

**Characterization of groundwater in the reference of arsenic and nitrate  
mobilization, Kathmandu Basin, Nepal**

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**ABSTRACT**

The groundwater is an important source of drinking water in the Kathmandu Valley, and is presently fulfilling about forty five percent of the total demand of water supply. However, the deteriorating groundwater quality is an emerging issue of concern. In this study attempt has been done to characterize the groundwater for the fate of arsenic and nitrate contaminations. Physico-chemical parameters as pH, Electrical Conductivity (EC), Oxidation Reduction Potential (ORP), Chemical Oxygen Demand (COD), total arsenic (AsT), nitrate (NO<sub>3</sub><sup>-</sup>), iron (FeT) and phosphate (PO<sub>4</sub><sup>3-</sup>) of sixty water samples were measured. The shallow and deep aquifers of the valley are contrast in groundwater-chemistry. ORP values are relatively lower in the deep aquifers compared to the shallow aquifers indicating the deeper part is under reducing condition. The shallow aquifers with high ORP values (up to 272 mV) is considered to be in aerobic and commonly contains elevated nitrate (up to 45 mg NO<sub>3</sub><sup>-</sup>/L). In contrast to nitrate, arsenic is higher (>5 µg/L) in the deep aquifers than those in the shallow aquifers (<5 µg/L). The commonly existing

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of arsenic in the deep aquifers and nitrate in the shallow aquifers reveals a good inverse relationship. The mobilization of arsenic in the deep aquifers (>200 m) is relatively high and the concentration could rise over time.

## INTRODUCTION

High concentration of arsenic and nitrate in drinking water is nuisance world widely for its detrimental effects on health. These effects of arsenic in health range from acute lethality, such as skin ailment to chronic diseases as cancer, and to death. Similarly, high nitrate consumption harms infant commonly causing methemoglobinemia or blue-baby syndrome and also can increase the risk of gastric cancer (Fewtrell 2004; Cantor 1997). The provisional limit of arsenic (As) and nitrate ( $\text{NO}_3^-$ ) in drinking water recommended by the World Health Organization (WHO) is  $10 \mu\text{g/L}$  and  $45 \text{ mg NO}_3^-/\text{L}$ , respectively. Dissolved arsenic in the groundwater is mobile in wide range of environment. Also, arsenic behavior is sensitive to the redox potential (Eh) that controls mainly its speciation commonly arsenite ( $\text{As}^{3+}$ ) and arsenate ( $\text{As}^{5+}$ ) (Smedley and Kinniburgh 2002; McAurthur et al. 2001 and others). In other hand, nitrate ( $\text{NO}_3^-$ ) changes to nitrite ( $\text{NO}_2^-$ ), and finally into ammonia ( $\text{NH}_3$ ) in sequential reduction. Thus, commonly high nitrate exists at near surface groundwater and high ammonia in the greater depth. The nitrate is concurrently responsible for the oxidation of  $\text{As}^{3+}$  to  $\text{As}^{5+}$  and plays the key controlling factor in cycling and speciation of arsenic.

Attention has not been paid to the arsenic concentration in the groundwater of Kathmandu Valley until high arsenic in groundwater in the Terai (Gangetic) Basin of Nepal was recognized. Arsenic in the Terai Basin was first time reported in the eastern three Terai districts of Nepal (Sharma 1999). Later, further tests identified that

groundwater in most of the Terai districts are contaminated with high arsenic, particularly the shallow aquifers (NASC/ENPHO 2003; DOI 2004, Gurung et al. 2005). About 24% samples (n=18,635) tested in the Terai Basin exceeds WHO limit (10 µg/L) (Shrestha and Shrestha 2004). The Kathmandu Valley contains Quaternary sediments similar to those in the Terai Plain, and thus the presence of arsenic in the groundwater is suspected. Most of the earlier studies in the Kathmandu Valley excluded arsenic from both analysis and discussion. One study of Kathmandu groundwater quality (Jha et al. 1997) also determined arsenic, and found that contents are within the Nepal's interim national guideline value (50 µg/L). However, the study explicitly pointed out the needs for study of sediment chemistry, and regular monitoring of As concentration in the Kathmandu Basin groundwater. Amaya (2002) identified As in few samples exceeding the national guidelines value. JICA/ENPHO (2005) has reported that Kathmandu groundwater is highly vulnerable to arsenic contamination, particularly the deep aquifers (>200 m) of the central part of the valley, where As contents of some samples exceeded 200 µg/L. Similarly, high nitrate content (>45 mg NO<sub>3</sub><sup>-</sup>/L) has been reported in the groundwater mainly from the shallow aquifers (Andrew 2000; BGS 2001). The studies made to date are based on the quantitative analyses of As concentrations in groundwater, and do not provide the information on the release mechanism and its controlling factors.

This study characterizes the groundwater of the Kathmandu Valley of both the shallow and deep aquifers, and discusses the possible mechanisms of arsenic and nitrate mobilization. There are two aquifer systems shallow and deep with contrasting groundwater-chemistry. The shallow aquifers are oxic condition and characterized by

higher nitrate, whereas the deeper aquifers are anoxic condition and accompanied with higher arsenic concentrations.

## **MATERIALS AND METHODS**

### **Study area**

The Kathmandu Valley is an intermontane basin, located in the central Nepal Himalaya (Fig. 1). This valley is elongated east-west, and covers the area of about 650 km<sup>2</sup>. The central part has more or less flat topography with elevation of 1,300 to 1,400 m, and is surrounded by high mountain ranges of more than 2,000 m. The drainage systems of the valley flow towards the centre and collected to the Bagmati River (Fig. 2). The Bagmati River exits the basin dissecting the mountains of the Mahabharat Range to the south. The sample collection for this study mainly covers the north and central parts of the Kathmandu Valley (Fig. 2).

