The Influence of Natural Organic Matter on the Transport and Bioavailability of Arsenic and Trace Metals in Groundwater in Lahore, Pakistan

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Summary: Samples of drinking water from wells situated in Lahore, Pakistan have been analysed for dissolved organic carbon (DOC), manganese, iron, copper and arsenic in a study on the role played by DOC in facilitating the transport of these elements. Filtered samples (64) were collected from five wells (depths 50-200 m) during the winter (31.12.09-21.02.10). During the period (2009 – 2010), the concentrations of DOC (0.02-2.89 mg/L) in water from wells 1 and 4 correlate positively with that of arsenic. In well 4 there is also a positive correlation between DOC and the manganese concentration. However, analysis of water extracted from well 5 shows a negative correlation between copper and DOC. The concentrations of arsenic (10-36 µg/L), which are high relative to the limit recommended by WHO; result from a combination of iron reduction and interactions between DOC and the arsenic-containing minerals that constitute part of the sediment. The results are consistent with DOC contributing to the release and transport of arsenic and trace metals in ground water. It is suggested that DOC may provide a means for evaluating the loadings of these elements in watercourses.

Key words: Arsenic, DOC, Correlation, Drinking water, Lahore, water contamination.

Introduction

The World Health Organisation (WHO) is a global driving force in providing access to clean drinking water in many parts of the world. [1] It is generally recognised that the availability of clean drinking water is paramount to economic development. [1] Until relatively recently the focus on providing clean drinking water was the eradication of water-borne diseases. Unfortunately, in some parts of the world, other potential risks that were initially ignored. These are the contamination of water by certain trace metals or non-metals that can be either geological or anthropologic origin. Well-cited examples are the serious consequences to health that caused by arsenic contamination in deep drinking water wells in Bangladesh. [2] This exposure led to extensive illness and many deaths. The source of this contamination is geological. Over millions of years, arsenic-containing minerals in sediment are washed down from the Himalayas and transported via waterways and aquifers into vast stretches of Asia, ranging from Pakistan to China and even as far as Vietnam in South-East Asia .[3] It is the release of arsenic into ground water and aquifers which gives rise to contaminated public water supplies.

It is important when formulating effective remediation strategies to understand the complex chemical processes that culminate in contamination by arsenic and trace metals. An important environmental factor is the wide range of organic compounds, collectively named natural organic matter (NOM), which greatly influences the behaviour of contaminants in aquatic environments. [4] Filella [5] has looked into the most widely applied terminology within this field and points out that one of the difficulties in studying NOM concerns terminology because a number of different acronyms and names are in use. For example, NOM can be quantified in terms of total (TOC) and dissolved organic carbon (DOC). NOM is a term that encompasses a wide range of organic compounds that have their origins in the biochemical processes of plants and animals and which occur throughout natural ecosystems. [6] NOM is a major factor in aquatic and terrestrial ecosystems because it results from ubiquitous decaying material from plants and animals. The material is crucial to the water chemistry and therefore to the transport of pollution and to the overall global carbon cycle. The complex and heterogeneous mixtures of organic compounds interact with ecosystems by a variety of processes. These include adsorption on mineral surfaces, photochemical reactions that alter reactivity and other properties, as well as microbial degradation. [7] Nutritional sources for microorganisms include natural organic material. In general, the nutritional value of ground water is very low because DOC is either degraded by a multitude of organisms near the surface of the soil or is bound to particles at the surface. [7]

However, there is another very important and widely accepted processes involved in the mobilization of manganese, iron, copper and arsenic

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in Asian aquifers. Previous studies reported positive correlations between dissolved arsenic and iron in groundwater. These points at an influence of redox reactions causing the reductive dissolution of Mn- and Fe-minerals. [8, 9] It is generally accepted that NOM is an important factor that affects the biogeochemistry of trace metals and some nonmetals. [10] It is apparent from the literature that the finer points behind the mechanisms governing adsorption and desorption on complex adsorbent surfaces are not fully understood. NOM found in water consists of both hydrophobic and hydrophilic components where the largest fraction generally consists of hydrophobic acids. These make up approximately 50% of the dissolved organic carbon (DOC) [11]

The active constituents of NOM are humic and fulvic acids. [12] Humic acid is a mixture of many different acids that contain carboxyl and phenolate groups which behave functionally as dibasic, and sometimes tribasic, acids. The fulvic acids, which impact similarly on ground water, are similar but of lower molecular weight and have higher oxygen content than humic acids. [13]

The importance of these acids is that they are ligands and can bind heavy metals. [14] To a large extent the complexation determines the mobility, bioavailability and toxicity of the heavy metals and some nonmetals, for example arsenic. Thus, the mobility of arsenic may be significantly increased by the presence of NOM in soil and this has an impact on toxicity. [15]

In aquatic environments it is important to identify the physicochemical processes that govern the interactions between DOC and mineral phases**.** In the case of aquatic environments it is important to study the formation, transformation and transport of organic material and to elucidate the relation between organic matter and trace elements if the dynamics of such systems are to be understood.

In terrestrial and aquatic environments, the dissolved fraction of organic material facilitates the transport of contaminants such as arsenic. This is particularly relevant to some anthropogenic sources of pollution such as croplands and grasslands where irrigation and drainage disperse fertilisers, pesticides and herbicides. [4]

There is health hazards associated with DOC in that these materials enhance the transport and bioavailability of arsenic and trace heavy metals into groundwater whether it be from natural or anthropogenic sources [16]. The adverse effects to human health of some water-borne metals and nonmetals expressed as cancers, skin lesions and other ailments are well documented [17]. For example, a UNICEF survey on hospital admissions in Lahore, Pakistan found that nearly 40% of patients admitted to hospitals suffered from some form of water-related disease. Nearly 30% of deaths are also caused by water-borne maladies. [18]

In particular, one study showed that children in the district of Kasur (55 km from Lahore) who were exposed to drinking water contaminated with arsenic exhibited intellectual capacities that were significantly lower compared to children who had access to arsenic-free drinking water. [19] In other areas of Pakistan, such as the southern part of Sindh, respiratory diseases have been reported.[20] and skin lesions have been found in Khairpur Pakistan.[21] Thus, arsenic is insidious and is also a carcinogen in addition to causing still-births, chronic airway obstruction and hypertension and also elevates levels of post neonatal mortality, diabetes mellitus, and nephrosis. [22] High concentrations of iron, although not actually hazardous to health, give water a brown colouration and impart an unpleasant odour and taste which not only detracts from its aesthetic quality but also increases the cost of water treatment.

