

**DISTRIBUTION OF SELECT NUTRIENTS AND METALS IN THE
SOILS OF A WETLAND-TERRESTRIAL ECOSYSTEM
COMPLEX: A CASE STUDY OF KEOLADEO NATIONAL PARK,
BHARATPUR, INDIA**

Thesis submitted to the
BHARATHIAR UNIVERSITY, COIMBATORE

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DEGREE OF DOCTOR OF PHILOSOPHY
in
ENVIRONMENTAL SCIENCES

by
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CERTIFICATE

This is to certify that the thesis entitled “**Distribution of select nutrients and metals in the soils of a wetland-terrestrial ecosystem complex: A case study of Keoladeo National Park, Bharatpur, India**” is a record of original research work done by **Mr. B. Anjan Kumar Prusty** in the Division of Environmental Impact Assessment, Sálím Ali Center for Ornithology and Natural History, as full time Research Scholar during the period of study 2003 – 2007 under my guidance and supervision for the award of the Degree of **Doctor of Philosophy in Environmental Sciences**. I further certify that this research work has not previously formed the basis for the award of any other Degree or Diploma or Associateship or Fellowship or other similar title to any candidate of this or any other University.

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DECLARATION

I, **B. Anjan Kumar Prusty** do hereby declare that thesis entitled “**Distribution of select nutrients and metals in the soils of a wetland-terrestrial ecosystem complex: A case study of Keoladeo National Park, Bharatpur, India**” submitted to the Bharathiar University, Coimbatore, for the award of the Degree of **Doctor of Philosophy in Environmental Sciences**, is a record of original and independent research work done by me during 2003 – 2007 under the supervision and guidance of **Dr. PA Azeez**, Senior Principal Scientist, Sálím Ali Center for Ornithology and Natural History, Coimbatore, and it has not previously formed the basis for the award of any other Degree or Diploma or Associateship or Fellowship or other similar title to any candidate of this or any other University.



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List of abbreviations used in the text

ANOVA	Analysis of Variance
CEC	Cation Exchange Capacity
CEMDE	Centre for Environmental management of Degraded Ecosystems
CPOM	Coarse Particulate Organic matter
CSIR	Council of Scientific and Industrial Research
CSIRO	Commonwealth Scientific and Industrial Research Organization
DOM	Dissolved Organic matter
DRDO	Defence Research and Development Organization
DTRL	Defence Terrain Research Laboratory
FPOM	Fine Particulate Organic Matter
GEER	Gujarat Ecological Education and Research
GLM	General Linear Model
GUIDE	Gujarat Institute of Desert Ecology
GUIDE	Gujarat Institute of Desert Ecology
IICT	Indian Institute of Chemical Technology
IUCN	International Union for Conservation of Nature and Natural Resources
JNU	Jawaharlal Nehru University
KNP	Keoladeo National Park
LSD	Least Significant Difference
MoEF	Ministry of Environment and Forests
NIO	National Institute of Oceanography
PCA	Principal Component Analysis
SACON	Sálim Ali Centre for Ornithology and Natural History
SAR	Sodium Absorption Ratio
SET	Sequential Extraction Technique
SOM	Soil Organic Matter
TAP	Total Available Phosphorous
TAS	Total Available Sulphur
TN	Total Nitrogen
TOC	Total Organic Carbon
TOM	Total Organic Matter
ULBS	Upper-most Layer of the Bottom Sediment
UNESCO	United Nations Educational Scientific and Cultural Organization
WHO	World Health Organization

1. INTRODUCTION

1.1. BACKGROUND

Wetlands, integral to large landscapes in almost all parts of the world, offer various ecological services and goods (commodities) to the humankind, perform several valuable functions and are ecologically unique (Gopal et al. 1993). In wetlands, hydrologic regime is the most important factor that determines or alters the physico-chemical properties of the system, which in turn directly affects the biotic systems of the wetland. Slight changes in the hydrologic conditions in wetlands may lead biota to respond with substantial changes in species composition and richness, and ecosystem productivity. The process of organic matter (detritus) decomposition influences the soil / sediment physico-chemical properties largely. The study of the nutrient distribution in soil / sediment in different habitats in turn will throw light on detritus dynamics and its role in the general ecology of each system.

Trace metals occur naturally in soils, mostly at comparatively low concentrations, because of weathering and other pedogenic process acting on rock fragments from which soils build up (Mohanraj et al. 2000a). Physical, chemical and biological settings are vital in determining absorption of nutrients including trace metals from soil, the natural medium for plant growth. Trace metals are generally associated with pollution and toxicity and their toxic potency is largely dependent on the ambient conditions. Total concentration, distribution and reactivity of trace metals in the sediment (or soil) are a function of organic matter, mineralogy and textural qualities of sediments (Li et al. 2000b, Martin and Calvert 2003, and Silva et al. 2003). Trace metals have different geochemical forms in the environment, may be water, soil and / or sediment, resulting from a process known as speciation (Florence 1982), which is central in determining their bioavailability and mobility and ultimately their impact on living organisms (Prusty et al. 1994, Boruvka et al. 1997, Chandra Sekhar 2003, and Le et al. 2004). The measurement of the total concentration of an element provides little information about its bioavailability or its interaction with sediment and / or suspended particulates. Thus, the evaluation of potential risks in soil requires an appraisal of the proportion of the metal in different geochemical forms.

Spatial and temporal dependence is widely considered to be a core characteristic of many ecological phenomena. Nevertheless, in most of the ecological studies, independence of observations in space and time is often assumed rather than explicitly investigated (Yankelevich et al. 2006). Based on this principle, soils of semitropical systems as like that of Keoladeo National Park (KNP) can evince patterns at least four different scales, both spatial and temporal. First, soils may differ among the habitats (usually associated with vegetation types). Second, soils may differ spatially among different locations within a vegetation type. Third, soil may differ on seasonal basis also within a vegetation type. This factor assumes significance especially in seasonal wetland systems. Fourth, soils may differ along depth profile in each location in a site. Variability at these scales could affect structural and functional characteristics (e.g., diversity and productivity, Cox et al. 2002) of the system. These four assumptions form the basis of this thesis. All the nutrient and metal distribution was studied in view of these points and accordingly the goals for this study were set and specific technical chapters were prepared. To our knowledge, no such study has been undertaken in KNP on soil characterization, despite several years of scientific exploration under in the Park focussing on various ecological aspects.

1.2. QUESTIONS ASKED

The present study based at KNP, Bharatpur, a multi habitat system, is an attempt to explore the following:

1. The background level of nutrients and their distribution pattern on a spatio-temporal scale in the Park.
2. The background level of alkali and alkaline earth metals and their distribution pattern on a spatio-temporal scale in the Park.
3. Any specific enrichment of alkali and alkaline earth metals in general and saline-alkaline patches in particular in KNP.
4. Background level of select trace metals and their distribution in the soil profile in different habitat system; and the pattern of association of metals to specific operationally defined geochemical phases in the soil.
5. Any effect of detritus and/or habitat type on the soil characteristics in the soil layers along the depth profile.

It is believed that these questions have been answered satisfactorily under specific chapters that follow the general introduction and description of the study area.

1.3. STRUCTURE OF THE THESIS

The thesis is structured into 9 chapters. Following the **1st Chapter**, the introduction, **2nd Chapter** describes the Keoladeo National Park regarding its formation, existence and physio-climatic features. The chapter also describes the general sampling protocol followed during the study. The **Chapter 3** provides details about the soil characteristics and distribution of nutrients on a spatial scale. The spatial heterogeneity was studied in at two levels, one examining the heterogeneity horizontally (i.e. among the habitats, on the basis of vegetation types) and the second vertically (i.e. depth wise distribution of nutrients in the soil profile in all the habitats). The **Chapter 4** presents and discusses the distribution of nutrients in the wetland sediments and its variations on a temporal scale (i.e. seasonal and/or bi-monthly variation). A picture of depth wise nutrient distribution up to a depth of 20 cm, the layer directly and immediately influenced by seasonal water regime, is also given. The **Chapter 5** furnishes details of the distribution of alkali and alkaline earth metals (base cations) in different habitats. The depth wise distribution and their relation with the geochemical or ecological and/or biological reasons are also discussed. It distinguishes the base cation enrichment among the habitats, i.e. terrestrial and aquatic areas. The **Chapter 6** presents a comparative account of base cation availability in wetland sediment on bimonthly basis, and deliberates upon the influence of water and other ecological factors on the variations of metals / cations in soil. The **Chapter 7** discusses about the availability and distribution of select heavy metals, such as Cu, Pb and Zn in this multiple habitat system. Depth wise distribution of these metals is also presented. This chapter also reports the chemical partitioning of these heavy metals amongst defined fractions in soil in different habitats. The **Chapter 8** is a consolidated summary presenting the salient features of the whole exercise, while the **Chapter 9** lists out the relevant literatures cited in the thesis.

2. STUDY AREA AND GENERAL STRATEGY OF SAMPLE COLLECTION

2.1. STUDY AREA

The Keoladeo National Park (Figure 2.1.1), a world heritage and Ramsar site, is famous for its wintering palearctic waterfowl and is a known wintering ground in India for the highly endangered Siberian Crane *Grus leucogeranus*. It is an important tourist destination and is located on the major sightseers' route of Delhi-Agra-Jaipur.

2.1.1. Location

Keoladeo National Park, one of the renowned waterfowl habitats and freshwater wetland in the world is situated in eastern Rajasthan, between 27° 7.6' to 27° 12.2' N and 77° 29.5' to 77° 33.9' E about 2 km south-east of Bharatpur city (Plate 1.), 56 km west of Agra. It is equidistant from New Delhi and Jaipur on either side (approximately 180 km, Plate 2.). It falls in the Punjab plains biotic province of semi-arid biogeographical zone (Rodgers and Panwar 1988), which is a flat dry area of the Indus-Yamuna watershed. The area also falls under Aravalli region.

2.1.2. History

The history of Keoladeo National Park (KNP) is an example of man's credit of the interference with natural system, which had benefited not only man but also the wildlife in an area. The beginning of artificial flooding was the turning point in the Park's history. One of the most striking features of KNP is its origin from a natural depression, which was an evanescent rain-fed wetland some 250 years ago. This periodically/seasonally flooded natural depression was converted into a permanent water body by harnessing the water from Ajan Dam, a temporary reservoir, situated half a kilometre south of the present border of the Park. Maharaja Surajmal, the second Raja of the erstwhile Princely State of Bharatpur constructed the Ajan Dam during his reign, i.e. during 1726-1763 (Gasquire 1927, and Pandey 1970). Since the construction of this bund, entry of water into the Park has been regulated and

maintained at a level, encouraging growth of aquatic vegetation. Water was brought in from Ajan Dam through a canal, called Ghana Canal and regulated inside the Park by means of earthen dykes and sluice gates. Along with the water, millions of fry also entered the Park, growing up attracting a variety of piscivorous colonial birds for nesting. The vegetation changes that followed provided the ideal habitat for waterfowl. Thus water management, which was initiated during 1726 - 1763, was the beginning of the formation of the present world famous National Park at Bharatpur (Middleton 1989).

From the available records, it appears that the area was being under active protection since 1857, when the then ruler of the state Maharaja Jaswant Singh enclosed the jheel and the surrounding forest area – popularly known as Keoladeo-Ghana with fencing supported by stone pillars. The entire Park area belonged to the rulers of the princely state of Bharatpur until its declaration as a bird sanctuary in 1956. The main objectives of the then rulers in converting the rain fed wetland into a permanent waterfowl reserve were sport hunting, protecting the “sacred” cow from hostile farmers as the cow often grazed agricultural crops, providing grazing land for buffaloes, and protecting Bharatpur town from deluges that were frequent in those days.

The main reason for the construction of Ajan Dam does not appear to be promoting the waterfowl habitat of the Park, as it is popularly believed. It was only a part of an ingenious network of detention reservoirs constructed to harness the flow of the rivers, Ghambhir and Banganga, for flood irrigation, necessitated by the frequent and at times catastrophic deluges during the rainy season (Middleton 1994). Water stored in the dam during rainy season particularly during July-August is gradually released to empty the reservoir by October. Once the reservoir is drained out, the area is utilized for raising kharif crop, mainly wheat. The then rulers constructed a canal to bring in water from Ajan Dam and build several dykes to contain water. The management of water regime encouraged luxuriant growth of aquatic plants, providing habitats for wildfowl, and when millions of fish fry entered the Park along with the water from Ajan Dam, fish eating birds were lured in, and the present Park was developed. Earlier, the villagers around the Ghana (currently KNP) were allowed to graze their cattle inside the Park. The area of the Ghana was much larger than what

it is presently, as encroachments by the neighbouring villages has reduced it to the present day size.

During 1905, a European forest officer GM Mathew visited the forests of the state and made a detailed report. He recommended creation of a forest department by amalgamating existing departments for grass production and distribution, grazing ground for cattle, wild cattle management and wildfowl shooting reserve and production of firewood and charcoal. He also suggested management of the Ghana on standard coppice system and rotation period was fixed at 20 years. In 1925, the Forest Act of Bharatpur came into effect and the Shikar department was brought under the forest department. In 1932-33, nurseries and plantations were taken up. In 1935, fire protection work in Keoladeo Ghana was taken up along with other areas.

An assessment in 1941, reported that the conditions of the forest had deteriorated since 1905 attributing it mainly to unregulated grazing. Artificial regeneration of *Acacia nilotica* on the banks in the Park was recommended. A working plan was prepared for 1944-45 to 1963-64 and prescription of plantation for whole state was given. Numerous bunds and roads in the Park were constructed during the reign of Maharaja Brijendra Singh and his father. It is presumed that the *A. nilotica* plantation on the mounds was raised during early 1960 or late 1950. There were no heronries in the Sapan mori or in the area behind the Shanti Kutir before 1958 (Saxena 1975).

The KNP passed through a very crucial period immediately after independence in 1947, as there was a high demand / mounting pressure to convert the refuge into agricultural land. However, the Bombay Natural History Society through the efforts of Dr. Sálim Ali could impress upon the then Prime Minister of India, Pt. Jawaharlal Nehru and the erstwhile Maharaja of Bharatpur the need for declaring the refuge as a Bird Sanctuary. This effort of Dr. Sálim Ali, Mr. Horace Alexander and Gen. Williams and the determined timely action of the Forest Department of Rajasthan led to the declaration of the area as a Bird Sanctuary on 13th March 1956, under the State Wild Animals and Birds Protection Act, 1951. Nevertheless, the Maharaja retained shooting rights until 1972. Subsequently during 1967, it was declared a Protected Forest under the provisions of the Rajasthan Forest Act, 1953. It was designated as a Ramsar Site under the Ramsar Convention ("Convention on Wetlands of International

Importance especially as waterfowl habitat", Ramsar, 1971) in October 1981 (Mathur et al. 2005). It was declared a National Park on 10 March 1982 under the Wildlife Protection Act, 1972 (Sharma and Praveen 2002). During 1987, the Park was inscribed in the UNESCO (United Nations Educational Scientific and Cultural Organization) World Heritage list. The KNP is IUCN (International Union for Conservation of Nature and Natural Resources) Management Category II National Park and X World Heritage Site. Presently KNP is the only place of wildlife importance, which has all the four statuses, viz., Sanctuary, National Park, Ramsar Site and World Heritage Site in the country.

2.1.3. Topography

The total area of this Park is about 29 km², out of which the central submersible area (the central dotted area in the Figure 2.1.1), the wetlands cover about 8.5 km² and the grassland and woodland cover the rest (Azeez et al. 2000). The average elevation of area is about 174 m above mean sea level. The grassland system is mostly of savannah type with thickets. The wetland system (Plate 3 and Plate 4) of the Park is wholly dependent on the monsoon. The total Park is segmented into 15 blocks or compartments, named alphabetically from A to O, separated by earthen dykes or trails, for the ease of management and tourism. The bottom of each block is more or less flat except the narrow stretch along the dykes, around mounds and some patches towards the centre of some blocks. The large number of migratory waterfowl and the range of habitats (Prusty et al. 2006a) clearly distinguished by vegetation types (Davis and van der Valk 1988) are the distinctive features of the Park. Sluice gates are used to regulate water in the blocks that fall under the wetland area. It is the only National Park in India with a wall (2 m high) around it, which is about 36 km long, separating the Park from the vast agricultural landscape (agricultural fields of over 15 villages) surrounding it.