### **Geology and hydrogeology**

The Kathmandu Valley is a tectonically controlled basin, filled with Quaternary fluvio-lacustrine sediments, the succession more than 600 m thick. The northern part of the valley is bounded by Sheopuri Gneiss. The central part and other slopes of the valley are comprised of low-grade metamorphic rock of the Phulchauki Group, mainly slate, phyllite, limestone (Stöcklin 1980). The basal part of the basin-fill sediments consist of lower Pleistocene lacustrine clay and gravel Lukundol Formation (Yoshida and Igarashi 1984) which is equivalent to the Bagmati Formation (Sakai 2001, Fig. 1). This basal sequence is comprised of lignite beds, bituminous pebbly mud (Dangol 1985; Binnie and Partners 1973) and represents the shallow lacustrine marginal facies (Sakai 2001). Thick black lacustrine clay locally called the Kalimati Clay overlies the basal Lukundol

Formation. The Kalimati Clay is rich in organic matter and diatom, plant fossils and natural gas (Fujii and Sakai 2001; JICA 1990). The uppermost basin-fill sediments are covered by extensive fluvio-lacustrine terraces and fan deposits dominantly of sand and gravel of the Gokarna, Patan and Thimi formations (Yoshida and Igarashi 1984). The ages of these terrace deposits ranges from 40,000 to 11,000 yrs BP (Igarashi et al. 1988; Yoshida and Gautam 1988). The coarse sediments of the northern part of the valley represent delta deposits and the facies of which are influenced by the process of delta progradation and the paleo-lake fluctuation (Sakai T. 2001).

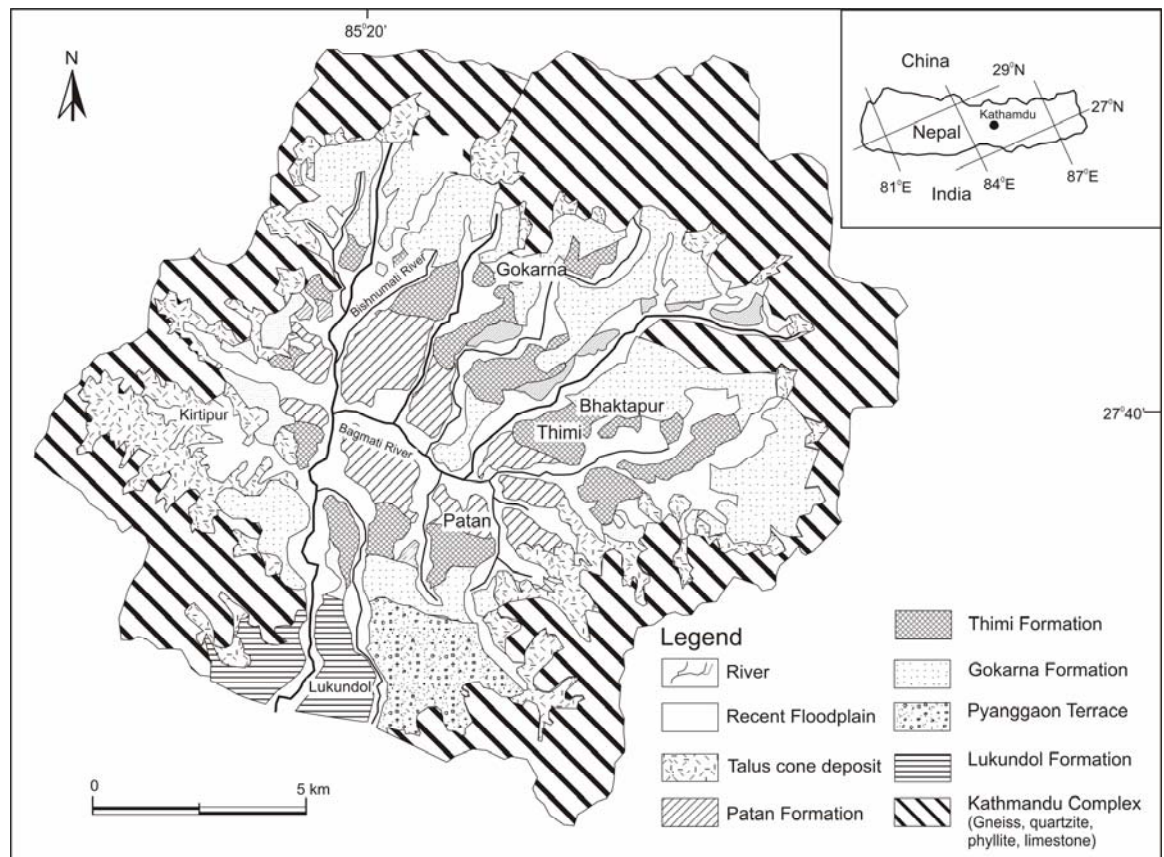


Fig. 1. Geological map of the Kathmandu Valley, Nepal. (after Igarashi et al. 1988).

Average precipitation in the Kathmandu valley is 2,000 mm/year, about 80% of which falls in the monsoon period during June and July. Surface runoff is high during the monsoon. The mean monthly discharge of the Bagmati River at Chobhar gorge is 15.81 m<sup>3</sup>/sec; the rate of evaporation is 3.70 mm/day (JICA 1990). Recharge to the shallow aquifers (<60 m) occurs mostly along basin margins, directly from precipitation and a number of small rivers. However, recharge to the deeper aquifers is considered limited due the presence of the clay beds that significantly restricts the downward percolation. Because the Kathmandu Valley is a closed basin with gentle slopes towards the centre, the groundwater flow is assumed slow, particularly in the deep aquifers.

