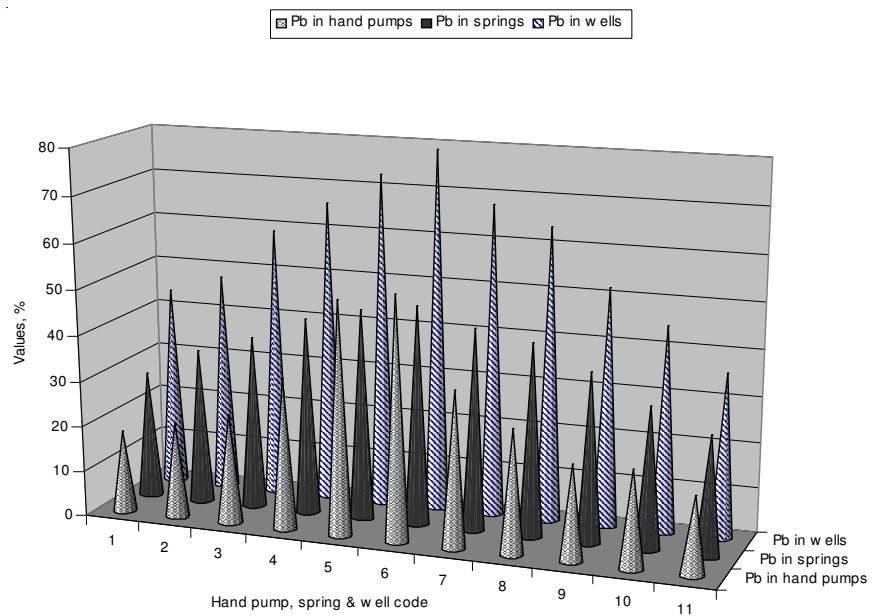


Fig. 4 Relative distribution of Pb in representative wells, springs & hand pumps

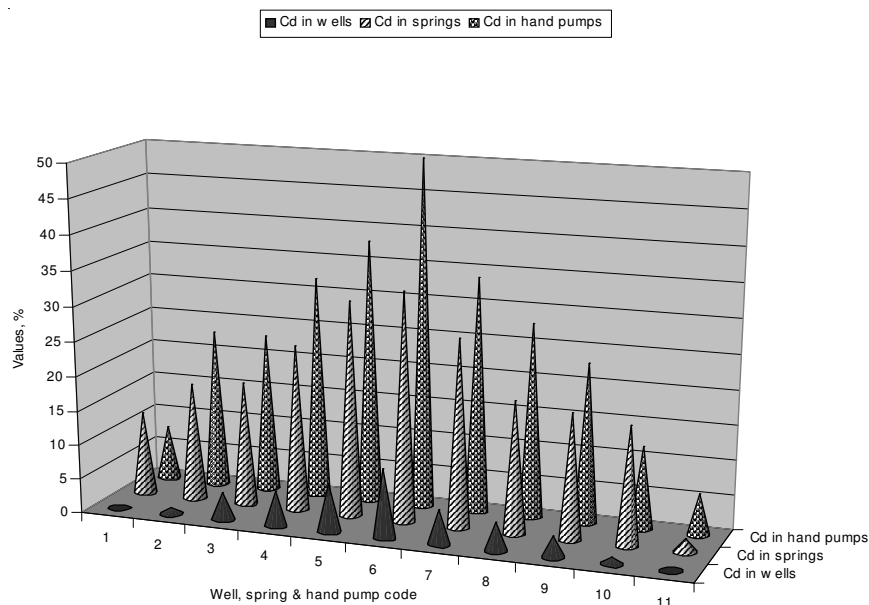


Fig. 5. Relative distribution of Cd in representative wells, springs and hand pumps

presence. For major metals their solubility and availability at soil-aqua interface is significant. Bicarbonates is the major sequestering agent for speciation of  $\text{Ca} > \text{Mg}$ , next in order is  $\text{Cl}$  for  $\text{Ca} > \text{Na} > \text{Mg}$ .

For metal availability (mg/L) the mobility and transfer mode appears different. Organic acid of leaf leachate absorbed on soil surface increases its cation exchange capacity and catalyze the whole process. A two stage pathway is most likely followed. At the two-phase interface the metals are immobilized through their adsorption or mineralization. Later organic acids-humic and fulvic acid, form aqueous complexes through water sequestering of metals thereby facilitating their mobility and replenish lower levels of minerals from soil to aqueous phase. This is further supported by the fact that the study area is clay rich capable of holding sufficient water molecules for demineralization of organic matter. Since micro metals are especially susceptible to ion exchange and facilitated by pH based humic acid and fulvic acid catalysis<sup>13</sup>.

As a corollary to present metal availability study, it was interesting to calculate the proportion of RDA, the residents of the study area acquire through water intake (Figs. 6-8). Each person was assumed to have been drinking 1.5 L of water per day.