We report here on the interactions between dissolved organic carbon (DOC) and the elements manganese, iron, copper and arsenic in five drinking groundwater sources located within the Municipality of Lahore, Pakistan. The groundwater was analysed for these elements. The environmental impact is due to the speciation of the various trace element ions and their complexation with DOC. [23-25]. The results of the present work are consistent with other studies in Asia and the wide spread distribution of arsenic is attributed to rivers and waterways flowing across the Indo-Pakistan border, thereby linking these areas both geologically and anthropologically. [26] One of the aims of the present study is to assess the quality of the drinking water in Lahore because this is an important prerequisite if remedial actions are to be implemented. [27] We have therefore paid particular attention to DOC, arsenic and selected trace heavy metals and have carried regression analyses between DOC and these elements.

Aside from the aesthetics of the presence of NOM (colour, taste and odour) there are additional health effects that arise from the reactions between DOC and the disinfectants used for purification [28, 29] Other important factors affecting the impact of arsenic on the environment include redox potentials, the presence of sulphides and certain types of bacteria. Another negative effect of NOM is that the material promotes microbiological growth because this corrodes the pipes of the distribution system. [29]

In order to understand the part played by NOM in the geochemical processes that lead to contaminated ground water, it is necessary to map the geology of the relevant area, and the present study concerns the influence of DOC on metal solubilities and transport and hence on the quality of the drinking water.[30]

Sample Collection and Methods

The Area of Collection

Lahore is the capital city of the Punjab province of Pakistan and is the second largest city and metropolitan area in the country by virtue of population which in 2013 was estimated to be 9 million. [1, 31] The city lies on the Indus Plain and covers an area of 684 sq. miles (1,772 km^2) mainly on the left bank of the Ravi River which flows through a flat alluvial plain. The rapid increase in the urban population has resulted in the city spreading to the left bank and the lower alluvial plains. The city plays a major role in the economic development of the country.

Lahore is built on an undulating loess plain i.e. predominantly silt-sized sediment formed by accumulations of wind-blown dust [32] from the late Pleistocene with mounds and low alluvial plains that are a result of more recent unconsolidation and aggradation. The flood plain deposits of the Ravi River are sub-recent to recent in age. [33] Harland *et al*. dated the silty loess to be 1-6 million years (my). These sediments are mainly silt, loamy clay, clay and sand [23] with the loamy clay tending to increase gradually with distance from the river bed. [34] In the southern parts of the Ravi River the thickness of the silt and loamy clay of the flood plains reaches several meters. Flooding due to the annual monsoon leads to fresh sediment being deposited which keeps the clay free of salinity. These sediments are approximately 375 m deep above a foundation of rock of the Indo-Pakistan Plate, outcropping in the Sargodha and Chiniot areas of Punjab, as the Kirana Hills of the Precambrian era. The generalised stratigraphic sequence of the Quaternary sediments of the Lahore Metropolitan Area (LMA) has been described by Akhtar *et al*. [34] as shown in Table-1.

Table-1: Description of quaternary sediments exposed in LMA. [34]

Quaternary Sediments	Description	Age
River bed and sand bars	Unconsolidated sand, silt, loamy clay and clay	Early Recent
Meander belt deposits	Unconsolidated sand, silt and loamy clay	
Younger flood plain deposits	Sand, silt and silty clay	
Older flood plain deposits	Silt, loamy clay and clay	Sub-Recent
Meander belt deposits of ancient streams	Silt and loamy clay	
Silty loess	Silty clay, clay and silt	Late Pleistocene

There are significant changes in lithologies in the direction in which the stratigraphy becomes younger, manifested in particular by the grain size fractions becoming coarser. For example, the coarser sand fraction appeared for the first time in the younger flood plain deposits and the loamy clay of the meander belt deposits from ancient streams. However, clay and silt are present in all sediments regardless of age. [35, 36]

Over 17 percent of the total area of the LMA is prone to flooding. Landform units have been previously studied with respect to genesis, and subdivided into those formed by sediment deposition and those subjected to erosion. [35] These areas are:

Riverbed and Sandbar: This unit develops in low lying land on a broad valley floor that is reshaped annually by flowing water. Slopes are less than 4%.

Meander Flood Plain: This unit forms along a belt parallel to both sides of the Ravi River. The unit is characterised by the formation of numerous bars, meander scrolls, levees and oxbows. These features are repeated as and when the river changes its course. Slopes are less than 5%.

*Active Flood Plain***:** This unit occurs in the form of benches lying slightly above the stream channels on the valley floor. The active flood plains are above water level for most of the year but are commonly flooded when the river overflows, Slopes are less than 4%.

*Covered Flood Plain***:** This is an important landform unit that occurs north of the Ravi River. Its surface material is composed of fine grained sand, silt and clay with little organic matter and is prominently marked by 3-7 m rise in height from the active flood plain.

*Loess Plain***:** A loosely compacted yellowish-grey deposit of windblown sediment of fine silt and clay that has a gentle slope**.** The loess plain, which is the more prominent unit of the LMA, mostly covers the southern stretches of the Ravi River with part also covering the northern reaches.

The soil is fertile and is easily eroded by water and wind. Wells (4) and (5) are situated on the loess plain.

*Basin and Channel Fill***:** This landform unit covers the meandering course of an ancient stream

that passed through the loess plain. There are basins defined by steep banks of the ancient stream that rise 2-3 meters above the active flood plain. Channel fills are broad and elongated depressions. Wells (1), (2) and (3) are situated in basin and channel fills.

Gully: This feature is defined by the steep banks of an old river terrace that rises 3-5 meters above the active flood plain. These have been subjected to severe erosion by monsoon rains so that original gully surface has been almost obliterated.

The tube wells are situated in various parts of the city, and are operated by the Lahore Development Authority's subsection WASA (Water and Sanitation Authority).The locations of the five wells from which the samples were taken are identified by the GPS coordinates listed in Table-2 The depths of the wells are also given.

Analytical Methods

During sampling, disposable powder-free nitrile gloves (VWR) were used to avoid contaminating the equipment and samples. Prior to use, all glassware and sample tubes were acid-washed by leaving them in acid solution (HNO_3, 0.1 M) for at least a day and then rinsing thoroughly with ultrapure water (Q-option, Elga, England) until the pH of the rinsing water was unchanged. In practice, intermittent withdrawal of water from the wells by users means that water is run irregularly over a period of 12 – 16 hours/day. This was taken into consideration by taking samples from flushing water.

Table-2: The depths and locations of the wells.