The water from monsoon flowing down the numerous ephemeral streams and stored in a temporary reservoir (Ajan Dam) to be released to the Park subsequently (Varshney 2005) is the lifeline of the Park. The input water brings in millions of fish fries (that grow to be food for the birds), sediments and detritus, to the Park

Ecosystem (Sebastian 2005). Minerals and nutrients including trace metals as an outcome of natural weathering, agricultural and other anthropogenic activities in the catchments finding their way into the wetland system with the incoming water, are settled in the inundated wetland blocks, and partly in the adjoining terrestrial areas such as woodlands and grasslands. During the years of abnormally high rainfall, the terrestrial (woodland and grassland) blocks bordering the aquatic blocks get partially inundated for certain duration of the year thus influencing the biogeochemical properties of the habitat. The Park administration, during the years with abnormally low rainfall, as a stopgap arrangement, floods some locations in the wetland pumping ground water from bore wells. This ensures the survival of the fish fauna and drinking water to other animals.

2.1.4. Vegetation

The major plants dominating the wetland vegetation are *Cyperus alopecuroides*, *Hydrilla verticillata*, *Ipomoea aquatica*, *Neptunia oleracea*, *Paspalidium punctatum*, *Paspalum distichum* and *Pseudoraphis spinescens* that are known for nutrient removal from the water and sediment system of the Park (Prusty et al. 2007). The wetland system has three different types of macrophytes, namely i) submerged species such as *Ceratophyllum* sp., *H. verticillata*, *Najas minor* and *Vallisneria* sp. ii) floating ones such as *Ipomoea* sp., *Lemna* sp., *Nymphaea* sp., *Nymphoides* sp., and *Spirodela* sp., and iii) emergent species such as *C. alopecuroides* and *P. distichum* (Azeez et al. 1992, Middleton 1989 and Middleton 1994). The detailed list of the plant species recorded in KNP until date is given in Appendix I.

Terrestrial area, that includes woodland and grassland, cover almost 20 km² Kadam (*Mitragyna parvifolia*) trees dominate large sized trees and the woodland (Plate 5 and Plate 6), while thorny *Acacia* sp. and *Prosopis juliflora* shrubs dominate shrub lands (Vijayan 1991). The major species found in woodland were *A. nilotica*, *Capparis* sp., *M. parvifolia*, *P. juliflora*, *Syzygium cumini*, *Salvadora* sp. and *Zizyphus* sp. (Azeez et al. 2007). The most widespread grasses (Plate 7 and Plate 8) in the Park were *Desmostachya bipinnata* and *Vetiveria zizanioides* (Sharma and Praveen 2002). *P. juliflora*, though an alien species, in due course of time because of the water scarcity

during 2000 - 2002 (due to lack of rainfall), has spread all over the Park irrespective of the habitat type competing with native plant species for resources including space.

2.1.5. Geology

Almost the whole of the northern portion of Bharatpur district is covered with alluvium. A few isolated hills of schist and quartzite belonging to the Aravalli and Delhi systems respectively are also seen (Azeez et al. 2000). The quartzites are well exposed in the Bayana hills where they are divided into five groups namely, Weir, Damdama, Bayana, Badalgarh and Nithar. To the south-east, sandstone of Upper Vindhyan Age is faulted down against the quartzites, forming a horizontal plateau over-looking the alluvium of the Chambal River. Bharatpur forms part of the alluvial basin of the river Yamuna and the Ganges. Consequently (Figure 2.1.2), the great majority of the exposed rocks are alluvial, consisting of modern alluvial deposits with brown sand, which the wind carries from the desert of Rajasthan. The hills west of Bayana and divided from the Sidgir Pahar by the catchment basin of Gambhir River are formed of quartzite sandstone. The Vindhyan sandstone formations cover most of the rocky parts of Bharatpur district.

The soil in the KNP, which is predominantly alluvial, has some clay formations resulting from periodic inundations. Patches of saline soils are many in terrestrial area of the Park. The present investigation has found that the saline patches in the woodland and grassland are mostly due to the Na salts while those in the wetland are due to the salts of Ca. The soil type has textural differences in different areas in the KNP. In terrestrial areas, it was silt clay loam and in aquatic areas, it was clayey. Scattered saline patches are seen in the terrestrial areas. The soil characteristics of the Park are elaborated in the next chapter.

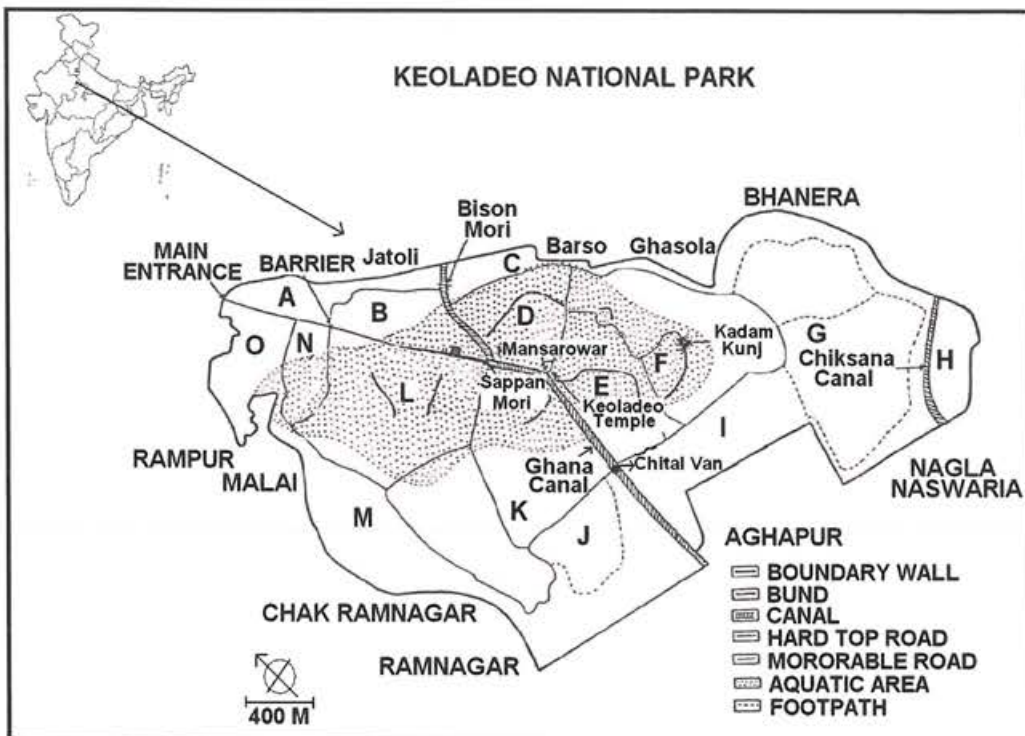


Figure 2.1.1. Study Area Map



Plate 1. Location map of Bharatpur city in India



Plate 2. Location map of Keoladeo National Park near Bharatpur city

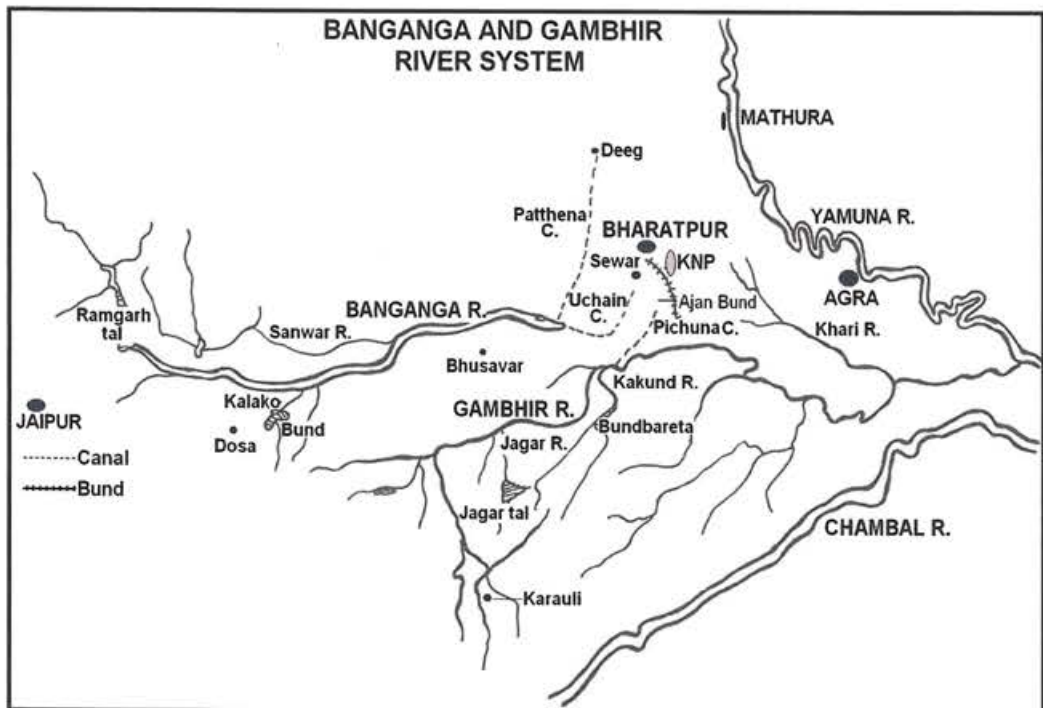


Figure 2.1.2. Map of Banganga-Ghambhir river network



Plate 3. A view of the KNP wetland system (B Block)



Plate 4. A view of the KNP wetland system (E Block)



Plate 5. A view of the KNP woodland system (C Block)



Plate 6. A view of the KNP woodland system – Litters (C Block)



Plate 7. A view of the KNP grassland system (G Block)



Plate 8. A view of the KNP grassland system (G Block)

2.1.6. Water management in the Park

Keoladeo National Park is a monsoonal wetland (Azeez et al. 2000). Its main water supply is from an outside source, the Ajan Dam, an earthen dam that stores water from its catchment basin. Two rivers systems namely Banganga and Gambhir have their network in the basin area of the dam (Figure 2.1.2), supplying nutrients and other autochthonous materials to the Park. Water from the dam is released into the Park by end of August every year through a canal, the Ghana Canal, which is connected to most of the wetland blocks on either side by sluice gates (Plate 9.). Most of the wetland area remains inundated during monsoon and post monsoon season (i.e. up to October) the turning point so far as the Park's limnochemistry is concerned (Prusty and Azeez 2004), after which water starts drying up.



Plate 9. The Ajan Dam releases water to KNP through the sluice gates

2.1.7. Climate

The Bharatpur area is a part of the Aravalli Super group and falls under semi-arid hot dry zone of India (Pal et al. 2000). However, the climate of the area is sub-humid to

semi-arid. KNP experiences four distinct seasons; summer / pre-monsoon (April to June), rainy / monsoon (July to mid-September), post monsoon (mid-September to mid-November) and winter (mid-November to March, Prusty and Azeez 2004). Usually the temperature in the Park varies from 05 °C to 49 °C, showing strong diurnal and seasonal fluctuations i.e. chilling winter and scorching summer.

The summer season (March-June) in Bharatpur is characterised by hot dry weather, dust storms, low humidity and scanty drizzles of only a few millimetres. The Park receives most of its precipitation from the south-west monsoon, which usually sets in during early July. The transitional period between the hot and the cold season, (the post monsoon) is characterized by a gradual decrease in temperature and occasional showers. The winter is very cold with chilly winds and fog. Scanty showers due to disturbances also occur during this period.

2.1.7.1. Temperature

The minimum temperature recorded during the period of the study was 05 °C in November 2003 and the maximum was 49 °C in June 2003 (Meteorological Department, Bharatpur, 2003 - 2005). The annual mean minimum temperature and annual mean maximum temperature ranged between 5.3 °C and 8.9 °C, and 42.7 and 42.3 °C. January 2004 showed the lowest average minimum (5.3 °C) and June 2003 had the lowest average maximum (32.2 °C) temperature. In contrast, January 2004 had the highest average minimum temperature (18.1 °C) and June 2003 had the highest average maximum temperature (42.7 °C). The mean minimum temperature started rising gradually from January 2004 (5.3 °C) until July 2004 (28.4 °C) and thereafter declined. The mean maximum and minimum temperature increased gradually from January until May and thereafter declined gradually until January (Figure 2.1.3). The average maximum temperature differed by approximately 7.0 °C between February and March, the transition period between winter and spring.

2.1.7.2. Relative Humidity

The average relative humidity ranged from 42.8 to 91.8 %, the minimum being in summer (June 2003) and the maximum in winter (January 2004, Figure 2.1.4).

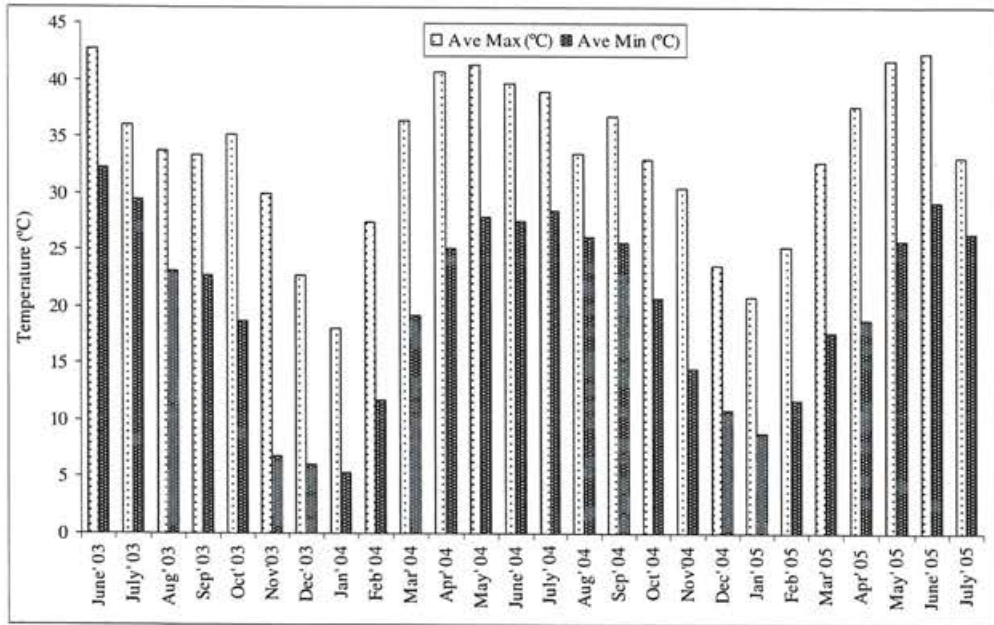


Figure 2.1.3. Seasonal variation of Temperature KNP during the period of the study

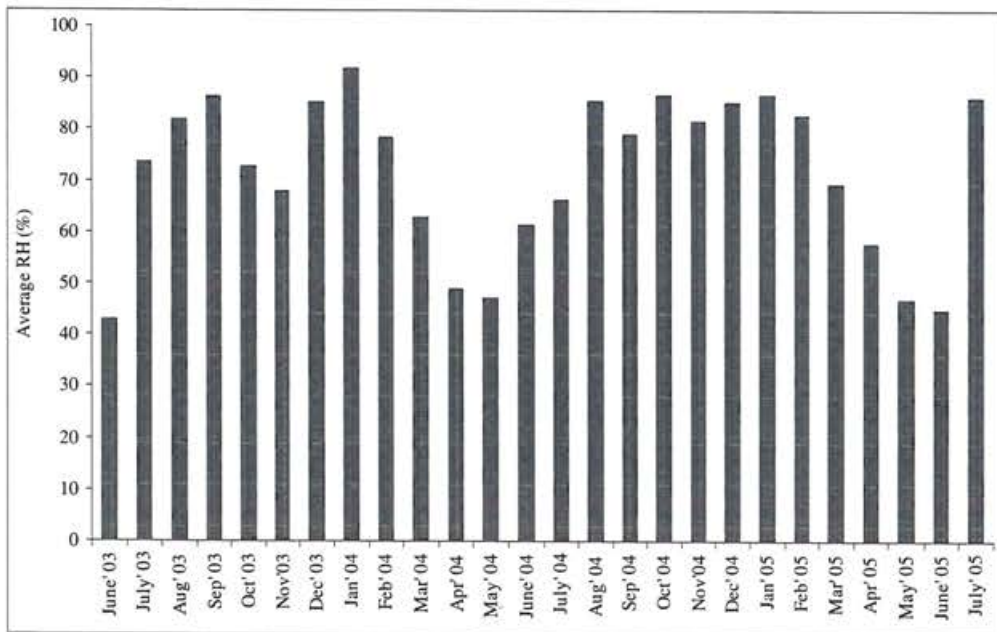


Figure 2.1.4. Seasonal variation of Relative Humidity in KNP during the period of the study