The groundwater supplies about 45% of the total demand (122 million litre/day, 2001) of water supply of the Kathmandu Valley (Acres 2003), withdrawn from both the shallow and deeper aquifers. Shallow aquifers typically extend from less than 5 to 60 m, and deeper aquifers below 60 m. Groundwater from the shallow aquifers is drawn from dug wells, hand pumps, roar pumps, whereas the deeper aquifers are exploited from deep wells. Traditional stone spouts (locally called as the Dhungedhara) are also common, drawing water from shallow aquifers. Groundwater from both the shallow and deeper aquifers has been extensively used for drinking and industrial purposes. The static water table generally lies within a meter of the ground surface, but in some area in the northern part of the valley it is as low as 60 m (Kharel et al. 1998). Dug wells and stone spouts in the central and southern parts of the valley are most dry in dry season (April-May) due to the lowering of water table.

## **Sampling and field measurements**

Sixty water samples were collected from different sources as hand pumps, dug wells, water spouts, deep wells, roar pumps and river (Fig. 2). Pumps were run to remove all standing water in the wells before sample collection. Temperature, pH, Oxidation Reduction Potential (ORP), and Electrical Conductivity (EC) were examined at the time of water sample collection by using portable field kits. Chemical Oxygen Demand (COD), Nitrate ( $\text{NO}_3^-$ ), Phosphate ( $\text{PO}_4^-$ ) were measured by Pack Test. Pack Test consist of small soft polyethylene tube with chemicals (dried) inside which is immersed into the water samples to fill it halfway. The colour of the water changed, which is compared with the standard colour chart. Each sample was also tested for arsenic with a Hironaka Kit. In this kit, water is treated with reagents that produce Arsine gas ( $\text{AsH}_3$ ), which reacts with Bromide paper ( $\text{HgBr}_2$ ). The stain thus produced in the paper ranges from yellow to brown, showing low to high concentrations of As (Hironaka 2000). The detection limit of the kit is  $10 \mu\text{g/L}$ . At each site 200 mls water sample was collected and acidified with 1N HCl and taken for further tests to laboratory.

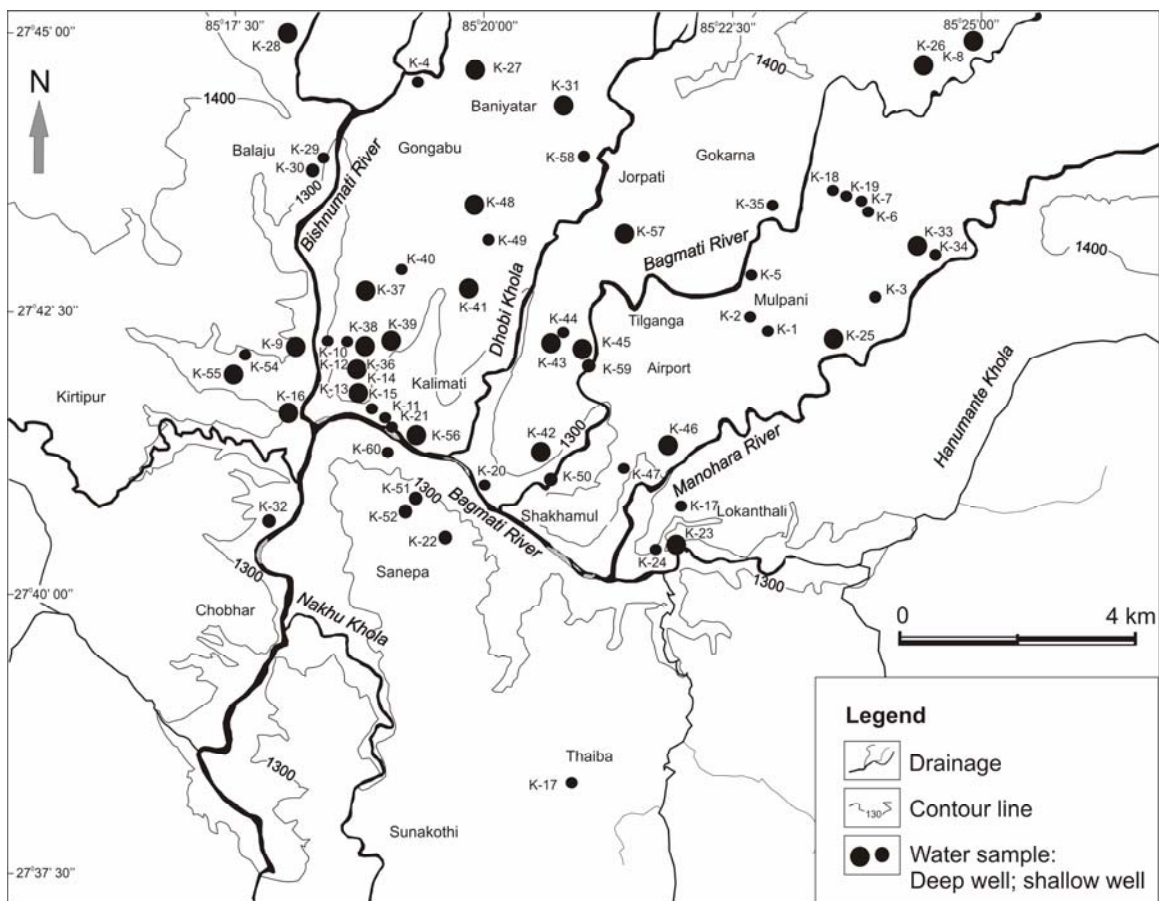


Fig. 2. Location of water sample collection, Kathmandu Valley, Nepal.