Sample point	Location	Depth	Latitude	Longitude
Well 1	**P-block, Wahdat colony, Lahore**	**650ft, 199m**	**31.515867**	**74.304646**
Well 2	**P-block, Wahdat colony, Lahore**	**150ft, 46m**	**31.518122366395524**	**74.30026352405548**
Well 3	**H-block, Model Town, Lahore**	**550 ft, 168m**	**31.47867622129598**	**74.33710634708405**
Well 4	**17- Kiran Street, Taj Bagh, Lahore**	**250ft, 77m**	**31.56156520462974**	**74.41638708114624**
Well 5	**Taj Bagh, Lahore**	**650 ft, 199m**	**31.562465668345574**	**74.4165962934494**

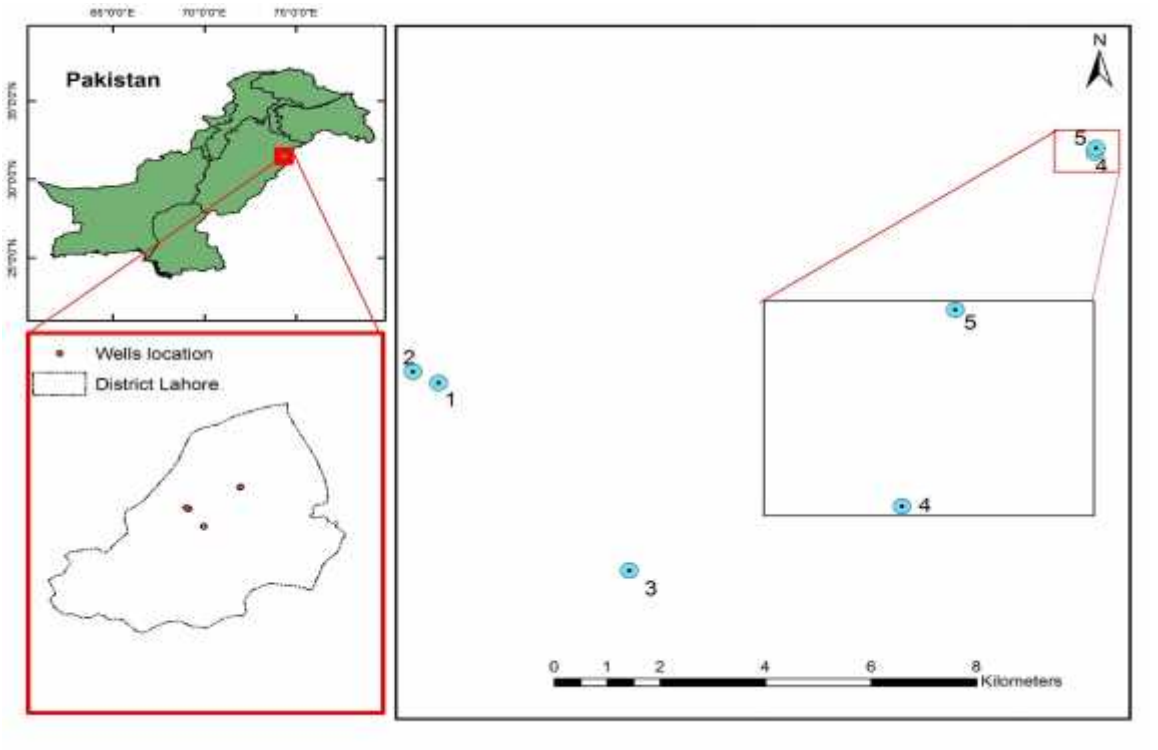

Fig. 1: The locations of the five wells in Lahore.

Water samples for the metal analyses by ICP-MS were extracted using 30 ml sterile syringes (Henke-Sass. Wolf, GMBH and CO) and filtered through 25 mm syringe filters of polyethersulfone with pore size 0.45 microns (VWR) into polypropylene tubes (14 ml, Sarstedt). Quality control of the filters were performed using ultrapure water and multielement standard solutions at different element concentrations. Filtration of ultrapure water showed that the filters did not add significant amounts of elements to the water. Using multielement standard solutions at environmentally relevant concentrations, no substantial differences in element concentrations were found between filtered and unfiltered samples (the recoveries were with very few exceptions in the range 90-110%). Samples were conserved by nitric acid (Merck, supra-pure) to a final pH of 1.

Samples for analysis of dissolved organic carbon were extracted (using the same syringe) into 40 ml open tubes of borosilicate glass with Teflon membrane (QEC) caps. Prior to use the borosilicate glass tubes were washed with phosphoric acid and ultrapure water. Immediately before sampling the tubes were rinsed twice with filtered samples prior to the actual sample being taken. The variations in the measurements were assessed by taking two parallel controls between sampling.

Elements were analysed by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) ,using a Thermo Finnigan model Element 2 instrument (Bremen, Germany). The radio frequency power was set to 1400 W. The samples were introduced using a CETAC ASX 500 autosampler with a peristaltic pump (1 ml/min). The instrument was equipped with a concentric PFA-ST nebulizer connected to a Scott PFA spray chamber, platinum sample and skimmer cones and a demountable torch of quartz with a guard electrode. The instrument was calibrated using 0.6 M HNO_3 solutions of multielement standards at 3 different concentrations.

An aqueous certified reference material containing 66 elements (SPS-SW-2, Spectrapure Standards, Norway) was analysed at the beginning and end of each analytical sequence to check the calibration of the instrument. For the elements used in the present study, the concentrations found in the reference material were always in the range of 85-115% of the certified values. Three blank samples (ultrapure water with suprapure nitric acid) were analysed in each analytical sequence, and all blank levels obtained were negligible.

Measurements of pH, conductivity and temperature were conducted by a handheld Multi 350i system from WTW, supplied with a SenTix pH electrode and a ConOx combined conductivity and oxygen sensor (WTW). Dissolved organic carbon was analyzed by IR spectroscopy using a Torch Combustion TOC Analyzer from Teledyne TEKMAR.

Dissolved organic carbon (DOC) was measured on samples that were were filtered through a 0.45 μm polyethersulfone filter (VWR) and kept in precleaned borosilicate vials (40 mL, QEC). The analyses were carried out using a Torch Combustion Analyzer from Teledyne Tekmar using a NDIR detector with static pressure concentration technology and absorption wavelength 4.26 micrometers. Halogens which might affect the detector were removed by a halogen trap (Cu and Sn loop), and interfering water vapour was removed by a moisture system consisting of a condensing loop, cooling fan, mist trap and a permeation dryer. Inorganic carbon was removed by adding ACS grade phosphorous acid (21%) to the samples until a final pH below 2 was attained, and purging for 1 min with synthetic air (5.5 Plus, Yara Praxair). The combustion temperature was 750°C; the NDIR pressure was set at 50 psig for the detector chamber. All other instrumental parameters were set in accordance with the Teledyne Tekmar Torch application for Total Organic Carbon.