Table 2.1.1. Details of water release into the Park

Year	Total annual rainfall (mm)	Quantum of water released to the Park (million m ³)
2005*	873.8	16.14
2004*	630.0	0.51
2003*	849.8	8.15
2002	503.5	0.0
2001	612.8	5.18
2000	445.6	4.02
1999	NA	9.71
1998	965.0	8.40
1997	709.2	5.11
1996	998.4	12.25
1995	974.2	10.57
1994	657.2	14.30
1993	603.6	13.73
1992	787.8	16.51
1991	NA	13.30
1990	NA	13.30
1989	520.4	5.21
1988	392.83	13.73
1987	205.0	0.45
1986	220.0	0.37
1985	734.5	10.87
1984	396.4	9.74
1983	686.4	14.57
1982	781.5	9.79
1981	256.7	14.60
1980	638.1	14.59
1979	218.5	8.05
1978	590.2	8.05
1977	839.5	8.05
1976	775.7	14.58
1975	700.5	8.02
1974	621.0	14.58
1973	681.5	3.37
1972	678.1	3.37
1971	830.7	14.58
1970	624.2	14.58
1969	490.5	8.05
1968	619.9	14.58
1967	813.6	3.37
1966	641.1	14.58

Source: Irrigation Department – Bharatpur Circle, Govt of Rajasthan

* Study years, NA: Not Available

2.1.7.3. Rainfall

Bharatpur receives rain mainly from the south-west monsoon, which sets in during the late June and continues up to September. Scanty showers due to north-western disturbances also occur during the winter. The lowest rainfall was recorded during April 2004 and highest during July 2005 (Figure 2.1.5). During the present study from 2003 to 2005, the average rainfall was 83.6 mm. KNP, being a monsoonal wetland needs water for its very survival. The amount of water released varies from year to year depending on the rainfall in the catchment. During the whole study duration, the KNP received highest amount of water during 2005 (i.e. around 16.14 million m³, Table 2.1.1). Hence, the water inflow in the previous years (2002, 2003 and 2004) is significant as far as the wetland properties in 2003, 2004 and 2005 are concerned. The total rainfall during 2002, 2003, 2004 and 2005 were 503.5, 849.8, 630.0 and 873.8 mm respectively. As 2001 and 2002 were consecutive drought years, in 2002 there was no water inflow to the Park.

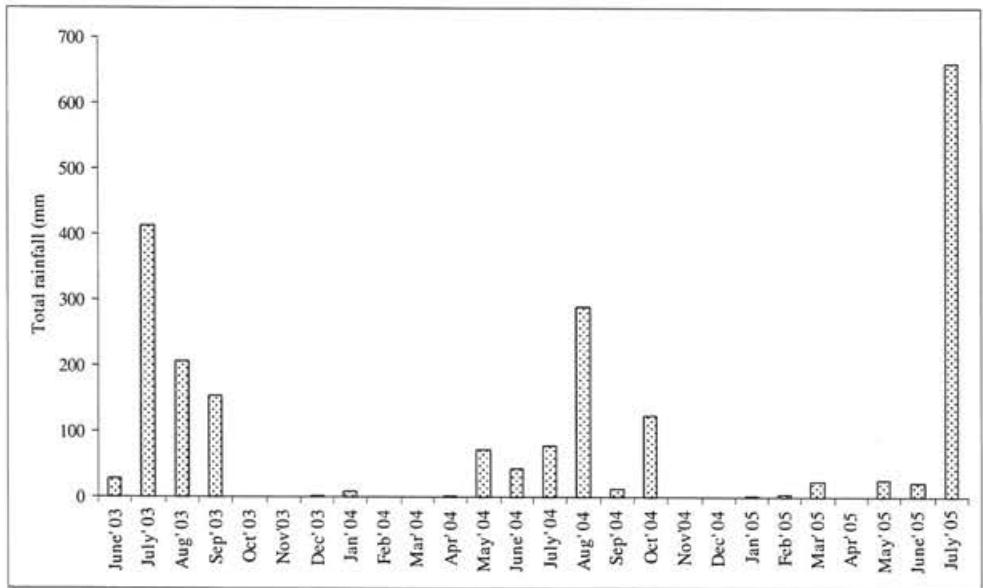


Figure 2.1.5. Seasonal variation of total rainfall in KNP during the period of the study

2.1.8. Present state of the KNP

For decades, Keoladeo National Park has been attracting tourists mainly for its wetland system at its centre. The tourists flocked the area to watch the shimmering, bird-flocked wetland of the Park. This wetland system, once known as a marvellous haven for birds, now especially in summer, has restricted to pools and puddles nursed by a network of stuttering diesel-fuelled pumps, which pump out ground water from beneath the parched earth. Years of poor monsoon rains have left most of this World Heritage Site in the desert state of Rajasthan dry and cracked, while local farmers insist on getting the lion share of whatever little rainwater collected in the Ajan Dam to irrigate their fields. This has forced most of the thousands of migratory birds that would once spectacularly descend on Keoladeo every year for the winter to look for alternative sites that are very rare elsewhere. Few decades back, the skies above the Park were so full of birds to make one wonder how they do not collide with each other. Currently, the situation has changed so drastically. Although the Park has not yet been added to the United Nations' danger list, in 2005 the World Heritage committee warned of the risk of losing its status as a World Heritage Site if the KNP continues to dry up. The present situation as well as the future does not appear very encouraging, if the present condition is allowed to persist. When India succeeded in getting Keoladeo listed as a World heritage Site in 1987, the promise was to look after the unique wetland system for the conservation of the biodiversity. Nevertheless, the Park currently is in a precarious state that visitors apparently are showing up in ever-smaller numbers. It is common among the cycle-rickshaw pullers in the Park in these days to lament "No Water, No Birds, No Tourists".

Rajasthan's Forestry Department thinks the best solution for water scarcity is to top up the Park with piped water from the Chambal river, about 80 km (50 miles) away, or from the Goverdhan floodwater drain, about 20 km (12 miles) away. However, this has its own ecological implications. Financial constraint at the part of Rajasthan Forest Department also seems to be a major factor in this whole exercise. In the wheat fields behind the Park lie the relics of an unsuccessful attempt to bring water to the area in the form of rusting pipes that have almost abandoned since 2004 because of several legal wrangles. Therefore, piping water into the KNP remains a mirage for the time being. In the meantime, the Park waits in the queue for water from another

reservoir, the Panchana about 80 km (50 miles) away. Here in 2004, police had to use force to disperse angry farmers enraged to find that the local government opened sluice gates to release water into the Park. Since then, no dam water has been released to the Park, as commonly vented that unlike birds farmers have votes. The wetland system of KNP has now been going dry long enough for new woodland species of trees to take root and colonise, despite frantic attempts to remove the seedlings by the Park authorities. The KNP is deteriorating every year. It is believed that although the Park could partially recover, each dry year leaves more scars that are permanent on the system.

2.2. SOIL SAMPLING, PROCESSING AND ANALYSIS

2.2.1. For Spatial Variation Study

Of the total 15 blocks in the Park, 3 blocks each falling under the woodland, wetland and grassland habitats were selected to collect soil samples. The soil samples were collected up to a depth of 100 cm in mid June of the each year from 2003 to 2005. To estimate the mobile forms of nutrients like nitrogen and sulphur in soil, the samples are collected generally to a depth of 60 cm (SubbaRao 2001). However, in the present study, since species such as *Mitragyna* and *Syzygium* have roots traversing deeper, samples were collected up to 100 cm depth consistently from all the three habitats. To maintain mounts for trees the Park administration removes soil from close vicinity of the mounts, prior to the onset of monsoon. Therefore, relatively undisturbed locations were identified for collecting soil samples for the study. After demarcating a location, the uppermost litter layer was removed by scrapping with a plastic scrapper and a trench of 1 m³ was dug (Plate 10). After removing the litter, samples were collected using a plastic scoop at 0, 25, 50, 75 and 100 cm depths. The soil samples were then spread over a plastic tray for colour matching with Munsell Soil colour chart and the colour codes and notations were recorded. Subsequently, the samples were packed in pre-cleaned, acid treated and airtight plastic bags and transferred to the laboratory for further processing and analysis. In total 162 samples (after pooling) of soil was collected in June of all the three years (2003 - 2005).

In the laboratory, a portion of the soil samples was air-dried at room temperature (Jackson 1958), homogenized / gently crushed using an agate mortar and pestle, and

sieved through a standard sieve of 2 mm mesh size (Tandon 2001). The soil samples with particle size of < 2 mm were stored in acid washed plastic containers. A portion of the air dried original sample was hand crushed and analyzed for the soil texture and grain size (sand, silt and clay) after sieving through a series of standard sieves of different mesh sizes using a mechanical sieve shaker. The fractions were reported on percentage basis. The results of the soil texture analysis are discussed in the third chapter. The detailed methods of the soil processing for specific analysis are discussed under concerned chapters. Thus, the results and discussion of the spatial distribution of nutrients and alkali metals in KNP presented under the chapters 3 and 5 is based on the same sample set.

2.2.2. For Temporal Variation Study

Study of the temporal variation of select parameters was done only in the case of the wetland soils / sediments. The wetland soils / bed sediments samples were collected bimonthly, during September 2003 to July 2005, using a core sampler. The sampler of size 75 x 10 cm² (Length = 75 cm, Internal diameter = 10 cm, Plate 10) was made of galvanized iron lined internally with PVC (pre-cleaned and acid treated). The core sampler was forced into the wetland bed up to 20 cm depth at nine randomly selected locations (i.e. three each in D, K and L blocks). The cylindrical sediment core was taken out of the sampler and sliced into four sections each of 5 cm length using a thin plastic string to obtain representative samples from each of 0-5, 5-10, 10-15 and 15-20 cm depths. The sediment slices were packed immediately in laboratory pre-cleaned polythene bags, transferred to the laboratory, and stored at 4 °C until further processing and analysis.

Similar to the soil samples collected for spatial variation study mentioned earlier, the bed sediment samples for temporal variation study were air dried at room temperature (Jackson 1958), homogenized / crushed gently in a porcelain mortar and pestle. The samples thus processed were sieved through a standard sieve of 2 mm mesh size (Tandon 2001) and particles less than 2 mm were separated for further characterization. All the triplicate soil samples from the same block from each depth were mixed homogeneously to make composite samples from the block and stored in

pre-cleaned and acid treated plastic containers. The results of specific analysis of the sediment samples are discussed in chapters 4 and 6.

The major chemical characteristics of the samples used in the study were estimated / analysed by standard procedures and techniques as given in Table 2.2.1. The chapters 4 and 6 that discuss about the temporal (bimonthly) variation in the distribution of nutrients and alkali metals in KNP soil respectively, is based on the analysis of same sample set. In total the 144 soil samples (after pooling) was collected bimonthly from September 2003 to July 2005. It may be noted that the results presented in the chapter 3 and chapter 5 are based on one sample set collected annually while those presented in chapters 4 and 6 is based on the sample set collected bimonthly.



A



B

Plate 10. A: Trench dug for soil sampling (Spatial variation study) and B: Core sampler used for wetland bed sediment sampling (Temporal variation study)

Table 2.2.1. Methods used in the analysis of samples collected for the study

Parameter	Method	Reference	Instrument/Apparatus
Soil Colour	Colour Comparison	-----	Munsell Soil colour Chart
Soil Texture	Standard Sieve Method	-----	Mechanical Sieves of different mesh sizes
pH (1:5, soil: water)	Potentiometry	Tandon (2001)	Digital pH meter- Model- Digisun-7007
EC (1:5, soil: water)	Conductometry	Tandon (2001)	Digital Conductivity Meter- Model- Digisun -D1 9001
TDS (1:5, soil: water)	Conductometry	Tandon (2001)	Digital TDS Meter- Model- E1-651 E
Total Organic Matter	Wet Digestion Method	Walkley and Black (1934)	-----
Carbonate content	Rapid titration method	Allen (1989)	-----
Total Nitrogen	Indo Phenol Blue Method	Kaplan (1965) Raveh and Avnimelech (1979)	Spectrophotometer (Model- Perkin Elmer Lambda 35)
Total Available Phosphorous	Olsen's Method	Jackson (1958)	Spectrophotometer (Model- Perkin Elmer Lambda 35)
Total Available Sulphur	Turbidimetry	Tandon (2001)	Spectrophotometer (Model- Perkin Elmer Lambda 35)
Available Sodium	Ammonium Acetate Method	SubbaRao (2001)	Flame Photometer (Systronics-128)
Available Potassium	Ammonium Acetate Method	Allen (1989)	Flame Photometer (Systronics-128)
Available Lithium	Ammonium Acetate Method	Allen (1989)	Flame Photometer (Systronics-128)
Available Calcium	EDTA Titration Method	Allen (1989)	-----
Available Magnesium	EDTA Titration Method	Allen (1989)	-----
Cation Exchange Capacity	Empirical Estimation	Darmody and Marlin (2002)	-----
Sodium Absorption Ratio	Empirical Estimation	Azeez et al. (2000)	-----
Copper	Aquaregia Digestion	Ure (1990)	AAS
Lead	Aquaregia Digestion	Ure (1990)	AAS
Zinc	Aquaregia Digestion	Ure (1990)	AAS
Chemical Partitioning	Sequential Extraction	Tessier et al. (1979)	AAS

2.3. STATISTICAL ANALYSIS

To find the range, distribution and association of different metals among themselves and with the metal ratios, basic descriptive statistics and two-tail Correlation matrix were performed on the analytical data using MEGASTAT 8.8 (Orris 2000). Univariate tests to assess variations of the distribution of the metals among different sediment layers and months were performed following the General Linear Model (GLM). When significant values from *F*-tests were obtained separation of means was achieved using a Least Significant Difference (LSD) test as post-hoc analysis, at the $\alpha = 0.05$ level. These statistical tests were performed using SPSS 13.0 (Norusis 1990). The parameters were further examined with a Principal Component Analysis (PCA) using the SPSS 'FACTOR'. The factors were retained in the analysis based on the criterion that each retained factor had an Eigen value >1

3. SPATIAL VARIATION OF MAJOR NUTRIENTS IN THE KNP HABITATS

3.1. INTRODUCTION

Soils are considered as highly heterogeneous in both space and time, and that this heterogeneity has strong consequences for both plant performance and in turn on ecosystem function (Huber-Sannwald and Jackson 2001). The intent in spatial studies of soil is to describe soil properties off a landscape that is a function of vegetation and other ambient factors from the sample data (Agbu and Olson 1990). At a landscape level, the spatial patterning of soil resources affects the distribution (Pan et al. 1998), productivity (Mou et al. 1995) and diversity (Anderson et al. 2004) of plant communities. At smaller scales, it influences plant establishment (Maestre et al. 2003) and the outcome of plant–plant interactions (Robinson et al. 1999). Evidence on the role of spatial heterogeneity of soil nutrients has been acquired mainly from studies of horizontal heterogeneity. Other components of soil heterogeneity, such as temporal variations and vertical patterns, are less commonly described (Fransen et al. 1999, and Fitter et al. 2000), although they can exert strong influence on community structure (Maestre and Reynolds 2006). Vertical heterogeneity in soils may be especially relevant in arid and semiarid ecosystems (Sala et al. 1997, and Reid et al. 1999) due to phenomena such as hydraulic lift (Caldwell and Manwaring 1994), accumulation of litter and plant material (Zaady et al. 1996), plant rooting behaviour (Soriano et al. 1987) and bioturbation by animals (Whitford 1993).

Habitat wise (generally categorized based on vegetation) variation in soil properties indicates the variations in the biogeochemical and ecological processes (Gupta and Malik 1996, Hagedorn 2001, Singh et al. 2002, and Goma-Tchimbakala and Bernhard-Reversat 2006) on a spatial scale. Holding environmental conditions constant, residue composition (litter quality) has been seen to influence the rate and extent of residue decomposition (Martens 2000) and nutrient mineralization. However, studies exploring the response of roots to small-scale vertical heterogeneity in nutrients are lacking (Hodge 2004).