### Laboratory analysis

Water samples were analyzed for As by using an atomic absorption spectrophotometer (AAS, Shimadzu AA-660G) with a graphite furnace atomizer (GFA-4B) at Shimane University. Calibration of the AAS was made using a blank solution (1N HNO<sub>3</sub>, 0.01 ml/L) and standard arsenic solution (1000 µg/L). The detection limit of the AAS used is less than 1µg/L.

### RESULTS

The physico-chemical parameters of the groundwater measured in this study are given in Tables 1 and 2. All water samples have nearly neutral pH ranging from 6.0 to

7.6. EC in the shallow aquifers water averaged 502  $\mu\text{S}/\text{cm}$ . However, two samples from shallow wells (at Tripureshwor, K-11 and Kalimati, K-53) show exceptionally high EC, 955 and 1102  $\mu\text{S}/\text{cm}$ , respectively. The water from deep aquifers generally has high EC (average 676  $\mu\text{S}/\text{cm}$ ) with some samples very high values ( $>1000$   $\mu\text{S}/\text{cm}$ ; Table 1). Generally, EC of the groundwater in the northern margin of the valley such as Gokarna, Jorpati, Mulpani is lower (around 400  $\mu\text{S}/\text{cm}$ ) relative to the central valley such as at Kalimati and Tripureshwor (around 800  $\mu\text{S}/\text{cm}$ ), particularly in the deep tubewells. The highest value of EC observed (2100  $\mu\text{S}/\text{cm}$ ) at Balaju industrial area (K-30) clearly indicates the intense local effect. The COD is higher ( $>30$  mg/L, mostly) in the deep aquifers compared to the shallow aquifers ( $<10$  mg/L), and follows a trend similar to EC (Fig. 3a), both increase with depth. ORP is relatively lower in the deep wells (average 75 mV) than in the shallow wells (average 132 mV). The ORP shows inverse relationship with EC (Fig. 3b) and COD (Fig. 3c).

All the deep aquifers water samples showed high dissolved total iron (FeT), commonly ranging from 5 to 10 mg/L (Table 2), with some exceptional low values (as K-26, K-27, K-45, K-52). Whereas, FeT in the shallow wells is generally low ( $<0.2$  mg/L) with few exceptional high values (up to 10 mg/L). Phosphate as  $\text{PO}_4^{3-}$  is low to high in the shallow wells (ranges  $<0.2$  to 10 mg  $\text{PO}_4^{3-}/\text{L}$ ). However, phosphate is generally high in the deeper wells (5 to 10 mg  $\text{PO}_4^{3-}/\text{L}$ ).

Arsenic in most of the water samples from shallow aquifers was not detected ( $<10$   $\mu\text{g}/\text{L}$ ). In few samples (K-10, K-11, K-49, K-53) arsenic was detected by AAS analyses, however, the content was less than 5  $\mu\text{g}/\text{L}$ . Arsenic was detected in the most deep wells samples by the field kit. AAS analysis also showed low As values ( $<10$   $\mu\text{g}/\text{L}$ ) in the deep

well samples. Only in one sample (at Tahachal, K-9) arsenic value exceeded the WHO limit (18  $\mu\text{g/L}$ ). However, some samples from deep tubewell were slightly turbid with fine suspended particles which may make slight variation in As concentration measured in laboratory. In contrast to arsenic, nitrate is low to high in shallow aquifers (ranges <1 to 45  $\text{mg NO}_3^-/\text{L}$ ), whereas it is low in all the deep wells (<1  $\text{mg NO}_3^-/\text{L}$ ) (Fig. 3d). The river water checked by field kits showed the high COD (>50  $\text{mg/L}$ ), phosphate (>10  $\text{mg/L}$ ) and EC (average 731  $\mu\text{S/cm}$ ) indicating they are highly polluted.