The specifications for the standard solution used for calibration are: certified standard KHP 1000 mg/l (Teledyne Tekmar) diluted to 50 mg/l with DI water (Milipore MilliQ gradient, 18 Mohm). The calibration curve (R^2 better than 0.995) was obtained for concentrations 0.500, 1.00, 5.00, 10.00 and 20.00 mg/l. Calibrations were repeated after 20 samples and with 3 parallel runs per sample. Part of the measuring protocol was the determination of the system blank and baseline corrections together with a frequent detector check.

A separate washing routine (sample syringe and sample chamber) was performed between measurements on individual samples.

Statistical Methods

The data were analysed statistically using the regression analysis tool of the free-trial licensed version of the MiniTab Statistical Analysis Software. The analysis made use of hypothesis testing where the alpha (α)value determines the maximum acceptable level of risk for rejecting a true null hypothesis (type I error) and is expressed as a probability ranging between 0 and 1.

The value of α (usually referred to as the level of significance) is set before beginning the analysis and compared with p-values in order to determine the significance.

The most commonly used α-level is 0.05, which means that the probability of finding an effect that does not really exist is only 5%. The value used for analysis in this paper was set at α=0.1.

Results and Discussion

Since dissolved carbon plays an important role in mobilising or immobilising elements such as manganese, iron, copper and arsenic. [37] We found it necessary to analyse the water samples for these contaminants and Table-3 summarises the results and statistics for the DOC and ICP-MS analyses.

The number of samples and duration of sampling from wells is reported in Table-4.

whereas Table 3 contains the median and average values for DOC and trace elements, Table 5 lists the ranges of the latter.Table 5, which defines and lists the guideline or reference values pertaining to the elements under study, shows that the concentrations of arsenic are generally high, whereas the general trend for the concentrations of manganese and iron are just above the values given by the guidelines, although for some of the wells the concentrations of these metals, except for copper, are higher than the reference values.

Table-3: The pH, DOC and trace element (Mn, Fe, Cu, As,) concentrations in filtered samples over the period 31.12.09-21.02.2010.

Sample Point	PH	DOC mg/L median/ average	Mn(µg/L) median/ average	Fe (µg/L) median/ average	Cu(µg/L) median/ average	As(µg/L) median/ average
Well 1	7.53	0.90	41.4	26.3	0.36	22.6
		1.04	41.7	25.98	0.42	22.77
Well 2	7.87	1.3	29.6	17.8	11.0	7.2
		1.19	40.75	39.32	11.50	7.5
Well 3	8.05	0.66	42.4	327	0.61	23.8
		0.76	42.21	260.31	0.62	23.85
Well 4	8.13	1.06	78.0	168	0.87	26.9
		1.15	67.25	137.28	3.75	21.97
Well 5	8.15	0.67	55.9	189	0.79	32.1
		0.76	55.78	197.80	0.90	32.28

The number of samples and duration of sampling from wells is reported in table 4.

Table-4: The number of samples and duration of sampling from wells. .

Sample points	Duration	No of samples
Well 1	1/1/10-19/2/10	9
Well 2	31/12/09-21/2/10	15
Well 3	31/12/09-17/2/10	9
Well 4	31/12/09-15/2/10	13
Well 5	31/12/09-21/2/10	18

Table-5: Comparison of trace elements concentrations with WHO guideline values for Cu and As, and with EU water quality standards for Mn and Fe. [1, 38]

Elements	Mn	Fe	Cu	As
Guideline value by WHO	20-50 µg/L	50-200 µg/L	100-300µg/L	10 µg/L
Well1	39.5 - 45.8	19.7 - 32.2	0.16 - 0.74	21.6 - 24.1
Well2	5.70 - 109	0.16 - 162	0.02 - 2.25	5.32 - 13.2
Well3	37.6 - 45.7	47.2 -260	0.08 - 1.59	22.7- 25.2
Well4	16.1 - 113	15.9 - 266	0.01 - 10.5	6.50 - 36
Well5	48.7 - 62.9	154 - 260	0.12 – 2.04	29 - 36

The data presented in Table 5, show that the water quality is not in accordance with the EU and WHO standards for drinking water. Hence, over time, the level of arsenic contamination found in these wells is likely to have adverse effects on health, which could possibly be exacerbated by waterborne diseases. The latter are the subject of a report by USA Department of Health and Human Services which tracked diseases in Pakistan that are attributed to waterborne causes. These include lung cancer, skin, prostrate, kidney, nose and liver, still births, post neonatal mortality, bronchitis, diabetes mellitus, chronic airway obstruction, lymphoma, ischemic heart diseases, nephritis (chronic, inflammation of kidneys), hypertension, emphysema, black foot disease.[18] USAID estimates that 250,000 child deaths from waterborne diseases occur each year in Pakistan .[18]

The arsenic and metal concentrations vary with location and moreover these variations appear to be influenced by interactions with DOC. Fig. 2 and 3 indicate that the concentrations of DOC and arsenic are positively correlated for Wells (1) and (4). Similarly, in Well (4), the concentrations of DOC and manganese also appear to correlate positively (figure 4). On the other hand, in the case of Well (5), the correlation between the concentrations of DOC and copper is apparently negative. We do not find a significant correlation between DOC and iron in any of the wells.