An understanding of the soil nutrients such as soil organic matter, Total Nitrogen and C: N ratio is very important for proper management of a wetland-dominated system, as they greatly influence their productivity (Mitsch and Gosselink 2000, and Bai et al. 2005) and possible successional changes. The estimation of available nutrients in soil has pedological as well as ecological importance, as only a small fraction of what the soil contains is in the plant available form and this small fraction may not be directly proportional to the total nutrient content of the soil. An exhaustive survey of past studies revealed that studies on the soil characterization, especially nutrient distribution and mobilization along the depth profile, in protected areas in India are wanting. Horkar and Totey (2002) has reported depth wise variation in soil properties in Navegaon National Park, Maharashtra. GEER and GUIDE (2001) report the textural characteristics of soil in Narayan Sarovar Wildlife Sanctuary in Gujarat, India. The study by Garg and Singh (2005) investigates the available nutrient status in soil and plants in the hill ranges of Garo, Khasi and Jantia in Meghalaya, India, while Bisht and Lodhiyal (2005) did soil characterization in reserve forests of Kumaun in central Himalaya. Another study by Neeraj et al. (2004) examines carbon dynamics in relation to plant diversity and soil biological activity in tropical successional grassland systems at Kurukshetra, India.

In this chapter, we discuss the issue on a spatial scale (both horizontal and vertical) in KNP, Bharatpur, India. The horizontal scale refers to different habitats in the KNP and the vertical scale refers to the depth wise variation along the soil profile at each locations.

3.2. METHODS

The details about the sampling and preliminary processing are discussed in the section 2.2.1. The total number of soil samples, collected in June of every year (2003 – 2005) after processing and packing in plastic containers, was 162. In these samples, the portion meant for chemical characterization was analyzed for several parameters. The list of parameters and the protocol followed in this study for their estimation are given in Table 2.2.1. pH, Electrical conductivity (EC, $\mu\text{s}/\text{cm}$) and Total Dissolved Solids (TDS, mg/kg) were analyzed from the soil water extract in the ratio of 1:5 using respective digital electrodes. The electrodes were calibrated using required standards

and standardized prior to the experiment. All the chemicals used in the study were of AR grade and all the reagents were made in double distilled water prepared using quartz double distillation assembly. Total Organic Carbon (TOC, %) was estimated following the Wet Digestion method of Walkley and Black (1934), wherein the organic matter in the soil is oxidized with a mixture of Potassium Dichromate ($K_2Cr_2O_7$) and concentrated Sulphuric Acid (H_2SO_4) utilizing the heat of dilution of Sulphuric Acid. The unspent Potassium Dichromate is back titrated against Ferrous Sulphate ($FeSO_4 \cdot 7H_2O$) solution.

Total Nitrogen (TN, %), Total Available Phosphorus (TAP, %) and Total Available Sulphur (TAS, %) were estimated spectrophotometrically using Perkin Elmer Spectrophotometer, model Lambda 35. TN was estimated following the Persulphate Oxidation Method of Raveh and Avnimelech (1979) and Indophenol Blue method of Kaplan (1965). As per this method, the soil is first oxidized with persulphate salt of K. This converts all the nitrites to nitrates. In the second step, all the nitrates are reduced into ammoniacal form by the addition of Devarda's alloy. The final total amount of ammoniacal nitrogen is estimated by following the standard Indophenol Blue method of Kaplan (1965). A multipoint standardization curve between the ranges 0 and 28 $\mu g/ml$ is prepared after reading the absorbance of the standards at 625 nm.

TAP was estimated following the standard Olsen's method (Jackson 1958) after extracting with 1M Sodium bicarbonate solution ($pH = 8.5$). Sodium Bicarbonate releases exchangeable forms of phosphate into the solution, with which Ammonium Molybdate reacts and forms Phosphomolybdic Acid. Ascorbic Acid leads to the formation of deep blue colour complex, which can be read at 882 nm. The intensity of the colour is directly proportional to the concentration of the phosphate (plant available phosphorus) present in the extract (Tandon 2001). The multipoint standardization curve was prepared using standard solutions ranging from 0 to 50 $\mu g/ml$ after reading the respective absorbances at 882 nm.

TAS was estimated turbidimetrically (SubbaRao 2001). The soil was extracted with 0.15% $CaCl_2$ and turbidity developed using Barium Chloride was subsequently measured using a spectrophotometer at 340 nm. The turbidity of the suspension was kept constant using a conditioning reagent. A multipoint standardization curve

ranging from 0 to 250 $\mu\text{g/ml}$ is prepared after reading the absorbance of the standards at 340 nm. The concentrations of nitrogen, phosphorous and sulphur in the samples were determined using linear regression. In the present case, the average regression coefficients were 0.98, 0.96 and 0.99 for nitrogen, phosphorous and sulphur respectively. The nutrient ratios, C: N, C: P, C: S and N: P, were calculated empirically.

3.3. RESULTS

3.3.1. Soil characteristics

Colour is the most obvious and easily determined soil property. There was no prominent and clear-cut difference in the colour among different soil layers or across the years, and therefore the soil colour of the habitat wise profile of only one year is presented in Table 3.3.1. Irrespective of the habitat type, in terrestrial areas the upper soil layers were of low chroma and dark grey in colour that lightens towards deeper layers. In the wetland, the surface layers were dark coloured (low chroma) and persisted more or less until the bottom of the profile. The soil texture (percentage of sand, silt and clay) in the soil profile along the depth in the three habitats is presented in the Table 3.3.2. Overall, in all the three habitats, the upper soil layer was clayey compared to the lower layers. The coarse fractions (sand and silt) were found increasing down the profile (Table 3.3.2). The lower layers were silty loam in texture. In grassland and wetland, the surface was more clayey compared to the woodland sites.

Table 3.3.1. Colour codes and notations of the soil layers

Habitat	Depth (cm)	Colour codes	Colour notation
Woodland	0	10YR4/2	Dark greyish brown
	25	2.5Y6.5/3	Light yellowish brown -Light olive brown
	50	2.5Y6/3	Light yellowish brown
	75	2.5Y6.5/3	Light yellowish brown -Light olive brown
	100	2.5Y5/3	Light olive brown
Wetland	0	2.5Y4/2	Dark greyish brown
	25	2.5Y4/2.5	Dark greyish brown -Olive brown
	50	2.5Y4/2	Dark greyish brown
	75	2.5Y4/2	Dark greyish brown
	100	2.5Y4/2	Dark greyish brown
Grassland	0	2.5Y4/2	Dark greyish brown
	25	5Y6/2	Light olive grey
	50	5Y6/2	Pale olive
	75	5Y6/2	Light olive grey -Pale olive
	100	5Y6/2	Pale olive

Table 3.3.2. Soil texture along the depth profile in KNP

Habitat	Depth	Clay (%)	Silt (%)	Sand (%)
Woodland	0	43.0	53.0	4.0
	25	71.0	22.0	7.0
	50	66.0	25.0	9.0
	75	66.0	25.0	9.0
	100	62.0	29.0	9.0
Wetland	0	58.0	34.0	8.0
	25	45.0	35.0	20.0
	50	47.0	34.0	19.0
	75	54.0	30.0	16.0
	100	54.0	33.0	13.0
Grassland	0	80.0	20.0	0.0
	25	57.0	28.0	15.0
	50	76.0	23.0	1.0
	75	48.0	33.0	19.0
	100	58.0	31.0	11.0

The soil pH, EC ($\mu\text{s}/\text{cm}$) and TDS (mg/kg) in the three habitats across the three years are presented in Figure 3.3.1, Figure 3.3.2 and Figure 3.3.3 respectively. Overall, pH was in the range of 5.20 - 9.97. The highest and lowest values were recorded in grassland during 2004 (100 cm depth) and 2003 (50 cm depth). EC ($\mu\text{s}/\text{cm}$) was in the range of 2.7 - 1336.0, the lowest and highest values being in the woodland. TDS (mg/kg) was found to be in the range of 90.0 - 8073.3 and the respective locations were at the woodland during 2004 (50 and 75 cm layer) and 2003 (25 cm layer). Among the three basic parameters, pH showed a gradual trend of rise towards deeper soil layers, except in certain cases. For instance, during 2003 pH in the grassland at 50 cm depth was lesser than its preceding layer. EC and TDS were found to show a trend of decline in all habitats except grassland; in grassland, an initial decline up to 25 cm depth was followed by a gradual increase. pH differed significantly among the years, habitats and soil layers (GLM-ANOVA, Table 3.3.3., $P < 0.05$). However, the post-hoc test reveals that none of the years was found distinct as far as variation of pH was concerned. In the case of habitats, woodland differed significantly from the other two habitats (LSD, Table 3.3.4., $P < 0.05$). Litter layer and upper layer of the soil profile (0 cm) differed from the rest of the layers. Both EC and TDS varied significantly in all the aspects, i.e. among the years, habitats and soil layers (GLM-ANOVA, Table 3.3.3., $P < 0.05$). As far as their variation in soil among years is concerned, the year 2003 was distinct and differed significantly from rest of the years (LSD, Table 3.3.4., $P < 0.05$). Among the habitats, wetland was found to differ significantly from the rest of the habitats. No significant variation was seen with in the soil layers with respect to the EC and TDS level in soil.



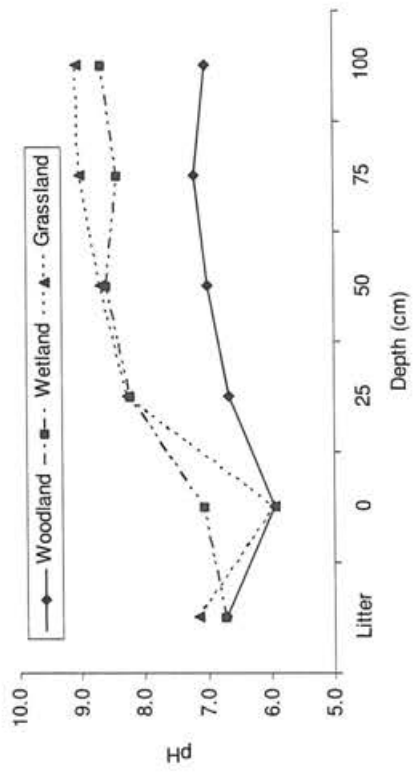
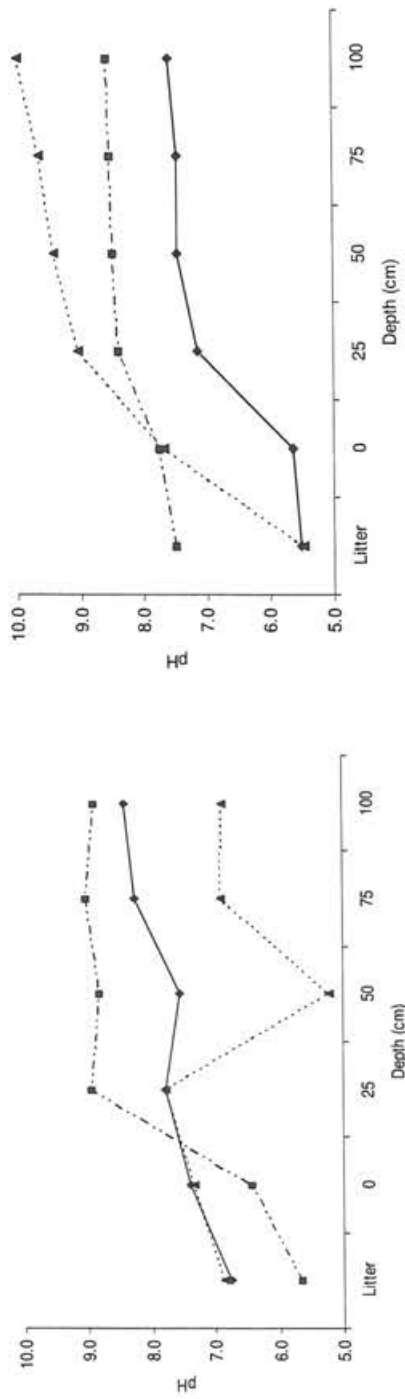


Figure 3.3.1. Year wise variation in pH in the KNP soil

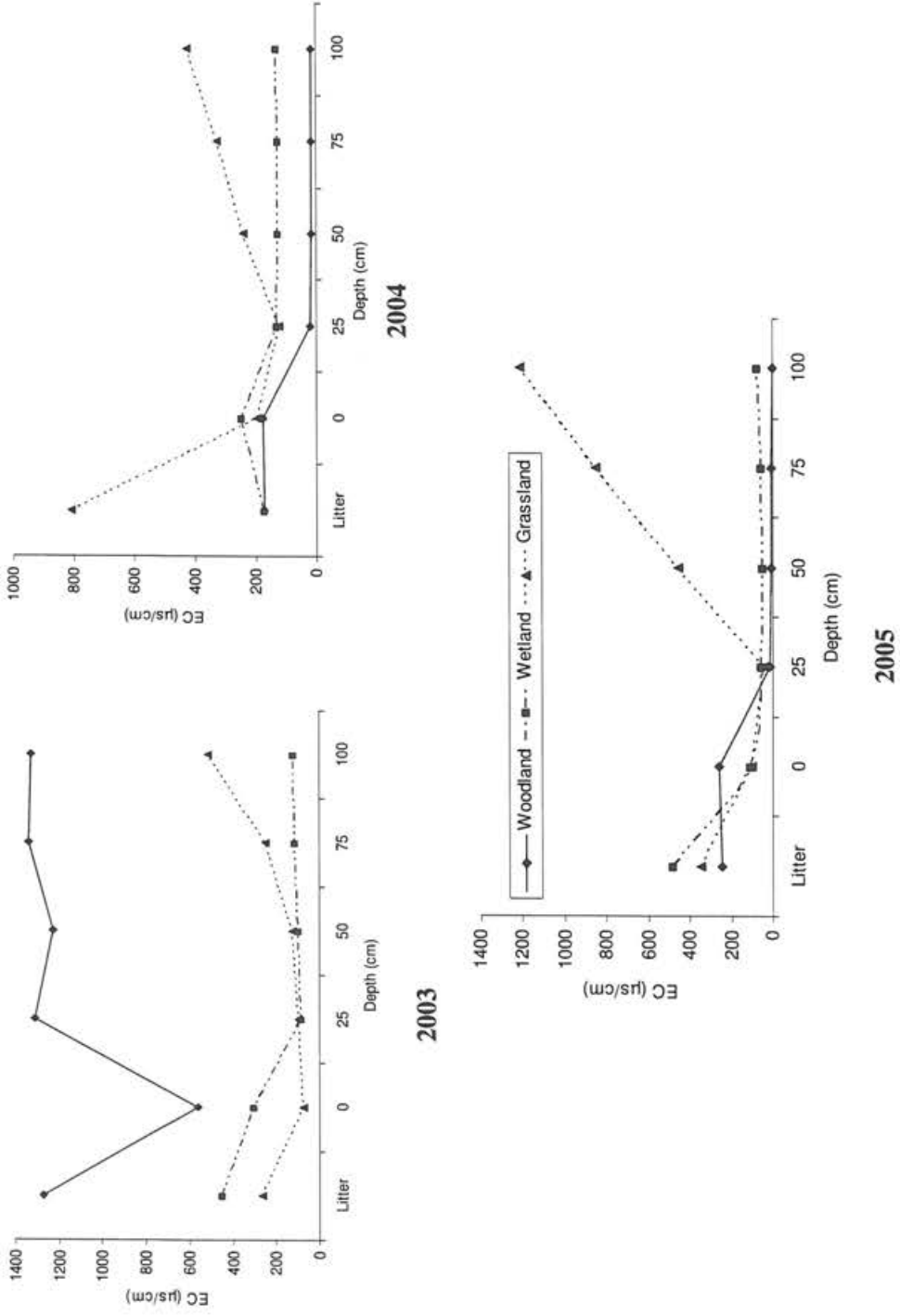
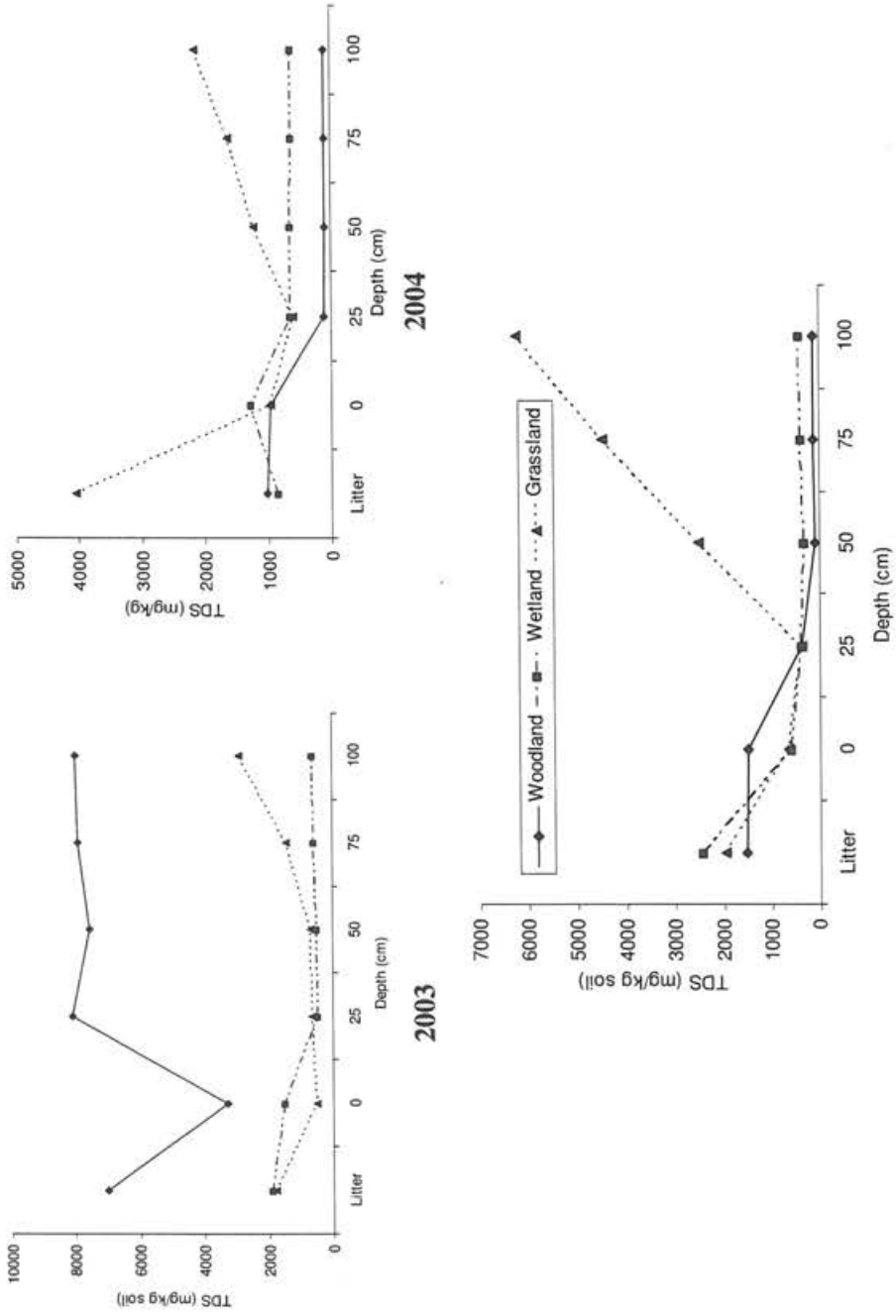