**Table 1** Groundwater-chemistry, shallow aquifer, Kathmandu Valley, Nepal

SN	ID	Loction	Well	Depth (m)	pH	EC ( $\mu\text{S/cm}$ )	As ( $\mu\text{g/L}$ )		FeT (mg/L)	$\text{NO}_3^-$ (mg N-/L)	$\text{PO}_4^{3-}$ (mg P-/L)	COD (mg/L)	ORP (mV)
							Kit	AAS					
1	K-1	Gothatar	Dug well	8	6.6	493	<10	—	0.2	45	0.2	—	234
2	K-2	Gothatar	Dug well	10	6.1	367	<10	—	7.0	<1	0.5	5	100
3	K-4	Baniyatar	Shallow well	8	6.5	374	<10	<1	10.0	<1	5.0	5	16
4	K-11	Tripureshwor	Hand pump	10	7.0	955	<10	3.15	10.0	5	5.0	10	13
5	K-7	Mulpani	Roar pump	8	6.0	132	<10	—	0.2	1	1.0	5	261
6	K-6	Mulpani	Roar pump	8	6.0	251	<10	—	5.0	1	0.5	5	144
7	K-18	Dhaksindhoka	Roar pump	6	6.3	416	<10	—	10.0	1	0.5	10	115
8	K-19	Dhaksindhoka	Roar pump	8	6.3	392	<10	—	6.0	2	0.2	4	143
9	K-15	Tripureshwor	Shallow well	30	6.7	792	<10	<1	5.0	45	4.0	5	120
10	K-17	Thaiba	Shallow well	15	6.8	523	<10	—	<0.2	20	0.5	5	168
11	K-20	Shankhamul	Shallow well	6	6.5	463	—	<1	4.0	<1	1.5	6	141
12	K-29	Balaju	Hand pump	8	6.9	686	—	<1	5.0	<1	1.0	10	95
13	K-35	Jorpati	Shallow well	75	6.5	461	<10	<1	<0.2	45	0.5	5	150
14	K-36	New Raod	Dug well	10	6.9	644	<10	<1	0.5	1	10.0	7	132
15	K-44	Puranobaneshwor	Shallow well	30	6.2	578	—	<1	<0.2	45	2.0	5	125
16	K-47	Koteswror	Hand pump	14	6.6	341	—	—	10.0	<1	1.0	13	83
17	K-53	Kalimati	Dug well	9	6.9	1102	—	4.82	7.0	<1	7.0	—	61
18	K-51	Pulchowk	Dug well	10	7.2	597	<10	—	<0.2	2	1.5	—	117
19	K-55	Thimi	Hand pump	8	6.5	348	<10	—	<0.2	5	1.0	5	131
20	K-60	Kupandol	Dug well	8	7.3	458	—	—	0.5	5	2.0	—	137
21	K-5	Jorpati	Shallow well	18	6.3	632	<10	—	<0.2	5	0.5	5	101
22	K-24	Lokanthali	Dug well	5	6.8	473	<10	<1	0.2	1	1.5	10	145
23	K_40	Babarmahal	Shallow well	27	6.6	207	—	—	10.0	—	1.0	5	97
<b>Spout</b>													
24	K-3	Mulpani	Spout	1	6.3	165	<10	—	<0.2	45	0.5	5	272
25	K-10	Bhimsensthan	Spout	4	7.0	936	<10	5.35	<0.2	45	10.0	5	151
26	K-21	Tripureshwor	Spout	2	7.2	745	<10	—	<0.2	30	0.7	9	148
27	K-22	Patan Darbar	Spout	3	6.6	490	<10	—	<0.2	20	2.0	5	155
28	K-34	Mulpani	Spring	1	6.5	242	<10	<1	<0.2	20	5.0	5	152
29	K-49	Bhatbhateni	Spout	1	6.5	510	<10	2.75	<0.2	45	7.0	5	130
30	K-58	Maharajganj	Pond	1	6.5	289	—	—	<0.2	10	<0.2	—	139
<b>River</b>													
31	K-32	Sundarighat	Bagmati River	—	7.6	776	—	—	1.0	<1	10.0	100	5
32	K-50	Shankhamul	Bagmati River	—	7.4	831	—	—	1.0	<1	10.0	100	128
33	K-59	Tilganga	Bagmati River	—	7.5	588	—	—	1.0	<1	10.0	50	32

**Table 2** Groundwater-chemistry, deep aquifer, Kathmandu valley, Nepal

SN	ID	Loction	Depth (m)	pH	EC ( $\mu\text{S/cm}$ )	As ( $\mu\text{g/L}$ )		FeT (mg/L)	$\text{NO}_3^-$ (mg N-/L)	$\text{PO}_4^{3-}$ (mg P-/L)	COD (mg/L)	ORP (mV)
						Kit	AAS					
1	K-9	Tahachal Campus, NWSC	274	6.9	1079	D	18.68	5.0	<1	7.0	30	108
2	K-14	Tripureshor, NWSC	244	6.7	1071	D	6.11	7.0	<1	10.0	50	10
3	K-12	Lagan, NWSC	247	7.0	974	D	5.3	5.0	<1	10.0	50	88
4	K-13	Lagan, NWSC (Repeat)	247	6.8	924	D	1.95	7.0	<1	10.0	50	28
5	K-16	Kuleshwor Awas, NWSC	192	6.9	1133	D	3.27	7.0	<1	10.0	25	77
6	K-23	Lokanthali, NWSC	259	7.3	885	D	< 1	5.0	<1	10.0	50	52
7	K-26	Nayapati, NWSC	>200	7.3	199	D	5.47	2.0	<1	2.0	7	140
8	K-27	Dhapasi, NWSC	>200	7.1	158	D	3.67	2.0	<1	7.0	10	66
9	K-30	Balaju, Cocacola factory	>200	7.1	2100	D	2.76	7.0	<1	10.0	50	14
10	K-31	Bansbari, NWSC	238	7.2	184	D	4.57	5.0	<1	5.0	7	105
11	K-41	Naxal, Police Head quarter	250	7.3	220	D	5.1	7.0	<1	10.0	50	100
12	K-42	Nayabanshwor, Tinkune	250	6.6	880	D	1.77	10.0	<1	10.0	50	39
13	K-39	Bir Hospital	283	6.8	782	D	1.88	10.0	<1	10.0	50	30
14	K-45	Tilganga, Soaltee Catering	200	7.0	689	D	2.92	<1	<1	5.0	30	122
15	K-46	Koteshwor, Pepsicola factory	150	7.0	506	D	4.96	5.0	<1	10.0	13	101
16	K-33	Mulpani, NWSC	>200	7.0	198	D	8.04	7.0	<1	7.0	13	108
17	K-43	Dwarika Hotel, Battishputali	268	6.7	572	D	3.9	10.0	<1	10.0	30	75
18	K-52	Pulchowk, DPTC	250	7.4	701	D	5.5	2.0	<1	7.0	5	73
19	K-54	Soaltee Hotel, Kalimati	300	6.8	1106	D	4.29	10.0	<1	10.0	50	6
20	K-57	Hayat Hotel, Baudha	267	6.9	825	D	4.85	7.0	<1	10.0	—	31
21	K-56	Thapathali, Prashuti Griha	300	7.1	633	D	6.2	7.0	<1	10.0	50	61
22	K-8	Sundarijal, Dege Carpet factory	>70	7.3	368	D	< 1	<0.2	<1	1.0	5	208
23	K-25	Mulpani, NWSC	>200	7.3	237	D	—	5.0	<1	5.0	10	122
24	K-28	Mahadev Khola, NWSC	>200	7.3	298	D	—	5.0	<1	10.0	10	12
25	K-37	Chhetrapati, Potala Guest House	>40	6.7	632	D	—	10.0	<1	5.0	10	97
26	K-38	New Road, Bishal Bazaar	300	6.9	644	D	—	7.0	<1	10.0	20	100
27	K-48	Baluwatar, Rastra Bank	250	7.0	242	D	—	5.0	<1	10.0	13	54