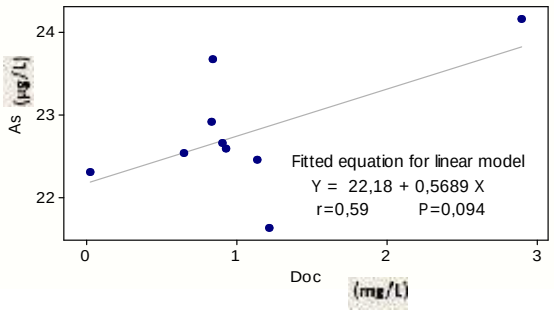

Fig. 2: Well 1 Positive Regression for DOC vs As

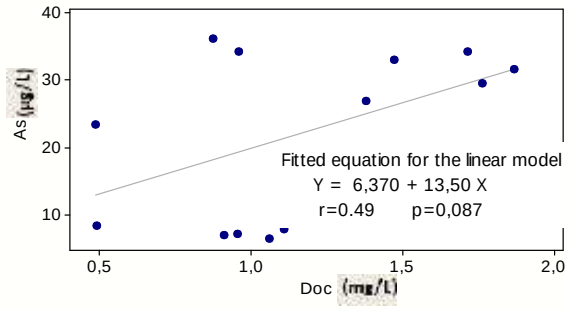

Fig. 3: Well 4 Positive Regression for DOC vs As

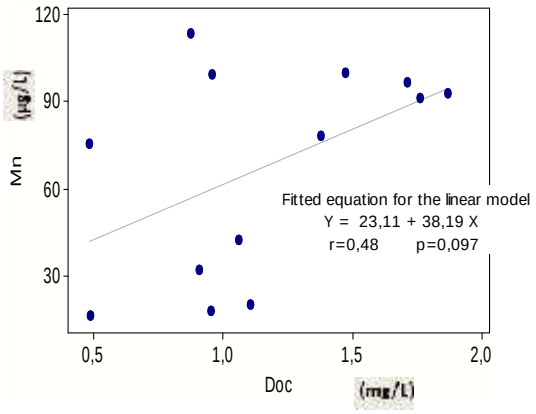

Fig. 4: Well 4 Positive Regression for DOC vs Mn.

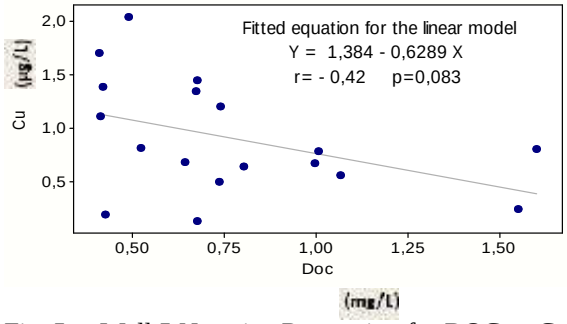

Fig. 5: Well 5 Negative Regression for DOC vs Cu.

The concentrations of iron in Wells (3), (4) and (5) are much higher than those found in Wells (1) and (2) with the maximum (260 µg/L) being observed in Well (3) which is in a residential area. Moreover, at these high iron concentrations there is no correlation with DOC. We attribute the high concentration of iron in Well (3) to contamination from slag deposited by local iron foundries and to a combination of discharge from a nearby sewage canal and from corroded iron pipes. The latter source of contamination is common for example in many North American cities, especially where aging water systems are more than a hundred years old. [39] Certainly, there are corroded iron pipes delivering water to the Lahore site.

The concentration ranges of manganese in Well (2) (5.7 -109 µg/L) and Well (4) (16.1-113 µg/L) are considerably wider and the maximum value significantly higher than in the other wells. The most common sources of iron and manganese in groundwater are natural, for example, from the weathering of iron- and manganese-bearing minerals and rocks. For most natural waters, manganese and iron are not considered to be a health risk by WHO. [40] However, in the wells studied here, we find high concentrations of iron and manganese. This leads to plumbing fixtures and laundry being discoloured and also to manganese-containing solids being deposited within pipes. These black solids break into particles that impart an unpleasant appearance and taste to the water. Both metals can increase the growth of unwanted bacteria that form a slimy coating within the pipes

The pH of the water at 170 m below ground in Well(3) is 8.05. At such depths, conditions are reducing and anaerobic and these conditions, coupled with the alkalinity, leads to iron(III) being reduced to iron(II). The overall effect is to release ferrous iron together with other metals or arsenic that might have been adsorbed on the original ferric hydro-oxide surfaces. [42] In Well (3), the total arsenic concentration is also very high due to the release of arsenic(V) that was originally attached to ferric hydro-oxides.[43, 44]

Both geological and anthropogenic sources play important roles as sources of various elements in ground water. An example of the former is the fact that Lahore is located on an alluvial plain made up of loamy clay soil. In general loamy soils contain more nutrients, moisture and humus than sandy soils. However, the actual contribution of these components to ground water depends on the permeability. The organic matter, which is mainly incorporated in loamy soils, has important consequences for the chemistry of sediments although; the significance of this is lessened when clay is dispersed throughout the fine earth fraction. [45]

Within the general geological description, there are specific sites, belonging to the “Loess Plain”, which include “Basic Channels and Fills”, which increases the probability that they are rich in DOC.

Wells (1) and (2), which are stratigraphically positioned in the Basic Channels and Fills, are in congested residential areas with

agricultural land being more than 1 km away. A river canal passes nearby. This land was converted into a residential area in 2008. Wells (4) and (5) are located in the loess plain and are close to both agricultural land and residential areas. A canal connected to the River Ravi is nearby.

In Wells (1) and (4), the concentrations of arsenic are high, and DOC and arsenic are positively correlated even at these concentrations. The complexing properties of DOCs are important for transporting metals and arsenic. In the process, metal solubility are enhanced and bioavailability reduced. Recently, it was reported [45] that high arsenic concentrations have been found in some localities in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India. These are among 21 countries in different parts of the world that are affected by groundwater being contaminated by arsenic. The largest population at risk is in Bangladesh followed by West Bengal in India.

Organic and inorganic arsenic compounds are based on the two valence states arsenic(III) and arsenic(V) which are represented by a number of species in the environment, with the inorganic compounds being frequently detected in water. The toxicity and mobility of arsenic depends upon valence state and the stabilities of the different forms of arsenic are influenced by pH. Arsenic is mainly found in groundwater as either inorganic in the form of arsenite (As(III)) and/or arsenate (As(V)), with the former predominating under anaerobic conditions and the latter under aerobic conditions.[46] Arsenic(V) is easily converted to, arsenic(III) under reducing conditions with the former being more soluble in water and hence more toxic. [47] According to Clifford *et al* , arsenic(V) is reduced to arsenic(III) over the pH range 7 – 9.[48] Within this pH range arsenic, originally bound to iron oxides and sulphides, is released and dissolved in water. [47] Arsenic is very likely present as arsenic(III) since the pH of the samples drawn from the five wells at depths ranging between 46-199 m under anaerobic conditions are in the range 7.5 - 8.2. This is significant because inorganic arsenic(III) is 60 times more hazardous than arsenic(V) [49] and also because arsenic(III) is more difficult than arsenic(V) to remove from drinking water. [50, 51] Our results also show that arsenic is present at relatively high concentrations in all of the samples. Such high arsenic concentrations reflect greater desorption at higher pH and the difficulty in removing arsenic(III) compared with arsenic(V). [41] Consequently, adsorption/desorption of arsenic is a major factor that affects the bioavailability and mobility of arsenic in soil and water. As the water becomes basic, hydroxyl anions neutralize the acid sites in the sediments thereby facilitating the release of arsenic(III) and arsenic(V). Therefore, it is the basicity of the water in the wells that causes the concentration of arsenic to actually increase. On the other hand, at Muzafrabad, also in the Punjab, anthropogenic sources (especially smoke from coal combustion by brick factories) of arsenic emissions are the major cause of ground water pollution. [52]