Figure 3.3.2. Year wise variation in EC in the KNP soil



2005
Figure 3.3.3. Year wise variation in TDS in the KNP soil

TOC was in the range of 0.28 - 27.78 % (Figure 3.3.4.), of which the lowest and highest values were found in woodland (50 cm layer) in 2004 and grassland (litter layer) in 2003 respectively. The lowest value of TN was 0.44 %, recorded in the woodland (25 cm in 2003) and the grassland (100 cm in 2004), while the highest value was 1.17, found in the litter layer of grassland in 2004 (Figure 3.3.5.). TAP (%) was found to be lowest (0.0004 %) in wetland (at 100 cm depth) and grassland (75 cm depth) in 2005. The highest TAP (0.0243 %) was recorded in the woodland litter layer during 2003 (Figure 3.3.6.). The lowest and highest values of TAS (%) were 0.007 and 0.049 (Figure 3.3.7.); in woodland at the depth of 50 cm (during 2005) and litter layer (during 2003) respectively. Among the four parameters (TOC, TN, TAP and TAS), TOC and TAP dropped sharply from the litter layer till 25 cm depth, thereafter following a gradual trend of declining. In the case of TN, the trend was of a rather gradual decline from the upper litter layer until 100 cm depth with a few exceptions. In 2004 and 2005, concentration of phosphorus in wetland soils in the top layers until 25 cm depth, was higher compared to terrestrial habitats. In the case of TAS in all the habitats, the values were falling at a faster rate until 25 cm. Further to that depth, the fall was gradual; the only exception being the grassland in 2005 where in the trend was reverse; increase in concentration after 25 cm depth.

GLM-ANOVA test reveals that TOC content in soil differed significantly only among the soil layers. However, among the soil layers, TOC content in litter layer and in the upper layer of the profile differed significantly among each other and was distinct from the rest of the layers (LSD, Table 3.3.4, $P < 0.05$). Unlike TOC, TN level in soil varied significantly among the years, habitats and soil layers. Further, within the years, the level during 2003 was found distinct from the rest of the years. Within the soil layers, TN level in the litter layer was distinct and significant from the rest of the layers in the soil profile (LSD, Table 3.3.4, $P < 0.05$). In contrast to the variations in TN, TAP varied significantly only among the years and soil layers and TAS did vary significantly among the habitats and soil layers. Nevertheless, the years did not vary significantly from each other as far as the TAP level in soil is concerned (LSD, Table 3.3.4, $P < 0.05$). Among the soil layers, litter was distinct and differed significantly from the rest of the layers in the profile. Similar to the results in the case of TAP, TAS also was distinct in litter layer and did differ significantly from the rest of the layers (LSD, Table 3.3.4, $P < 0.05$).