D= Detected (Complex color of dirty brown due to interference of other elements)

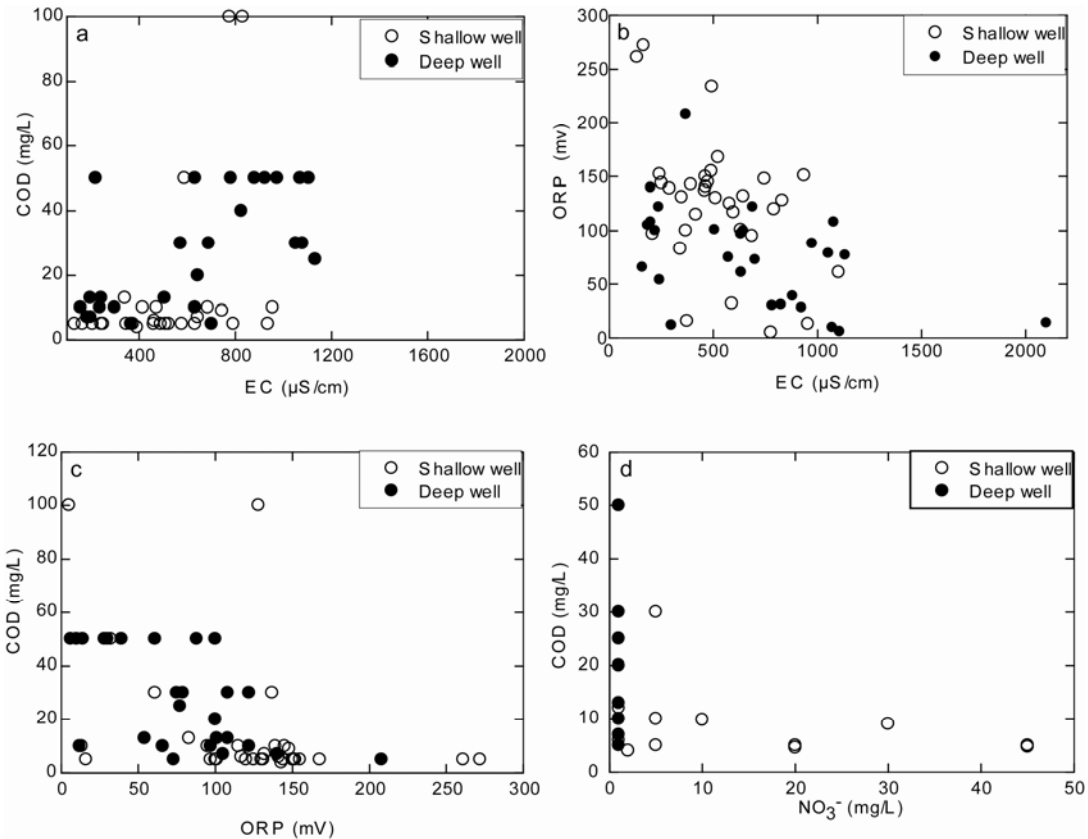


Fig. 3. Relations between: a. Electrical Conductivity (EC) and Chemical Oxygen Demand (COD), b. Oxidation Reduction Potential (ORP) and EC, c. COD and ORP, d. COD and Nitrate ( $\text{NO}_3^-$ ) of the groundwater samples, Kathmandu Valley, Nepal.

## DISCUSSION

### Groundwater chemistry

Two aquifer systems: shallow and deep with contrasting groundwater-chemistry is characterized. A schematic cross section of the Kathmandu basin indicating these two aquifers systems are shown in figure 4. The shallow and deep aquifers are virtually separated by lacustrine clay beds, which are thicker in the central and southern parts, whereas in the northern part of valley the clays occur as sporadic lenses (Fig. 4). This clay beds however occasionally consists of thin lamina of silts and fine sand that form aquiclude. Most deep wells of the central Kathmandu Valley extract water from this aquiclude. The groundwater-chemistry varies significantly between the shallow and deeper wells (Tables 1 and 2). The low ORP values (average 75 mV) in the deep aquifers clearly indicate reduced conditions relative to the shallow aquifers (average ORP 132 mV). The shallow aquifers (ORP up to 272 mV) are considered to be in aerobic condition, and the groundwater is commonly contaminated with high nitrate up to 45 mg  $\text{NO}_3^-/\text{L}$ . The widespread lacustrine clays probably restrict the downward diffusion of  $\text{NO}_3^-$ . Thus, the nitrate concentration diminishes below the limit of detection ( $<1$  mg  $\text{NO}_3^-/\text{L}$ ; Tables 1 and 2) in the deep aquifers. The earlier studies (e.g., Binnie and Partners 1973; JICA 1990; Jha et al. 1997; JICA/ENPHO 2005) have indicated the deep aquifers water is rich in ammonium ( $\text{NH}_4^+$ ) and bicarbonate ( $\text{HCO}_3^-$ ), more concentrated

in the central valley. Also, dissolved gases occur in the central valley that comprises methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) (JICA 1980). All these features demonstrate that the deep aquifers are under reduced conditions. Odour of H<sub>2</sub>S gas is commonly smelt in the water from all deep wells, which also indicates reducing conditions. Under such a reducing environment, organic matter may change to dissolved organic carbon (DOC) and inorganic nitrogen species that include humic acid and fluvic acid (Lovley 1995).