The variables defining the nature of the aforementioned sites that are linked to arsenic are specific to the localities of the five wells. Most of the binding sites are provided by oxidised species containing iron, aluminum or manganese. Within the observed pH range, the reduction of metal oxides leads to their metals being released to water and at the same time making arsenic(III) and arsenic(V) available to the environment. Other important factors affecting the impact of arsenic on the environment include redox potentials, the presence of sulphides and certain types of bacteria. From the viewpoint of toxicity, reduction of arsenic(V) to arsenic(III) increases the mobility of arsenic and hence toxicity. Under the present conditions, the presence of sulphides [35] influences the mobility of arsenic(III) (but not arsenic(V)) through the formation of insoluble As_2S_3. It is known that certain types of bacteria are capable of affecting the mobility of arsenic either through reduction of arsenic species or by reducing binding sites. Bacterial activity depends on the availability of nutrition. [53, 54]

In some areas, external factors such as natural and synthetic fertilizers provide additional sources of nutrition. [55, 56] In such systems, DOCs contribute to an environment in which arsenic(V) is reduced to arsenic(III) and iron(III) to iron(II). However, if oxygen is present in ground water there is the potential for arsenic to be released through oxidation. Some arsenic minerals contain sulphides which are a source of nutrition for some bacteria which, in presence of oxygen, oxidise sulphide to sulphate, thereby releasing arsenic. [57] The same process occurs at some mining sites where acid and metals are released into water with bacteria contributing to acid mine drainage. [58] These reactions can occur in the absence of bacteria but only much more slowly.

In the five wells sampled here, the concentrations of arsenic are found to be considerably higher (up to 36 µg/L) than the limit recommended by the WHO guideline (10µg/L);

Table 5. Such levels pose a serious hazard to health, as is exemplified by a study on cancers (e.g. lung and bladder) in male patients in southern Pakistan. These are attributed to the presence of inorganic arsenic in drinking water. [59]

Iron and manganese concentrations also exceed the limits recommended by the EU guidelines (table 5). However, the maximum copper concentration found (10.5 µg/L) is well below the guideline limit (300 µg/L) and hence is not a health hazard. In this case, the presence of copper is attributed to pollution from mining, farming and manufacturing operations, together with the release of municipal or industrial wastewater into rivers and lakes. The corrosion of copper pipes that are subjected to acidic environments is a significant source. [60, 61] When copper species are introduced into the soil, they become strongly attached to organic materials and minerals thereby inhibiting further transport of the metal into the groundwater and so the concentration of copper is low. [62]

However, copper can accumulate in plants and only a few species can grow or thrive on copper rich soils. [63, 64] Copper poisons soil fauna which are important for soil fertility [58] and are beneficial to the quality of water because they reduce the concentration of copper in water which comes at a price for agriculture and plant life in general. [65] Natural geochemical and anthropogenical processes can contribute to the copper concentration. These processes are thus consistent with the aforementioned negative correlation observed between copper concentration and DOC in Well (5).

Conclusion

The analyses of filtered water samples from the five wells show that there are variations in the concentrations of manganese, iron, and copper, arsenic. The latter element stands out both because the concentrations in all of the wells (10 – 36 µg/L) are above the level recommended by WHO (10 µg/L) and since the element may be mainly in the form of arsenic(III) which is more toxic than arsenic(V). Although the corresponding levels for manganese and iron are also high they do not represent a significant health risk; the main problem is low aesthetic quality. The concentrations of copper are well below the level recommended by WHO. The relatively high arsenic concentrations are most likely a result of the interactions between arsenic-containing minerals that constitute part of the sediment and DOC. The extraction of arsenic from the minerals is facilitated under anaerobic conditions by the high pH **(**7.5-8.2) of the water at depths of 50-200 m. The oxidation of arsenopyrite releases arsenic which is absorbed on, or occluded in, iron oxides with the arsenic being released to water under reducing conditions. For some of the wells, arsenic and manganese correlate positively with the DOC concentrations, and in one well a negative correlation is found for copper. It must be noted, however, that the correlations are not strong and only of borderline statistical significance, which may partly be explained by the low number of samples. In conclusion, the results provide some support for the notion that DOC influences the transport of arsenic, manganese and copper, but not iron, in the drinking water wells in Lahore.

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References

1. Guidelines for Drinking Waterquality,Chemical Face Sheet, **12**, 307 (2014).
2. J. McArthur, D. Banerjee, K. Hudson-Edwards, R. Mishra, R. Purohit, P. Ravenscroft, A. Cronin, R. Howarth, A. Chatterjee and T. Talukder, Natural Organic Matter in Sedimentary Basins and Its Relation to Arsenic in Anoxic Ground Water: The Example of West Bengal and Its Worldwide Implications, *Appl. Geochem.*, **19**, 1255 (2004).
3. N. M. Phuong, Y. Kang, K. Sakurai, M. Sugihara, C. N. Kien, N. D. Bang and H. M. Ngoc, Arsenic Contamination in Groundwater and Its Possible Sources in Hanam, Vietnam, *Environ. Monit. Assess.*,**184**, 4501 (2012).
4. W. Kordel, M. Dassenakis, J. Lintelmann and S. Padberg, The Importance of Natural Organiuc Material for Enviromental Processes in Water and Soil, *J. Pure Appl. Chem.*, **69**, 1517-1600(1997).
5. M. Filella, Freshwaters: Which Nom Matters?, *Environ Chem Lett*, **7,** 21 (2009).
6. Greenfacts, 22 April **2007,** Http://Www.Greenfacts.Org/Glossary/Mno/Natural-Organic-Matter-Nom.Htm
7. X. Xiang, Y. Huang, G. Madey, S. Cabaniss, L. Arthurs and P. Maurice, Modeling the Evolution of Natural Organic Matter in the Environment with an Agent‐Based Stochastic Approach, *Nat Resour Model*, **19**, 67 (2006).