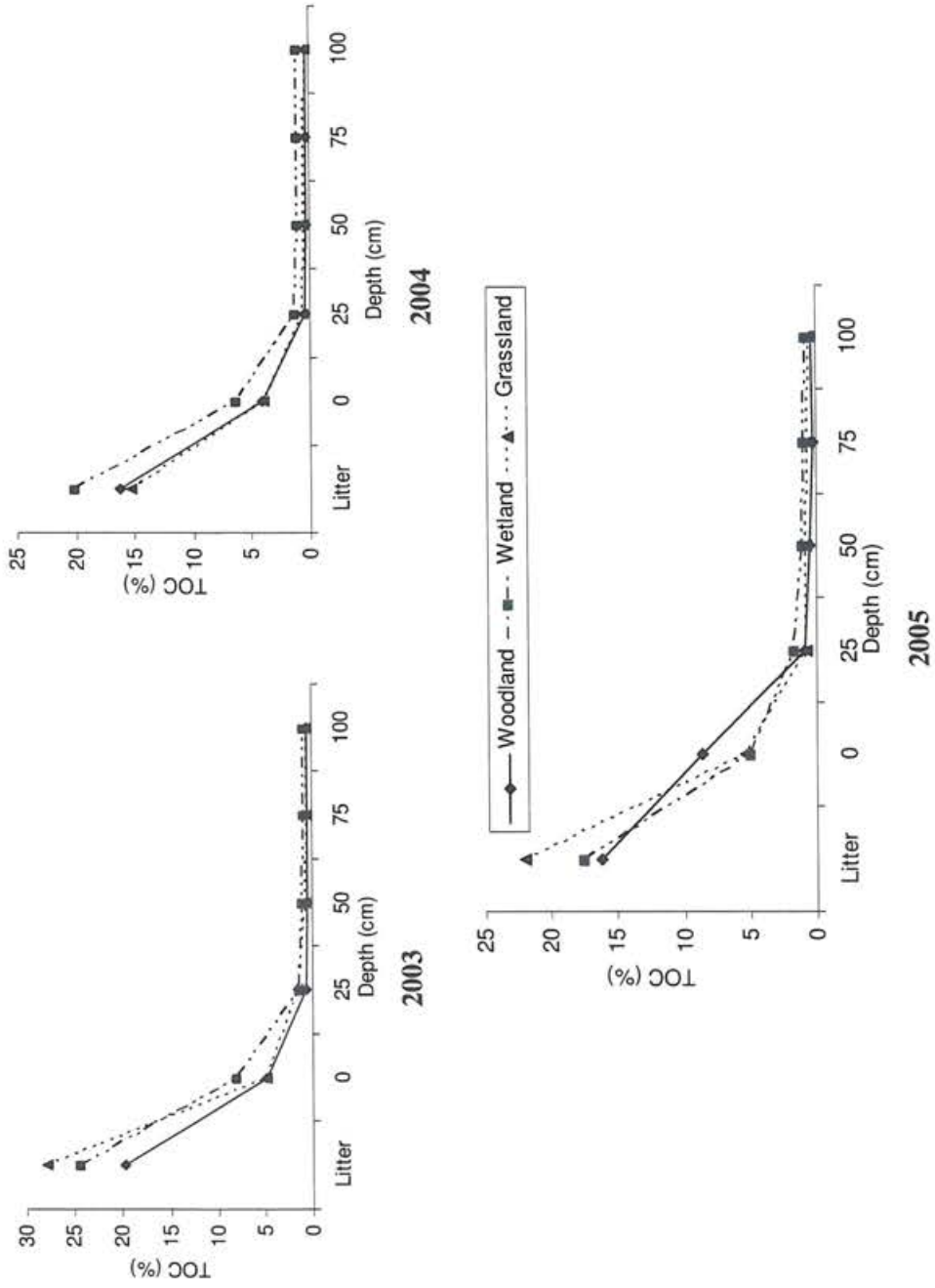


Figure 3.3.4. Year wise variation in TOC in KNP soil

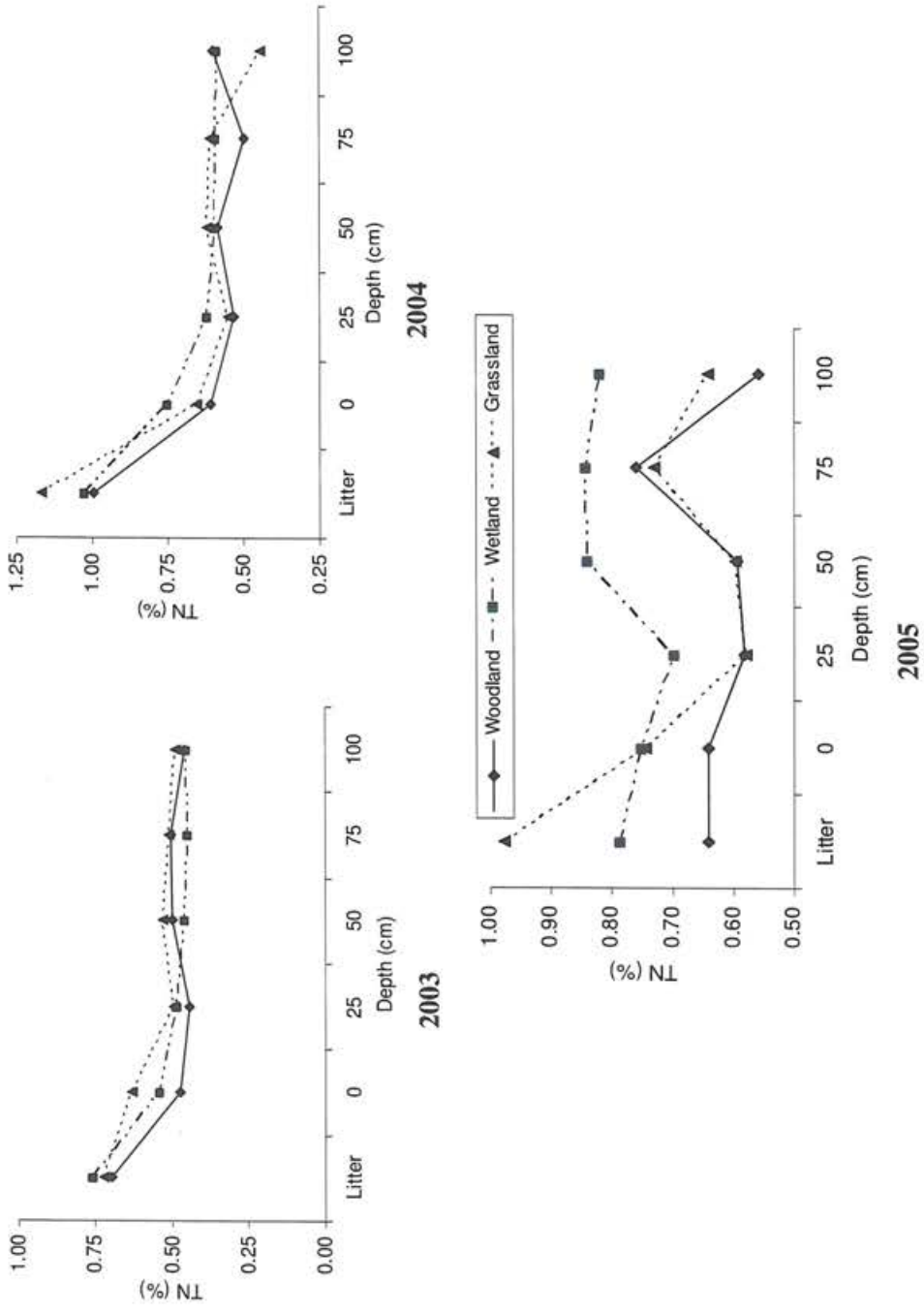


Figure 3.3.5. Year wise variation in TN in KNP soil

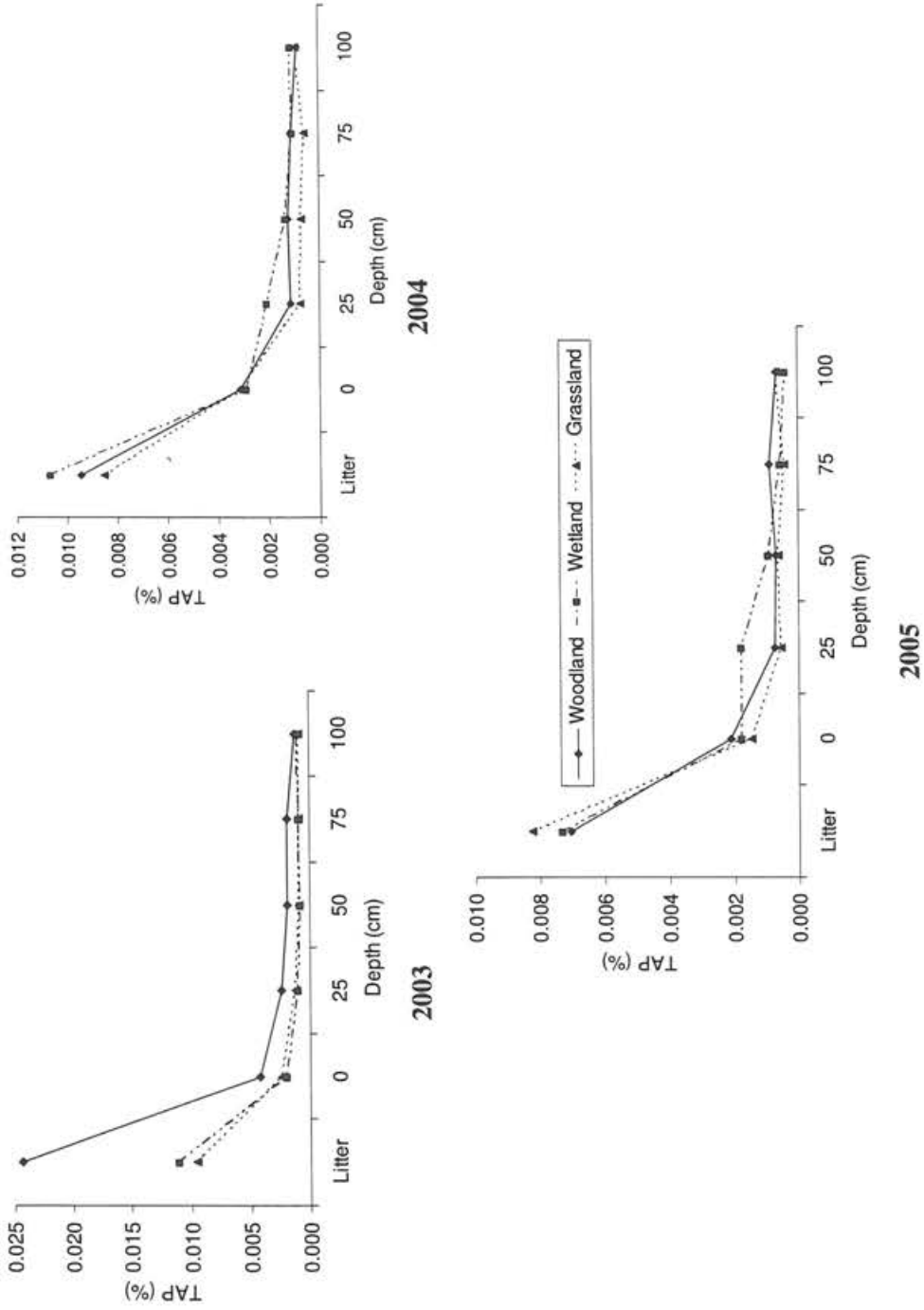


Figure 3.3.6. Year wise variation in TAP in KNP soil

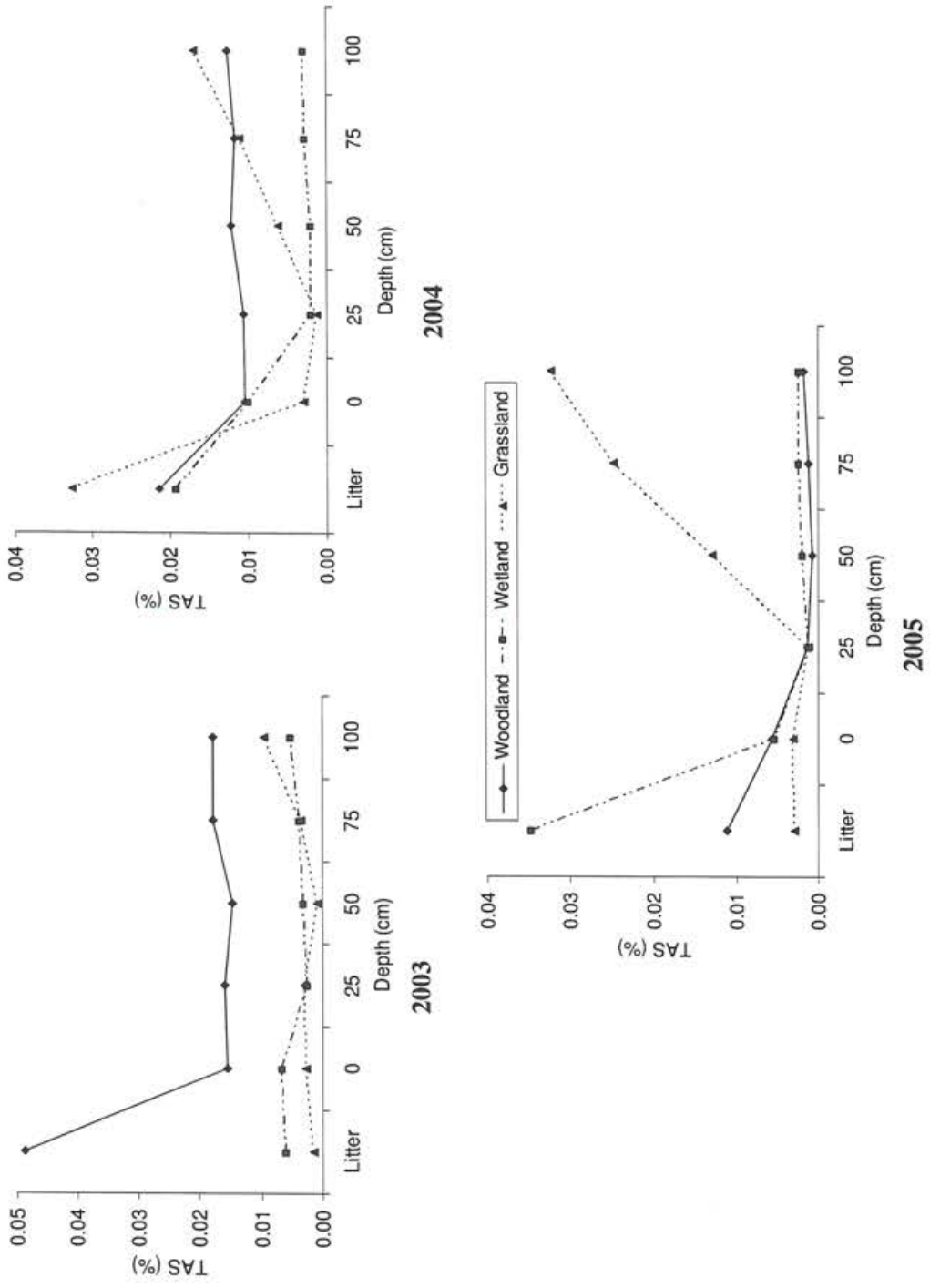


Figure 3.3.7. Year wise variation in TAS in KNP soil

3.3.2. Elemental Ratios in Soil

GLM-ANOVA (Table 3.3.3.) shows that of the four elemental ratios, C: P, C: S and N: P varied significantly among the years, habitats and soil layers. However, C: N ratio differed significantly only among the years and soil layers ($P < 0.05$). In the case of C: N ratio, none of the years did differ significantly from each other (LSD, Table 3.3.4., $P < 0.05$). However, among the soil layers, litter layer and the surface layer (0 cm) did vary from each other and from the rest of the layers in the profile (LSD, Table 3.3.4., $P < 0.05$). As far as the variation of C: P ratio is concerned, litter and surface layer of the profile differed significantly from the rest of the layers in the profile. In the case of C: S ratio, significant variation was seen within the habitats and soil layers. Among the habitats, grassland was found to be distinct differing from other habitats. Among the soil layers, litter layers were distinct (LSD, Table 3.3.4, $P < 0.05$). In the case of N: P ratio, the year 2005 varied from rest of the years; whereas among the habitats, woodland differed from others. Among the soil layers, the two upper layers (i.e. litter and 0 cm) differed significantly from the rest of the layers.

The details about the elemental ratios are given in Table 3.3.5. C: N was found to be in the range of 0.43 to 38.46. The lowest ratio was recorded in woodland (at 75 cm depth) and highest in grassland (in the litter layer). The lowest and highest values of C: P were recorded in the woodland at 50 cm depth (233.0) in 2004 and the surface soil layer (4090.3) in 2005. The lowest and highest C: S ratios (14.3 and 7396.7) were recorded in grassland in 2005, the former at the depth of 100 cm and the latter in the litter layer. The N: P ratio was the lowest (28.5) in the litter layer of woodland in 2003, and the highest (2073.6) in the bottom layer (100 cm) of the trench in wetland in 2005. Irrespective of habitats, the elemental ratios, C: N, C: P and C: S, were found to follow a trend of decline alike the TOC and TN. In contrast N: P ratio increased along the soil profile downward.

A test of correlation (Two-Tail test, Table 3.3.6) performed on the values of the nutrient elements and their respective ratios shows that TOC was positively correlated ($P < 0.05$) with all the nutrients and their ratios except N: P. pH was positively correlated with N: P, while EC and TDS were positively correlated ($P < 0.05$) with

TAP and TAS. The N: P ratio was negatively correlated with all the parameters studied, except pH and TN. TDS was positively correlated with TAP and TAS. TOC, TN and TAP were positively correlated with each other. Among the nutrient ratios, C: N ratio was found to be positively correlated with other elemental ratios such as C: P and C: S.

Table 3.3.3. Univariate analysis of variance of elements and their ratios

Parameters	Source of variation (P value)*		
	Years	Habitats	Soil Layers
pH	0.001	0.000	0.000
EC	0.000	0.000	0.000
TDS (Water extract)	0.000	0.000	0.000
TOC	NS	NS	0.000
TN	0.000	0.015	0.000
TAP	0.010	NS	0.000
TAS	NS	0.000	0.000
C: N	0.002	NS	0.000
C: P	0.033	0.039	0.000
C: S	0.027	0.000	0.000
N: P	0.000	0.000	0.000

*Post-Hoc test (LSD-Least Significant Difference) was performed only in the cases with P < 0.05; NS: Not Significant

Table 3.3.4. LSD (Post-Hoc) tests for the variables studied in the soils of KNP (Source of variation: Year, Habitat and Soil layers)

	Year	1	2	3			
	Description	2003	2004	2005			
	Mean	7.673	7.838	7.578			
	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	7.047	8.042	7.999			
	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	7.047	8.042	7.999	7.047	8.042	7.999
EC	Year	1	2	3			
	Description	2003	2004	2005			

	Mean	528.4	184.8	242.6			
	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	435.8	162.2	357.8			
	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	453.03	225.5	208.2	259.6	341.5	423.7
	Year	1	2	3			
	Description	2003	2004	2005			
	Mean	307.03	95.3	135.7			
TDS	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	263.6	81.5	193.01			
	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	246.1	125.03	129.7	150.9	190.4	233.9
TOC	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	19.9	5.6	1.01	0.7	0.6	0.5
	Year	1	2	3			
	Description	2003	2004	2005			
	Mean	0.5	0.6	0.7			
TN	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	0.591	0.667	0.648			
	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	0.862	0.642	0.551	0.591	0.608	0.560
	Year	1	2	3			
	Description	2003	2004	2005			
	Mean	0.004	0.003	0.002			
TAP	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	0.011	0.002	0.001	0.001	0.001	0.001
	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	0.013	0.006	0.001			
TAS	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm

	Mean	0.02	0.007	0.004	0.006	0.009	0.011
C: N ratio	Year	1	2	3			
	Description	2003	2004	2005			
	Mean	8.918	4.896	6.337			
	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	25.544	9.219	2.014	1.261	1.113	1.149
C: P ratio	Year	1	2	3			
	Description	2003	2004	2005			
	Mean	1577.8	1399.5	1905.6			
	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	1358.6	1852.9	1671.4			
C: S ratio	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	2299.1	2579.3	1041.9	1135.01	1283.2	1427.4
	Year	1	2	3			
	Description	2003	2004	2005			
	Mean	3653.9	930.8	2105.6			
C: S ratio	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	813.8	1222.1	4654.5			
	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	9800.7	1194.7	1328.3	599.9	264.6	192.4
N: P ratio	Year	1	2	3			
	Description	2003	2004	2005			
	Mean	390.2	548.7	875.8			
	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	456.7	680.7	677.2			
N: P ratio	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	109.3	316.5	607.5	758.5	921.4	916.2

The values with different colour shades in a same row differ significantly ($P < 0.05$)

Table 3.3.5. Habitat and year wise variation in C: N, C: P, C: S and N: P ratios

Habitat	Layer	C: N			C: P			C: S			N: P		
		2003	2004	2005	2003	2004	2005	2003	2004	2005	2003	2004	2005
Woodland	Litter	28.38	16.46	25.39	809.99	1731.06	2315.63	403.62	765.99	1462.36	28.54	105.18	91.20
	0	10.16	6.69	13.48	1139.26	1302.12	4090.33	307.09	389.68	1491.93	112.18	194.57	303.44
	25	1.40	0.87	1.53	255.09	420.14	1225.21	38.77	43.76	704.22	182.63	481.32	799.08
	50	1.08	0.48	0.87	286.52	232.94	733.49	36.55	23.24	713.48	266.16	482.10	841.75
	75	1.00	0.68	0.43	267.29	308.34	375.61	28.06	28.96	289.27	268.11	454.71	874.70
	100	1.21	0.50	0.72	479.20	358.25	604.82	30.96	23.81	224.68	395.95	719.89	841.99
Wetland	Litter	32.19	19.65	22.35	2214.09	1874.23	2404.12	4012.44	1045.70	506.56	68.79	95.39	107.56
	0	14.69	8.47	6.59	3978.20	2211.44	2809.48	1198.66	633.07	911.40	270.87	261.22	426.49
	25	2.59	2.06	2.52	1220.43	615.67	1003.27	515.45	636.71	1417.22	471.49	299.57	398.49
	50	2.01	1.71	1.30	1148.13	784.35	1190.52	303.14	520.66	576.57	571.29	458.41	913.96
	75	1.96	1.67	1.15	1018.65	982.64	1848.85	234.20	360.32	420.19	518.87	586.89	1602.35
	100	1.73	1.76	0.89	794.97	966.28	1852.74	151.76	354.12	318.74	459.28	550.34	2073.58
Grassland	Litter	38.46	13.09	22.58	2911.64	1796.34	2679.57	18719.59	468.25	7396.69	75.70	137.26	118.69
	0	7.68	6.08	7.16	2024.65	1267.28	3652.67	1759.49	1328.00	1715.80	263.54	208.48	509.81
	25	3.01	1.05	1.44	1232.19	783.45	1506.97	516.96	472.00	668.80	409.07	745.17	1048.35
	50	1.14	0.78	1.31	726.96	694.30	1256.30	735.46	78.22	60.65	638.52	889.94	959.31
	75	1.07	0.72	0.88	628.09	797.55	1567.24	151.64	39.77	25.92	588.98	1106.52	1783.02
	100	0.90	0.77	0.72	508.90	381.24	717.78	46.61	20.13	14.31	564.63	498.31	996.65

Table 3.3.6. Correlation matrix of select parameters in the soil system of KNP

	pH	EC	TDS	TOC	TN	TAP	TAS	C: N	C: P	C: S	N: P
pH	1.000										
EC	NS	1.000									
TDS	NS	.984	1.000								
TOC	-.491	NS	NS	1.000							
TN	-.332	NS	NS	.436	1.000						
TAP	-.396	.297	.295	.767	.290	1.000					
TAS	-.161	.601	.547	.310	.174	.412	1.000				
C: N	-.461	.194	.164	.958	.256	.807	.288	1.000			
C: P	-.196	NS	NS	.372	.244	NS	NS	.374	1.000		
C: S	NS	NS	NS	.484	.191	.239	NS	.441	.175	1.000	
N: P	.442	-.159	-.170	-.458	NS	-.434	-.187	-.453	NS	-.189	1.000

162 Sample size, $\pm .154$ critical value .05 (two-tail), NS: Not Significant

Table 3.3.7. PCA of soil variables from all the three habitats - Factor loadings

Parameters	Principal Components			
	I N: P/Soil P/C/pH	II EC/TDS/TAS	III C: S	IV Soil Nitrogen
PH	-0.734	0.101	0.0926	-0.27
EC	0.04	0.97	0.0549	-0.079
TDS	0.0368	0.952	0.0565	-0.121
TOC	0.739	0.137	0.494	0.342
TN	0.251	-0.111	-0.009	0.822
TAP	0.749	0.317	0.221	0.173
TAS	0.308	0.718	-0.249	0.268
C: N	0.727	0.186	0.525	0.224
C: P	-0.044	0.127	0.503	0.568
C: S	0.211	-0.129	0.814	-0.021
N: P	-0.777	-0.088	-0.069	0.361
Total loading*	2.986	2.582	1.565	1.493
% Variance explained	27.146	23.471	14.229	13.570
Extraction method: Principal Component Analysis, varimax rotation with Kaiser normalization (Rotation converged in 7 iterations). * Sums of squared loadings				

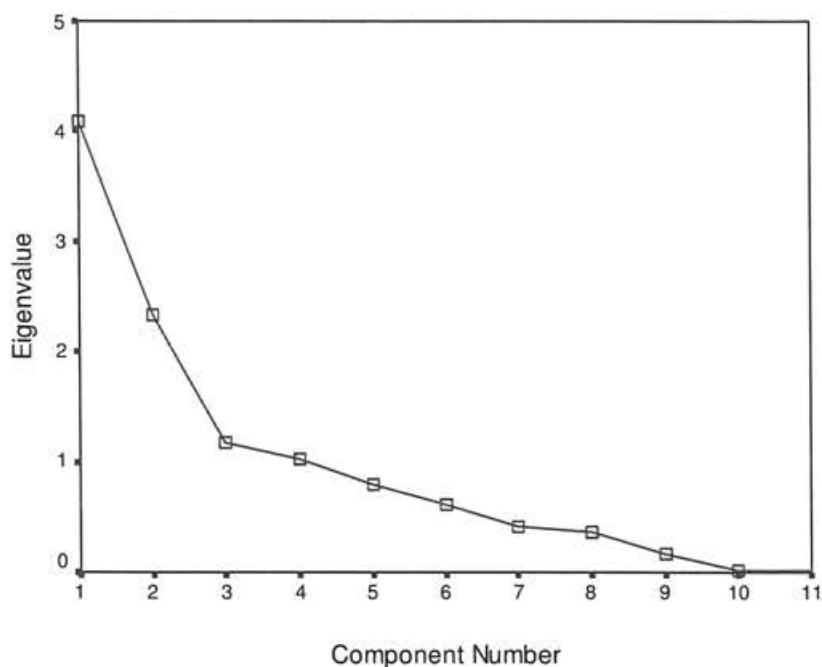


Figure 3.3.8. Scree plot of Principal Component Analysis

PCA was performed with the quantitative variables of the soil studied, in order to synthesize the variation patterns in those elements that are potentially associated with the biogeochemical processes in the soil. Table 3.3.7 shows that the PCA resulted in four components that explained or accounted for 78.416% of the total variance, selected based on a visual inspection of scree plots (Figure 3.3.8). Table 3.3.7 provides the original variables studied, the four factors generated by the PCA, as well as the respective factor loadings based on which the components are to be interpreted.