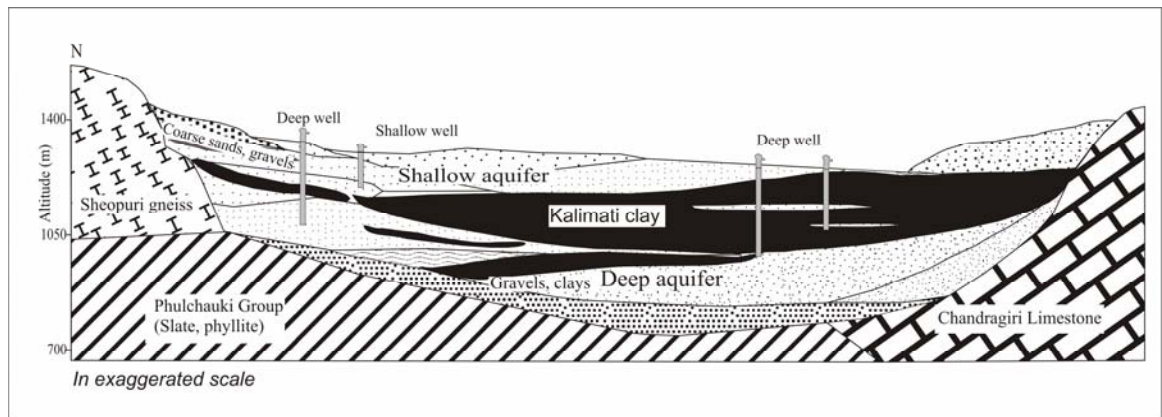


Fig. 4. Schematic cross section (N-S) indicating shallow and deep aquifers, Kathmandu Valley, Nepal.

The main source of high phosphate in the deep aquifers (7-10 mg PO<sub>4</sub><sup>3-</sup>/L) is probably organic matter, as phosphate is generally released during the process of organic matter change to its inorganic form (Buckau et al. 2000; Peretyazhko and Sposito 2005) and also from the domestic wastes at the shallow depth. Phosphate minerals such as vivianite are abundant (Dill and Melcher 2004) which may also contribute for such a high dissolved phosphate when dissolved. In the deep aquifer environment, the anaerobic organic matter changes the nitrate to ammonia (Lovley 1995; Cole 1996), and high level

of ammonia of the deep aquifers of the Kathmandu Valley could have accumulated by the similar mechanisms.

It is widely accepted that the role of organic matter is important for the mobilization of arsenic, and this is also valid in the many case studies from West Bengal (India) and Bangladesh (Nickson et al. 2000; McArthur et al. 2001; Akai et al. 2004; Anawar et al. 2003). Analyses of the organic matter were not attempted in this study. High concentration of organic matter can be expected to occur in the fine grained lacustrine sediments. Previous studies (e.g., Fujii and Sakai 2001; Dill et al. 2003) have indicated that the fluvio-lacustrine sediment in the Kathmandu Valley is rich in organic matter, especially the clayey sediments of central part of the valley, which could have enhance the arsenic mobilization.

The abundantly high concentrations of iron in the sediments ( $\text{Fe}_2\text{O}_3$ - 5 wt%, Dill et al. 2003) could be the source of high dissolved iron particularly in the deep aquifers groundwater (up to 10 mg/L). The iron release mechanism is not understood fully, but may be due to the reducing environment, in which iron oxides generally dissolve into soluble form (Lovley 1997). The iron oxide is the common host matter for arsenic, either adsorbed into the surface or co-precipitated (Pierce and Moore 1982), and under dissolution or desorption As could be released into groundwater (Bose and Sharma 2003; McArthur et al. 2001; Anawar et al. 2003). The generally low level of arsenic and iron in the shallow aquifer water (Table 1) could be due to in-situ iron mineralization forming Vivianite or Siderite (Dill and Melcher 2004), that significantly reduces the dissolved form (McArthur et al. 2004).

## **Release of arsenic and nitrate**

This study and other few previous studies have indicated that arsenic is not high (<50 µg/L) in groundwater of the Kathmandu Valley, although number of sample analyzed are limited. However, JICA/ENPHO (2005) has reported that about 12% of the 137 tested wells have arsenic above the Nepal standard of 50 µg/L, with some samples exceeding 200 µg/L. The study also has indicated wide seasonal variation of As concentrations in the deep wells (>200 m). The contrast geochemistry of groundwater in the shallow and deep aquifers (as discussed above) indicates that the percolation of the monsoon water to the depth more than 200 m is limited and thus, the dilution of arsenic concentration by monsoon as explained by JICA/ENPHO (2005) report may be less significant. Therefore, it is necessary to re-examine the As concentration of those deep wells showing high As values. No evidence of direct health impact from arsenic in drinking water has so far been reported from the Kathmandu Valley.

The pH measured in the study area is nearly neutral (6.0 to 7.6) indicating that arsenic release from pyrite is assumed less significant, as the pH could be lowered by  $\text{SO}_4^{2-}$  from sulfides (range from 2.3 to 5.9; Lengke and Tempel 2005).

The natural occurring of arsenic in the sediments and the human activities induced sources (such as solid wastes) both could contaminate groundwater (Van Leeuwen 2000; Keimowitz et al. 2005) and the arsenic concentrations vary over time due to continuous geochemical processes and the organic matter activities (Ishiga et al. 2000; McArthur et al. 2004; van Geen et al. 2003). Thus, understanding of the arsenic-release in the Kathmandu Valley is important to be considered. Two mechanisms of arsenic release are probable in the groundwater of the valley. First is the mobilization of arsenic due to the

change of redox condition. The groundwater displays clear redox gradient between shallow and deep aquifers as indicated by the diminishing trend of ORP downward from shallow to deeper depth. Khatiwada et al. (2002) reported negative ORP (-195 mV) in deep aquifers showing highly reduced environment. High dissolved iron of the deep aquifers also indicates the reducing condition (Lovley 1997).