8. J. McArthur, P. Ravenscroft, S. Safiulla and M. Thirlwall, Arsenic in Groundwater: Testing Pollution Mechanisms for Sedimentary Aquifers in Bangladesh, *Water Resour.Res.*, **37**, 109 (2001).
9. R. Nickson, J. McArthur, P. Ravenscroft, W. Burgess and K. Ahmed, Mechanism of Arsenic Release to Groundwater, Bangladesh and West Bengal, *Appl. Geochem.*, **15**, 403 (2000).
10. O. M. Saether and P. d. Caritat, *Geochemical Processes, Weathering and Groundwater Recharge in Catchments*, Brookfield, Rotterdam, p. 400 (1997).
11. E. M. Thurman, *Organic Geochemistry of Natural Waters*, Dordrecht : Springer Netherlands, p.497 (1985).
12. D. G. Kinniburgh, W. H. van Riemsdijk, L. K. Koopal, M. Borkovec, M. F. Benedetti and M. J. Avena, Ion Binding to Natural Organic Matter: Competition, Heterogeneity, Stoichiometry and Thermodynamic Consistency, *Colloids Surf., A*, **151**, 147 (1999).
13. M. Yamauchi, S. Katayama, T. Todoroki and T. Watanable, Total Synthesis of Fulvic Acid, *J Chem Soc Chem Comm*, 1565 (1984).
14. J. J. Morgen and W.Stumm, *Aquatic Chemistry : An Introduction Emphasizing Chemical Equilibria in Natural Waters*, Wiley, New York, p. 780 (1981).
15. A. D. Redman, D. L. Macalady and D. Ahmann, Natural Organic Matter Affects Arsenic Speciation and Sorption onto Hematite, *Environ. Sci. Technol.*, **36**, 2889 (2002).
16. R. A. Bell, N. Ogden and J. R. Kramer, The Biotic Ligand Model and a Cellular Approach to Class B Metal Aquatic Toxicity, *Comp Biochem Physiol C Toxicol Pharmacol*, **133**, 175 (2002).
17. K. G. Brown and G. L. Ross, Arsenic, Drinking Water, and Health: A Position Paper of the American Council on Science and Health, *Regul. Toxicol. Pharmacol*, **36**, 162 (2002).
18. Pakistans Waters at Risk, *Freshwater and Toxics Programme, WWF, Pakistan,*Lahore, (2007).
19. S. Abbas, E. M. A. Qureshi, F. Ahmad, S. Vehra and A. U. Khan, An Assessment of Relationship between Arsenic in Drinking Water, Health Status and Intellectual Functioning of Children in District Kasur, *Pakistan, J. Nutr.*, **11**, 150 (2012).
20. M. B. Arain, T. G. Kazi, J. A. Baig, M. K. Jamali, H. I. Afridi, N. Jalbani, R. A. Sarfraz, A. Q. Shah and G. A. Kandhro, Respiratory Effects in People Exposed to Arsenic Via the Drinking Water and Tobacco Smoking in Southern Part of Pakistan, *Sci Total Environ*, **407**, 5524 (2009).
21. Z. Fatmi, I. N. Abbasi, M. Ahmed, A. Kazi and F. Kayama, Burden of Skin Lesions of Arsenicosis at Higher Exposure through Groundwater of Taluka Gambat District Khairpur, Pakistan: A Cross-Sectional Survey, *Environ. Geochem. Health*, **35**, 341 (2013).
22. T. Yoshida, H. Yamauchi and G. Fan Sun, Chronic Health Effects in People Exposed to Arsenic Via the Drinking Water: Dose–Response Relationships in Review, *Toxicol. Appl. Pharmacol.*, **198**, 243 (2004).
23. W. B. Harland, *A Geologic Time Scale*, New York, Cambridge ,England, p. 131 (1982).
24. A. Hartland, I. J. Fairchild, W. Müller and D. Dominguez-Villar, Preservation of Nom-Metal Complexes in a Modern Hyperalkaline Stalagmite: Implications for Speleothem Trace Element Geochemistry, *Geochim. Cosmochim. Acta.,***128**, 29 (2014).
25. S. K. Sarker, S. Rashid, M. Sharmin, M. M. Haque, S. S. Sonet and M. Nur-Un-Nabi, Environmental Correlates of Vegetation Distribution in Tropical Juri Forest, Bangladesh, *Trop Ecol*, **55**, 177 (2014).
26. D. Mohan and C. U. Pittman, Jr., Arsenic Removal from Water/Wastewater Using Adsorbents--a Critical Review, *J Hazard Mater*, **142**, 1 (2007).
27. J. H. Reuter and E. M. Perdue, Importance of Heavy Metal-Organic Matter Interactions in Natural Waters, *Geochim. Cosmochim. Acta* ,**41**, 325 (1977).
28. R. J. Bull, *Toxicology*, Academic Press, San Diego, pp. 1041 (1999).
29. B. H. Kornegay, K. J. Kornegay and E. Torres, *Natural Organic Matter in Drinking Water : Recommendations to Water Utilities*, AWWA Research Foundation and American Water Works Association, Denver, Colorado, p.541 (2000).
30. K. H. Johannesson, J. Tang, J. M. Daniels, W. J. Bounds and D. J. Burdige, Rare Earth Element Concentrations and Speciation in Organic-Rich Blackwaters of the Great Dismal Swamp, Virginia, USA, *CHEM GEOL*, **209**, 271 (2004).
31. http://www.lahore.com/.
32. K. Pye, Loess, *Prog. in Phys. Geogr.*, **8**, 176 (1984).
33. S. M. I. Shah, Stratigraphy of Pakistan, *Mem. Geol. Surv. Pak.* **12**, 138 (1977).
34. M. Akhtar, M. I. Sheikh and T. A. Shuja in *Geological Map of Lahore, Vol. Punjab series map-4* **1998**.
35. S. Muhammad iqbal, Managment of Flood Hazards of Ravi River in and around Lahore, Pakistan, *J. Environ, Sci.* **2**, (2002).
36. A. Farid, P. Khalid, K. Z. Jadoon and M. S. Jouini, The Depositional Setting of the Late