The first component accounted for 27.1% of the total variance in soil characteristics among samples reflecting the influence of soil variables such as P, TOC and pH. The second component accounting for 23.5% of the total variance reflected the influence of the total dissolved solids (TDS and TAS). The influence of carbon to elemental ratio (C: S) was reflected by the third component that accounted for 14.2 % of the total variance. The fourth component accounted for 13.6% of the variance indicating the influence of soil nitrogen level (TN). Thus, the four PCA components can be characterized as 'N: P/soil P/C', 'TDS/TAS', 'C: S ratio', and 'soil TN' respectively.

3.4. DISCUSSION

In the present study, the soil properties were found varying drastically based on habitat and the principal vegetation type. Soil colour varied along the depth profile. Surface layers were dark coloured and in the subsurface and further lower layers the chroma were found increasing. Horkar and Totey (2002) have reported low chroma of the surface layer of soils of Navegaon National Park, Maharashtra. Soil colour is a function of clay mineralogy (Miller and Donahue 1997), texture (Foth 1984), organic matter content (Agbu and Olson 1990, and Winegardner 1995) and ultimately the drainage conditions (He et al. 2003) of an area. The colour patterns that include low chroma or grey colours are commonly used to predict the seasonal saturation of soils (He et al. 2003) and are distinctive of hydric soils (Clausnitzer et al. 2003). In the case of KNP soils, the surface layers in the wetland are dark coloured (low chroma), and could be attributed to the prolonged water logging and high accumulation of organic matter. The relatively high chroma in the terrestrial soils could be an indicator of good drainage condition with less accumulation of organic matter. This could also be because of the abundant salts and the saline nature of the soil (Miller and Donahue 1997).

The soil was fine textured in the upper layers and coarse in the lower layers, for the increasing proportion of sand and silt. Sahu et al. (2001) also reported drastic change in the particle composition of soil downward along the profile. The clayey nature of the surface layer could be associated with alluviation, the principal process that brings in sediments into the wetland system (Azeez et al. 2000). Horkar and Totey (2002) also reports the silt loam textured soil in terrestrial habitats under various vegetation stands, in Navegaon National Park, Maharashtra, India. Plant roots are known to change the soil properties including relative composition of the soil particles (Jama et al. 1998). GEER and GUIDE (2001) also reports textural heterogeneity among the terrestrial and aquatic areas in Narayan Sarovar Wildlife Sanctuary in Gujarat, India. Fine textured soil was reported in the aquatic area and coarse textured in other parts of this sanctuary.

Table 3.4.1. General concentration range of nutrients* in comparison with the concentrations recorded in the present study in the multiple habitat system

Parameters	Present observation	Concentration range	Authors	Locations
pH	5.2 – 9.97	6.7 – 8.1	Ajwa et al. (1998)	Tallgrass Prairie soil profile
EC ($\mu\text{S}/\text{cm}$)	2.7 – 1336.0	42 – 189		Navegaon National Park, Maharashtra, India
TDS (mg/kg, water extract)	90.0 – 8073.3	NA	NA	NA
TOC (%)	0.28 – 8.66	0.412 – 1.658	Horkar and Totey (2002)	Navegaon National Park, Maharashtra, India
TN (%)	0.44 – 0.75	0.11 – 0.48	Saha (2003)	Singalila range, Darjeeling
TAP (%)	0.0004 – 0.0042	0.00045 – 0.0008	Olufemi and Ikulamberu (2004)	Okeluse forest reserve, Ondo State Nigeria
TAS (%)	0.0007 – 0.032	1070 – 2650	Wesemael (1993)	Mediterranean forests in Southern Tuscany
C: N	0.9 – 14.7	1.76 – 9.96	Ajwa et al. (1998)	Tallgrass Prairie soil profile
C: P	255.1 – 3978.2	NA	NA	NA
C: S	28.1 – 1759.5	NA	NA	NA
N: P	112.2 – 638.5	NA	NA	NA
The values of the present observation exclude the concentration observed in the litter layer as it was predominantly plant materials and all the nutrients was found highest in the litter layer. NA: Not Available				

The trend of increasing pH along the depth profile is probably because of the closeness of the layers towards the parent material. Sahu et al. (2001) also reported similar results, a characteristic feature of Vertisols according to Subbaiah and Manickam (1992). The pH of KNP soil (5.2 to 9.97) was higher than that of Tallgrass prairie soil profile as reported by Ajwa et al. (1998). The pH range reported by Ajwa et al (1998) was from 6.7 to 8.1. EC and TDS were found to show a similar trend because of their obvious inter-relation. The trend in these cases was that of a gradual decline in all habitats except grassland. In grassland, EC and TDS were found to show a gradual trend of increase sustaining throughout the profile. The insignificant variation among the soil layers with respect to these above cited parameters is probably due to the homogeneity of the layers. The monsoonal flood in large areas of woodland and grassland, and the extended water logging in the wetland blocks may be the reason for the homogeneity. Brunet and Astin (1997) opine that woodland areas prone to flooding also provide a mechanism for the retention of sediment, associated nutrients, and hence act like aquatic systems to some extent. The EC in KNP soil exceeded the level reported from other protected areas in the country. Horkar and Totey (2002) reported EC ranging from 42 to 189 $\mu\text{S}/\text{cm}$ in Navegaon National Park, India (Table 3.4.1).

It is known that each tree species generates a particular soil environment under its canopy, and then under a diverse tree community, soil chemical properties will be spatially very heterogeneous. This is true for the top soil in particular, because in terms of nutrients availability and cycling, the surface soil seems to be where most plant-soil biochemical interaction occurs in forests. In the present case, also most of the nutrients in litter and top soil layer differed significantly from the rest of the layers in the soil profile. Single trees can create a zone of influence around itself by two main pathways (Yankelevich et al. 2006). First, litter from different tree species varies in quantities, nutrient quality and litter fall timing, which are determinant factors for the nutrient release to the soil. Second, trees regulate the proliferation and life span of fine roots according to nutrient availability in different areas, consuming and competing with each other plants for nutrients in a spatially heterogeneous manner.

The root litter seems to have added effect on the soil composition than leaf litter (Chen and Twilley 1999). Plant roots are known to be important in nutrient cycling,

improvement of soil texture and maintenance of soil organic matter (Jama et al. 1998, and Salas et al. 2003). Higher observed TOC content in the litter layer and soil surface layer in the grassland than in other habitats might be due to soil organic matter replenishment through aboveground litter and below ground root detritus (Srivastava and Singh 2002). Spatial variations in decomposition rates constrained by the soil texture and other micro environmental factors might be influencing the observed variation in the soil TOC and biological carbon cycling (Yoo et al. 2006). The higher values of TN and TAP along with soil organic matter (SOM) in the upper horizon and its subsequent decline indicated that N and P are largely associated with the SOM, which disappeared relatively fast through rapid decomposition (Aluko 1993) mediated by microbes (Arunachalam and Arunachalam 2005, and Hossain and Othman 2005) and abiotic processes (Vairavamurthy and Wang 2002). The higher concentration of TN in the upper layer may be due to the presence of immobilized nitrogen in the detritus on the soil surface (Barbosa and Fearnside 1996, and Kao et al. 2003), which is prone to microbial decomposition in soil in the subsequent layers (Gupta and Malik 1996, and Maharudrappa et al. 2000). Neeraj et al. (2004) also have observed high concentration of nitrogen in successional grassland systems at Kurukshetra, India, that was predominantly occupied by the grass species such as *Vetiveria* sp. and *Desmostachya* sp. Salas et al. (2003) also documents contribution of plant residues to the P concentration in soil. The decline in the TN along the depth profile in KNP may be due to the mineralization process, stimulating nitrogen mobilization in the plant available form (Aggangan et al. 1999, and Savin et al. 2001). It may be as well related with the agricultural runoff that carries phosphate fertilizers from the catchment of the Park, as reported by Doren et al. (1996) in which they found agricultural drainage water as mostly responsible for the phosphorus concentration. The relatively higher occurrence of organic acids in surface layer may also enhance release of P by competing for exchange sites (Maharudrappa et al. 2000). In the present case, TOC content in KNP soil was higher than the range reported by Horkar and Totey (2002). Similar to TOC, TN and TAP level in KNP soil also exceed the values reported from other environments (Table 3.4.1).

The TAS level in KNP soil was lower than the range reported by Wesemael (1993) from Mediterranean forests in Southern Tuscany (Table 3.4.1). The rapid decline of TAS in grassland, from the surface until 25 cm depth, seen in 2004 could be because

of the enhanced plant uptake resulting from the higher water availability in the previous year because of better monsoon. The roots of the dominant grass species *Vetiveria zizanioides* is known to reach that depth. The rise in the sulphur concentration with further depth is probably because of the sulphur derived from weathering of the parent material. The reported significant variation of most of the nutrients among the soil layers (Table 3.3.3) and in certain cases among habitats indicates that deposition of detritus and its subsequent decomposition driven by the regular rainfall and water input plays a crucial role in the nutrient dynamics in the Park. The Park received sumptuous quantity of water during 2003 monsoon after a year of drought (Table 2.1.1) and this might have brought in considerable amount of nutrients such as nitrogen and phosphorus and sediments.

The nutrients are likely to be distributed in the soil profile depth wise. However, it will be influenced by soil composition, vegetation, litter, and weathering and leaching processes. The lack of significant variation among the habitats could be related with the presence of certain dominant species such as *P. juliflora* in the vegetation and resultant litter type. In recent years, the species is found invading all the habitats in the Park. This species, in symbiotic association with rhizosphere bacteria, is known to be a proven nitrogen fixer (Felker and Clark 1980, and Reyes-Reyes et al. 2003).

Different nutrient ratios had high variability among the layers and habitats. Distributions of most of the ratios were found to be similar. The nutrient ratios C: N, C: P and C: S exhibited a gradual decline towards the bottom of the profile. The study conducted by Barbosa and Fearnside (1996) on carbon and nitrogen flows in an Amazonian forest reported the C: N ratio as an important indicator of litter decomposition and mineralization process with average C: N ratio above 20 indicating slow decomposition with lesser mobilization of nitrogen. A high (>20) C: N ratio was seen in the litter layer of the soil in the present investigation. The general range for this ratio is 1.8 to 9.9 as reported by Ajwa et al. (1998, Table 3.4.1) in the soil profile in a tall grass prairie. According to Barbosa and Fearnside (1999), relatively lower mobilization of nutrients from the decaying detritus layer gives rise to the higher values of C: N ratio. Srivastava and Singh (2002) had also similar finding of a declining ratio with increasing depth and this narrowing of the nutrient ratios downward in the soil profile may be because of the decomposition stage and age of

the horizons (Vejre et al. 2003). According to Brady (1996), commonly found range for this ratio is 10 – 12 that reflects a balance of high C: N from plant tissue and the lower values from microbial sources. Moreover, the lack of variation in the TOC content and C: N ratio reflects the uniformity of vegetation in the area (Brunet and Astin 1997). When mean concentrations of organic matter are considered at various sites, the C: S ratio did not show any sort of significant variation among the habitats during the whole study period, while the other ratios showed significant variation in certain years. This could be associated with the sedimentary source of sulphur; where as other nutrients more or less are brought in by the incoming water.

The statistical correlations among the nutrient elements and their respective ratios indicate TOC to be an important factor for the biogeochemical process related with nutrients in soil. It shows positive correlation with TN, TAP, TAS, C: N, C: P and C: S ($P < 0.05$) and negative correlation with N: P. The positive correlation of TDS with TAP and TAS indicates phosphate and sulphate salts as significant contributors of the soluble solids / salts in the soil (soil water extract). Moreover, the positive correlation of TOC, TN and TAP indicates the availability of recently shed plant litter, with high elemental ratios. The disintegration of the litter, in the course of time, results in fall of the ratios down the profile because of the loss of carbon (Vejre et al. 2003).

3.5. CONCLUSIONS

The present study reports the pedological characteristics downward the soil profile in a mixed habitat system (woodland, wetland and grassland) with emphasis on selected nutrient elements. Soil samples collected at depths of 0, 25, 50, 75 and 100 cm were found to differ considerably in their nutrient contents. Irrespective of the habitat type and year, most of the parameters, such as TOC, TN, TAP and TAS, were highest in the litter layer gradually declining along the depth in the soil profile. The major elemental ratios such as C: N, C: P and C: S also followed a similar trend. In contrast N: P ratio increased along the downward soil profile. The higher values of the elemental ratios in the litter layer indicate the relatively protracted mobilization of nutrients from the decaying detritus layer. While the variations of the nutrients and their respective ratios were significantly different among soil layers considering the entire period of study, among habitats it was not significant in several cases. This

could be associated with the distribution of some species of plants across the different habitats and the chief sources of these nutrient elements. The positive correlations of TAP and TAS with TDS indicate phosphate and sulphate salts to be chief contributors of the soluble solids/salts in the soil. TOC, TN and TAP were positively correlated with each other and with their respective elemental ratios. This suggest that recently shed plant litter with high elemental ratios getting disintegrated in the course of time result in low ratios down the profile because of carbon loss. Among the nutrient ratios, C: N ratio was found to be positively correlated with other elemental ratios such as C: P and C: S ratio. These may be resulting from the homogeneity of plant species distribution across the different vegetation types / the habitats.

Distribution of plant roots along the depth profile also would have significant influence on the nutrient input, mobilization and cycling in the soil. Both quality and quantity of plant residues incorporated in the soil determines the rate of decomposition, and dynamics and plant uptake of nutrient. Hence, understanding the litter and organic matter decomposition in soil along the depth profile influenced by biotic and abiotic factors would facilitate formulating long-term management practices in ecosystems within a given geographical realm.

4. TEMPORAL VARIATION OF MAJOR NUTRIENTS IN THE KNP WETLAND

4.1. INTRODUCTION

Monsoonal or rain fed wetlands receive notable amount of runoff from the surrounding areas, which bring in huge amount of allochthonous materials including sediments. The external inputs influence the wetland sediment characteristics largely. So far as the sedimentary biogeochemical process in the wetlands are concerned, human activities in the wetlands and their watersheds such as livestock grazing, agriculture, urbanization and road development are important (Kim et al. 2001). Wetland plants especially macrophytes occupying an important position in structure and function of aquatic ecosystems (Boston and Perkins 1982) play vital roles in both gaseous and sedimentary nutrient cycling. The occurrence and growth of macrophytes in wetlands is affected by various abiotic factors such as water quality (Mathew et al. 2002) and availability (Mann and Wetzel 2000), sediment properties (Kim et al. 2001), temperature conditions and water level fluctuations (Ellery et al. 2003, and Mäkelä et al. 2004). Variation in these factors may cause natural wetlands to changes such as rapid colonization by weeds such as *P. juliflora* and *P. distichum* that competes with native wetland vegetation for resources including space, a situation currently seen in the KNP (Sharma and Praveen 2002). Conservationists and naturalists are of opinion that wetland conservation depends on favourable condition created for native plant species and wildlife to thrive. The organic matter dynamics in the wetland soils that are tightly coupled to biogeochemical cycles of major nutrients such as nitrogen and phosphorous depend largely on the type of vegetation (Johnston 2003) and the subsequent process of decomposition, mineralization and plant uptake (Chen and Twilley 1999, and Bai et al. 2005) with in varying time scale. These whole processes are chiefly temperature driven and vary seasonally. Therefore, the major aim of temporal pedological studies in wetlands is soil characterization over a period of time that could be a function of growth and development of native plant species, ambient micrometeorological factors, water availability and the period of inundation and saturation.