Arsenic mobilization is high in the reducing conditions (Carbonell-Barrachina et al. 1999; McArthur et al. 2001; Smedley and Kinniburgh 2002), though not all reducing water contains arsenic. The arsenic adsorbed in the iron oxy-hydroxides in such reducing conditions could be released into groundwater, however the released arsenic could be re-adsorbed in to the residual iron oxy-hydroxides (McArthur et al. 2004; Pierce and Moore 1982). In the complete reduction, the room for the adsorption of arsenic as iron oxy-hydroxides is minimized, and thus the level of dissolved arsenic groundwater increases. Yet, low level of arsenic in the most of the deep wells of the Kathmandu Valley could be due to the incomplete reduction of iron oxy-hydroxides where there are enough residual oxides to adsorb arsenic released. The amount of iron oxy-hydroxides could gradually be lowered towards the end of the completing its reduction process i.e. sink of the arsenic as iron oxides will be minimized that could lead the rise As concentration over time.

Also, the mobilization of arsenic is low under strongly oxidizing or strongly reducing condition, but its mobility is high under intermediate or shifting redox condition (Bose and Sharma 2003; Carbonell-Barrachina et al. 1999). The redox environment of the deeper aquifers of the valley could have been changing, probably due to continuous pumping of water and gases, and also due to anaerobic organic matter activities (Lovley 1995) which could lead the favourable condition for As release. However, in the highly

reduced condition arsenic reacts with sulfur to form insoluble sulfides as FeAsS, AsS, As<sub>2</sub>S<sub>3</sub> (Carbonell-Barrachina et al. 1999). Therefore, in the very deeper part (probably >300 m) of the Kathmandu Basin, the As solubility is perhaps limited by the formation of insoluble As sulfide minerals. Systematic observation of change of redox gradient and change in the arsenic concentration in the groundwater could be useful for the confirmation of this idea. The low concentration of arsenic in the shallow aquifers could be due to the more oxidized condition (as indicated by high ORP, 132 mV) as arsenic in oxidized environment remains mostly into insoluble form (As<sup>5+</sup>) (Carbonell-Barrachina et al. 1999). The oxidized state of shallow aquifers is maintained by abundant nitrate (>45 mg NO<sub>3</sub><sup>-</sup>/L, Table 1) in the groundwater and diffusion of oxygen from the atmosphere.

The second probable source of arsenic is the municipal solid wastes, sewages and chemical fertilizers, which is not included in this study. Huge volume of municipal wastes of the Kathmandu Valley has been dumping openly without sealing until recently. Dumping site of Gokarna, about 20 km north from Kathmandu city is an example, which is not lined, and left not properly sealed after dumping the solid wastes for about 8 yrs that is estimated thousands of tons. This dumped waste is now under natural decomposition. Gases were emitted from this dumping site, which was used by local people for domestic purposes for some times. Unlined landfills could deliver strongly reducing leachate to associate aquifers (Keimowitz et al. 2005) and could enhance the leaching of arsenic in to the adjacent aquifers.

In contrast to arsenic, high nitrate (NO<sub>3</sub><sup>-</sup>) is abundantly found in the shallow aquifers (>45 mg NO<sub>3</sub><sup>-</sup>/L). Particularly in the northern areas of the valley such as Gokarna, Jorpati, Gongabu, Mulpani, which belong to sandy formation and high nitrate

above 45 mg NO<sub>3</sub><sup>-</sup> /L (Tables 1 and 2) occurs. Andrew (2000) identified a plume of high nitrate (63 mg NO<sub>3</sub><sup>-</sup> /L) in the shallow aquifers in the Jorpati. There are several sources of nitrates such as human and animal wastes, septic fields, leaky landfills, and agrochemicals in the Kathmandu Valley. The septic tanks rarely have adequate areas for soak pits for dilution in the most rural areas of the valley. The proximity of the septic tanks and the livestock corrals and the drinking water wells are not maintained, where the nitrate and ammonia could infiltrate into the shallow aquifers. Also, it's a common practice of freely disposing of domestic wastages and industrial sewerages without treatments. The ammonia of the untreated wastes when oxidized changed to nitrate. Agriculture activities are intensively using nitrate fertilizers. The high nitrate measured in the shallow aquifer water in this study area could have been accumulated from these different non-point sources. The river water is highly polluted as indicated by high COD, phosphate, EC (Table 1) and E-coli (>2500/ ml, Jha et al. 1997) which also could pollute the shallow aquifers particularly in the northern sandy zones.

## **CONCLUSIONS**

The dissolved arsenic in groundwater of the Kathmandu Valley mostly lies within the national guidelines. However, the concentration could be rise over time due to change in the underground redox condition and improper management of wastes. The shallow aquifers are considered to be in aerobic conditions, and the groundwater is commonly contaminated with high nitrate. Arsenic mobility is higher in the deeper aquifers due to redox potential. High nitrate of the shallow aquifers could be mainly due to human activities. The common occurrences of arsenic in the deep aquifers and nitrate in the

shallow aquifers reveal a good inverse relationship. The regular monitoring of groundwater quality for arsenic and nitrate is essential before it will be late.

### **ACKNOWLEDGEMENTS**

Our thanks to P. S. Tater, then Project Chief, Groundwater Resource Development Project (GWRDP/Govt/Nepal) for his valuable suggestion, Ms T. Singh and D. Tandukar (GWRDP/ Govt/Nepal) for their help in sample collection and field measurement, Mst. H. Bibi (Shimane University) for her guidance in analyzing samples. We are thankful to Dr P. D. Ulak for fruitful discussion and improvement in the manuscript. This study was supported by a MEXT (Monbukagakusho) graduate scholarship to JKG.

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