Quaternary Sedimentary Fill in Southern Bannu Basin, Northwest Himalayan Fold and Thrust Belt, Pakistan, *Environ Monit Assess*, **186**, 6587 (2014).
37. M. A. Rahman, M. M. Hasan and S. A. Alam, Mobilization of Arsenic with Iron, Manganese and Copper in Borehole Sediments of the River Jamuna, *J. Bangladesh Chem. Soc.*, **25**, 30-37 (2012).
38. S. Iftekhar, PhD. Thesis, *Trace Elements and Their Interactions with Natural Organic Matter in Water*, Norwegian university of science and technolgy ,Trondheim, (2015).
39. M. N. Nadagouda, C. White and D. Lytle, Lead Pipe Scale Analysis Using Broad-Beam Argon Ion Milling to Elucidate Drinking Water Corrosion, *MICROSC MICROANAL*, **17**, 284 (2011).
40. J. E. McLean and B. E. Bledsoe, *Behavior of Metals in Soils*, *540* (1992).
41. https://www.for.gov.bc.ca/hfd/library/documents/bib106076_iron_manganese.pdf.
42. A. Molinari, L. Guadagnini, M. Marcaccio, S. Straface, X. Sanchez-Vila and A. Guadagnini, Arsenic Release from Deep Natural Solid Matrices under Experimentally Controlled Redox Conditions, *Sci. Total Environ.*, **444**, 231 (2013).
43. A. H. Welch, S. A. Watkins, D. R. Helsel and M. J. Focazio, Arsenic in Ground-Water Resources of the United States, *USGS. Fact Sheet*, 63 (2000).
44. R. B. Johnston and P. C. Singer, Redox Reactions in the Fe-as-O2 System, *Chemosphere* **69**, 517 (2007).
45. R. K. Kaufmann, Cutler J, Cleveland. *Environmental Science, McGraw-Hill*, p.318 (2008).
46. Hua Zhang and H. M. Selim, Kinetics of Arsenate Adsorption−Desorption in Soils, *Environ. Sci. Technol.* **39**, p 6101 (2005).
47. K. Vanbroekhoven, S. Van Roy, C. Gielen, M. Maesen, A. Ryngaert, L. Diels and P. Seuntjens, Microbial Processes as Key Drivers for Metal (Im)Mobilization Along a Redox Gradient in the Saturated Zone, *Environ Pollut*, **148**, 759 (2007).
48. D. Clifford, L. Ceber and S. Chow, *Arsenic(III)/Arsenic(V) Separation by Chloride-Form Ion-Exchange Resins*, AWWA WQTC, Norfolk, Va., (1983).
49. J. F. Ferguson and J. Gavis, A Review of the Arsenic Cycle in Natural Waters, *Water Res*, **6**, 1259 (1972).
50. M. Z. López Paraguay, J. A. Cortes, J. F. Pérez-Robles and M. T. Alarcón-Herrera, Adsorption of Arsenite from Groundwater Using Titanium Dioxide, *Clean (Weinh)*, **42** ,*713* (2014).
51. S. K. Gupta and K. Y. Chen, Arsenic Removal by Adsorption, *J Water Pollut Control Fed*, **50**, 493 (1978).
52. R. T. Nickson, J. M. McArthur, B. Shrestha, T. O. Kyaw-Myint and D. Lowry, Arsenic and Other Drinking Water Quality Issues, Muzaffargarh District, Pakistan, Appl. Geochem, **20**, 55 (2005).
53. S. Shakya, B. Pradhan, L. Smith, J. Shrestha and S. Tuladhar, Isolation and Characterization of Aerobic Culturable Arsenic-Resistant Bacteria from Surfacewater and Groundwater of Rautahat District, Nepal, *J. Environ. Manage.*, **95**, 250 (2012).
54. H. M. Anawar, J. Akai, M. Mihaljevič, A. M. Sikder, G. Ahmed, S. M. Tareq and M. M. Rahman, Arsenic Contamination in Groundwater of Bangladesh: Perspectives on Geochemical, Microbial and Anthropogenic Issues, *Water*, **3**, 1050 (2011).
55. B. Das, D. Chakraborty, V. K. Singh, P. Aggarwal, R. Singh, B. S. Dwivedi and R. P. Mishra, Effect of Integrated Nutrient Management Practice on Soil Aggregate Properties, Its Stability and Aggregate-Associated Carbon Content in an Intensive Rice-Wheat System, *Soil Tillage Res*, **136**, 9 (2014).
56. K. K. Bandyopadhyay, A. K. Misra, P. K. Ghosh and K. M. Hati, Effect of Integrated Use of Farmyard Manure and Chemical Fertilizers on Soil Physical Properties and Productivity of Soybean, *Soil Tillage Res*, **110**, 115 (2010).
57. P. Smedley and D. G. Kinniburgh, In *Essentials of Medical Geology, Arsenic in Groundwater and the Environment*, Springer Netherlnad, p.279 (2013).
58. R. B. Thurman, C. P. Gerba and G. Bitton, The Molecular Mechanisms of Copper and Silver Ion Disinfection of Bacteria and Viruses, *Crit Rev Env Sci Tec*, **18**, 295 (1989).
59. S. K. Wadhwa, T. G. Kazi, N. F. Kolachi, H. I. Afridi, S. Khan, A. A. Chandio, A. Q. Shah, G. A. Kandhro and S. Nasreen, Case-Control Study of Male Cancer Patients Exposed to Arseniccontaminated Drinking Water and Tobacco Smoke with Relation to Non-Exposed Cancer Patients, *Hum. Exp. Toxicol*., **30**, 2013 (2011).
60. S. Gonzalez, R. Lopez-Roldan and J. L. Cortina, Presence of Metals in Drinking Water Distribution Networks Due to Pipe Material Leaching: A Review, *Toxicol. Environ. Chem*, **95**, 870 (2013).
61. J. Hu, F. Gan, S. Triantafyllidou, C. K. Nguyen and M. A. Edwards, Copper-Induced Metal

Release from Lead Pipe into Drinking Water, *Corrosion*, **68**, 1037 (2012).

62. M. I. Sáez, J. J. Casas, J. L. Guil-Gerrero, M. D. Gil, R. Cañero and M. D. Suárez, Effects of Organic Matter, Alkalinity and Ph on Acute Copper Toxicity to Mosquitofish, Gambusia Holbrooki: Implications for a Multipurpose Management of Irrigation Ponds, *Int Rev Hydrobiol*, **98**, 262 (2013).
63. H. Ali, E. Khan and M. A. Sajad, Phytoremediation of Heavy Metals Concepts and Applications, *Chemosphere*, **91**, 869 (2013).
64. H. Bothe, In *Detoxification of Heavy Metals, Plants in Heavy Metal Soils,* Springer Berlin Heidelberg, p.35 (2011).
65. M. Kargar, P. Jutras, O. G. Clark, W. H. Hendershot and S. H. and Prasher, Trace Metal Contamination Influenced by Land Use, Soil Age, and Organic Matter in Montreal Tree Pit Soil, *J Environ Qual,* **42**, 1527 (2013).