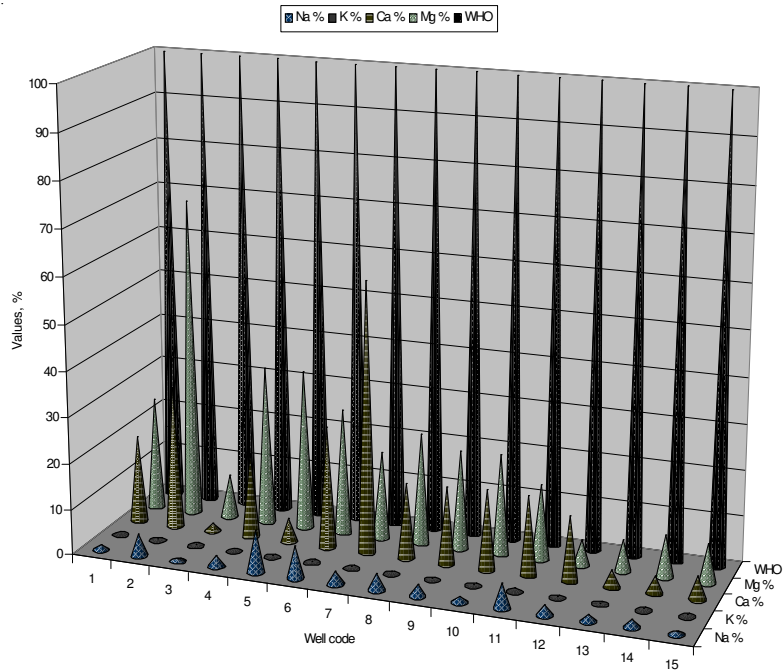


Fig. 6. Percentage of major nutrients in representative wells per 1.5 L (assumed average per capita water intake)

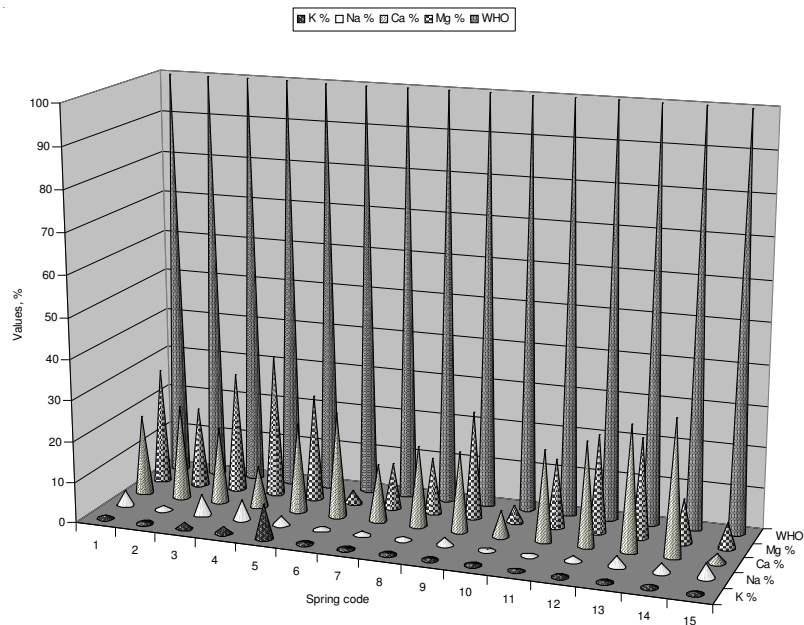


Fig. 7. Percentage of major nutrients in representative springs per 1.5 L (assumed average per capita water intake)

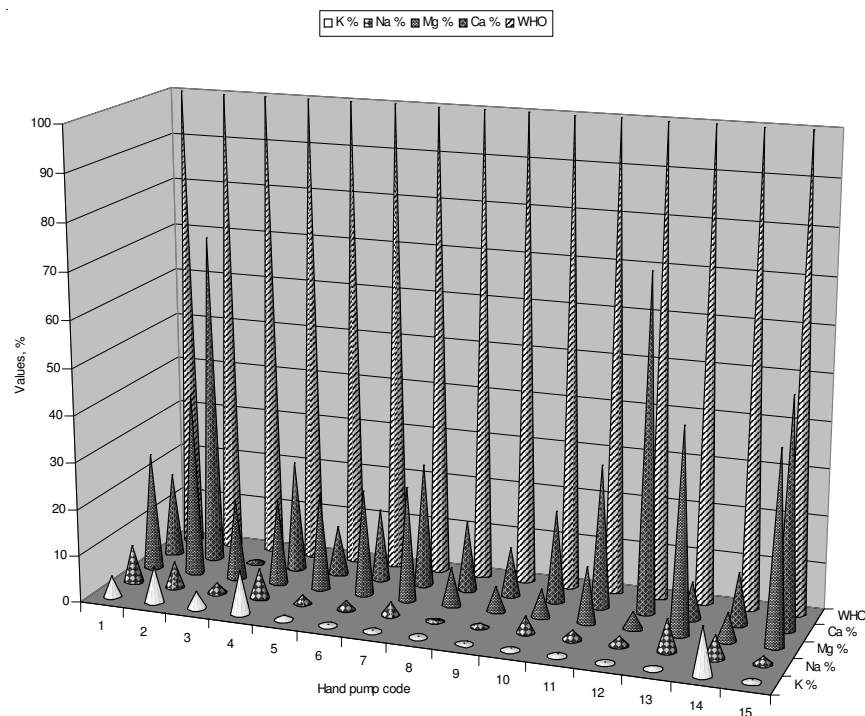


Fig. 8. Percentage of major nutrients in representative hand pumps per 1.5 L (assumed average per capita water intake)

### Conclusion

Presence of major nutrients Ca, Mg, Na, K, falls within WHO thresholds, their mass-charge balance is sustained through seasonal changes and hydro cycles. Alkaline earth metals precede the alkalis in distribution order with an occasional change of places due to residence time of water at soil-water interface.

Of the seven micro metals targeted, only Pb and Cd over spill WHO admissible limits. The elevated levels are of lithological origin and their availability in aqueous phase is catalyzed by organic acids especially humic and fulvic acids.

Since Pb and Cd presence is of lithological origin, later, when waste water of anthropogenic source also gets mixed up with the water stock, its pretreatment would be imperative.

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