In wetlands, the upper-most layer of the bottom sediment (ULBS) is of special interest (Ostrovsky et al. 1997), probably as it is rich in freshly deposited detritus and this in turn is subject intensively to biological and abiotic factors. Subsurface layers are important as far as the mobilization and redistribution of the elements along the depth of sediment profile is concerned. Soil Organic Matter (SOM), TN and their ratios are important in influencing the productivity of wetland soils (Mitsch and Gosselink, 2000, and Bai et al. 2005). SOM is a sensible indicator of climate and changes with respect to time and ambient climatic conditions (Bai et al. 2005). Nitrogen and Phosphorous are often the most limiting nutrients in wetlands or other aquatic systems. Several studies on nutrient content and nutrient retention in wetland soils are carried out (Chakrapani 2002, Kim et al. 2001, Mathew et al. 2002, Shanthi et al. 2003, Zak et al. 2004, Bai et al. 2005, Geng et al. 2005, and Opsahl 2005). Studies related with the temporal variation are equally scarce which is essential in view of plant germination, growth, death and decay, and its interrelation with the sedimentary nutrient cycling. A number of studies such as that of Chakrapani (2002), and Mathew et al. (2002) have been undertaken on wetland soils. The study of Chakrapani (2002) have addressed geochemical characterization of some of the major Kumaun Himalayan lake soils on a spatial scale, while the study of Mathew et al. (2002) has assessed the nutrient content in urban lake soils of Coimbatore city. Although all these studies have addressed the nutrient level in the surface sediments, depth wise as well as temporal variation was not examined that would have indicated the seasonal pattern in the sedimentary nutrient content and their mobilization along the depth profile. Studies by the authors (Azeez et al. 2007, and Prusty et al. 2007) in the KNP showed significant uptake of nutrients by certain macrophytes from the wetland system. Further to this, the present investigation was carried out to examine the issue depth wise on a temporal scale in this wetland system.

4.2. METHODS

The details of the sampling wetland sediment are discussed in the section 2.2.2. The samples from each layer (0-5, 5-10, 10-15 and 15-20 cm) collected bimonthly were pooled and homogenized. After pooling and homogenizing the sub samples from each layer the total number of samples were 144 for the whole study period. Except the

colour and texture, all other parameters were analyzed following the methods given in Table 2.2.1 and described in detail in the section 3.2.

4.3. RESULTS

4.3.1. Wetland sediment characteristics

The pH, EC ($\mu\text{s}/\text{cm}$) and TDS (mg/kg) varied widely in the sediments (Figure 4.3.1). The sediment was slightly acidic in the surface; the pH increased downwards along the core and the sediment was slightly alkaline at the bottom. However, the acidic or alkaline nature of the respective layers increased from monsoon to the summer months of the next year. EC ($\mu\text{s}/\text{cm}$) was found to be lowest (48.0 $\mu\text{s}/\text{cm}$) during September 2004 (5-10 cm layer) and highest (473.7 $\mu\text{s}/\text{cm}$) during May 2005 (0-5 cm). The minimum value for TDS was 243.3 mg/kg recorded during September 2003 (10-15 cm and 15-20 cm) and the maximum (2890.0 mg/kg) was recorded during May 2005 (0-5 cm). In the case of pH, minimum and the maximum values were recorded in the upper and lower layers. The pH, EC and TDS (Figure 4.3.1) were low in the month of September (immediately after the monsoon) and high during May (mid summer), when the temperature crosses 40 °C. These did differ significantly among months as well as among the sediment layers (GLM-ANOVA, Table 4.3.1, $P < 0.05$). Post-hoc analysis reveals that pH of soil did not vary with in the months and with in the sediment layers, upper two layers (0-5 and 5-10 cm) differed significantly from the rest two layers (10-15 and 15-20 cm, LSD, Table 4.3.2, $P < 0.05$). In the case of EC and TDS, May 2005 was seen as distinct and differed from the rest of the months; and within the sediment layers, surface layer (0-5 cm) differed from the rest of the layers.

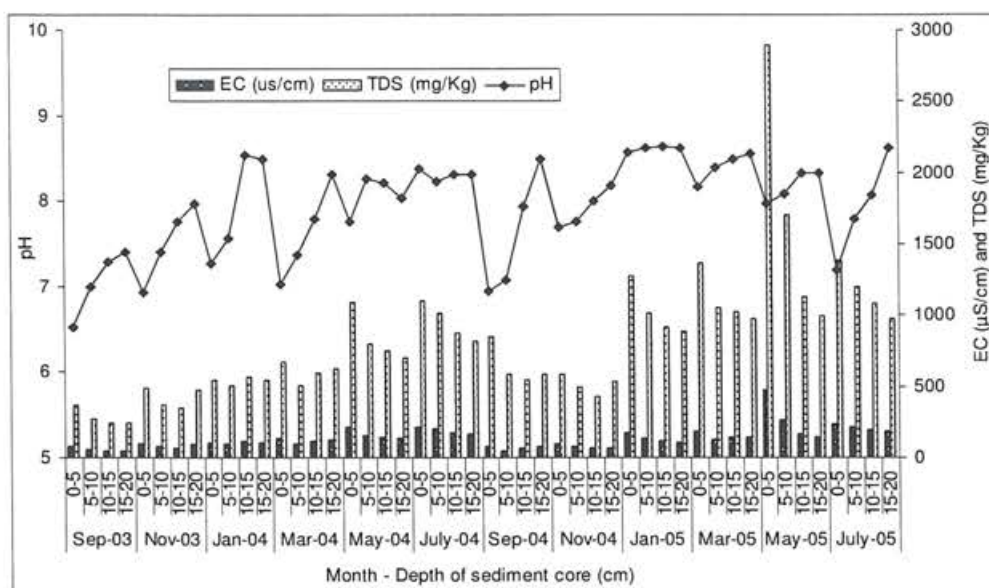


Figure 4.3.1. Seasonal variation in pH, EC and TDS in sediments

TOC was found to be lowest in July 2005 (0.61%) and highest in November 2003 (14.01%) and in the case of TN the highest and lowest values were seen in May 2004 and July 2005 respectively (0.26 to 0.68% Figure 4.3.2). In both the cases, the maximum value was recorded in the surface layer and the minimum value in the subsurface layers (Figure 4.3.2). TOC was found to have a sustained gradual depth wise pattern of decline in the sediment core throughout the study duration, irrespective of the months. Except in a few months such as January-May 2005, TN was found to show a trend of decrease along the sediment core in almost all the months. The minimum and maximum values for TAP with the corresponding months in parentheses were 0.001 (November 2003) and 0.034 (July 2005) (Figure 4.3.3). TAP showed a gradual trend of depth wise decline in most of the months. In the case of TAS, the range was from 0.0008% (September 2003) to 0.012% (July 2004, Figure 4.3.3). Although TAS showed a trend of gradual depth wise decrease throughout the study duration, March, May and July 2004 were exceptional months, wherein the trend was not sustaining throughout the depth profile. Among TOC, TN, TAP and TAS, only TOC and TAS varied significantly among months as well as among sediment layers, while TN and TAP varied only among months (GLM-ANOVA, Table 4.3.1, $P < 0.05$). As far as the variation within the months is concerned, TOC and TN did not show any variation within the months. However, within the sediment layers, the TOC level in 1st and 2nd layer did differ from each other and from the rest

of the layers (LSD, Table 4.3.2, $P < 0.05$). TAP varied significantly only among months, where as TOC varied only among sediment layers. Of these four parameters, only TAP was found to fall within the general reported concentrations elsewhere (Table 4.4.1). In the case of TAP, July-05 and in the case of TAS, July-04 were seen as distinct and differed from the rest of the months.

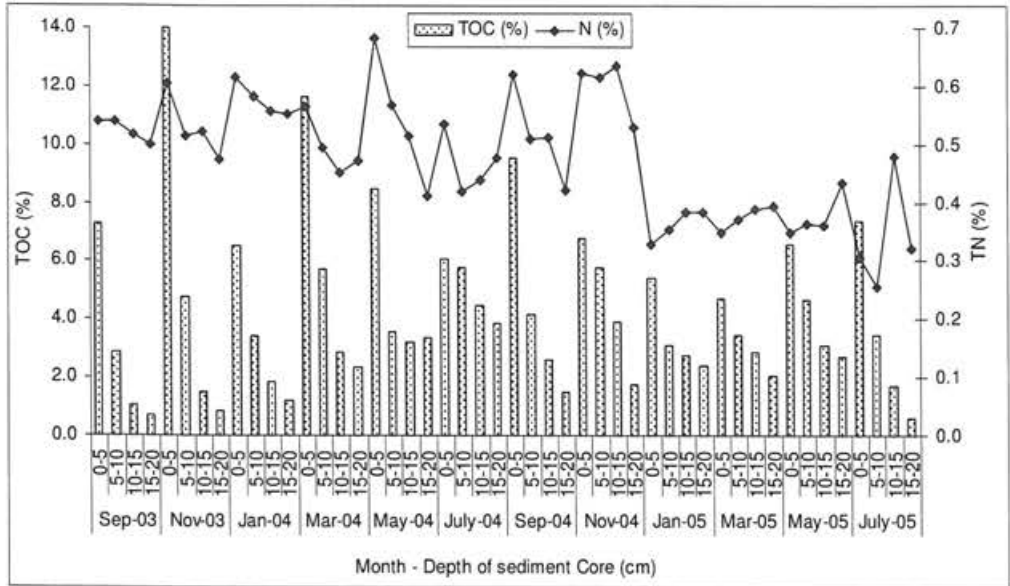


Figure 4.3.2. Seasonal Variation in the TOC and TN in sediments

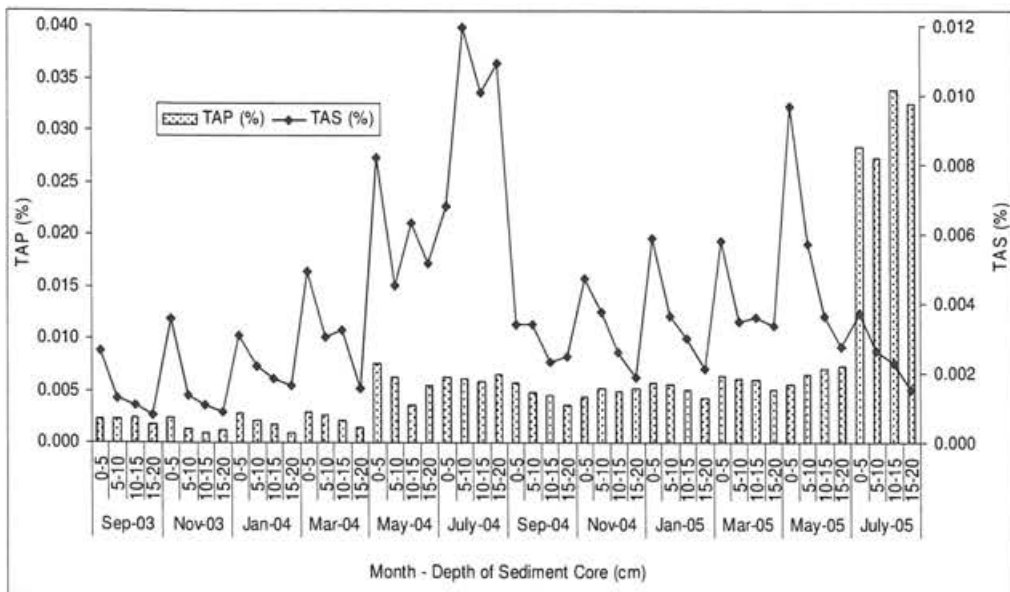


Figure 4.3.3. Seasonal Variation in the TAP and TAS

4.3.2. Nutrient ratios in the Sediment

The elemental ratios showed wide variability among the months and among the soil layers during the present study. C: N and C: P ratios were found to be in the range of 1.38 (September 2003) to 13.56 (March 2005) and 18.81 (July 2005) to 5995.83 (November 2003, Figure 4.3.4). C: S and N: P ratios were in the range of 352.2 to 3929.5 and 9.34 to 561.6 (Figure 4.3.5). Except N: P, all the elemental ratios were high in the surface layer (0-5 cm) and low in the lowest layer of the core (15-20 cm). N: P was found to be high at a depth of 5-10 cm and low in the lowest layer (15-20 cm). Of the four nutrient ratios, only C: P and C: S varied significantly among months as well as among the sediment layers. In contrast, C: N varied significantly only among the sediment layers, while N: P only among months (GLM-ANOVA, Table 4.3.1, $P < 0.05$). Detailed post-hoc analysis revealed that the C: N ratio in upper two layers did differ significantly from each other and from the rest of the layers (LSD, Table 4.3.2, $P < 0.05$). The C: P ratio during November-03 and March-04 were distinct and did differ from the rest of the months. As far as the variation with in the sediment layers are concerned, the ratio in 0-5 cm layer varied significantly from the rest of the layers. For C: S ratio, November-03 was seen as a distinct and different form the rest of the months. However, with in the layers, as like C: N ratio, C: P ratio in two upper layers varied significantly from each other and from rest of the layers. In the case of N: P ratio, the ratio in November-03 and January-04 differed from rest of the months (LSD, Table 4.3.2, $P < 0.05$)

The test of correlation (Two-tail, Table 4.3.3) performed on the values of all the above mentioned parameters show that, among these parameters, pH was significantly correlated with all the parameters except TAP, TAS and N: P ratio ($P < 0.05$). There was a significant correlation of EC and TDS with all of the parameters studied, except in certain cases. For instance, no significant correlation was seen between C: P and EC. TOC was significantly correlated with all the nutrients and their ratios except TAP and N: P. TAN was significantly correlated with others except TAS. Among the elemental ratios, C: N ratio was significantly and positively correlated with C: P and C: S ratios and negatively with N: P ratio ($P < 0.05$).

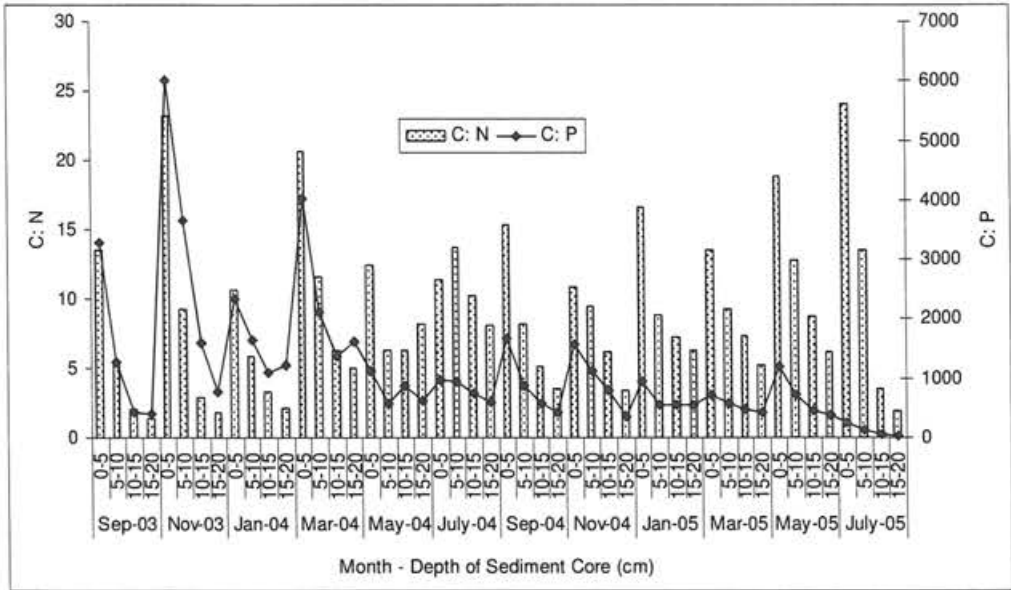


Figure 4.3.4. Seasonal Variation in C: N and C: P ratio

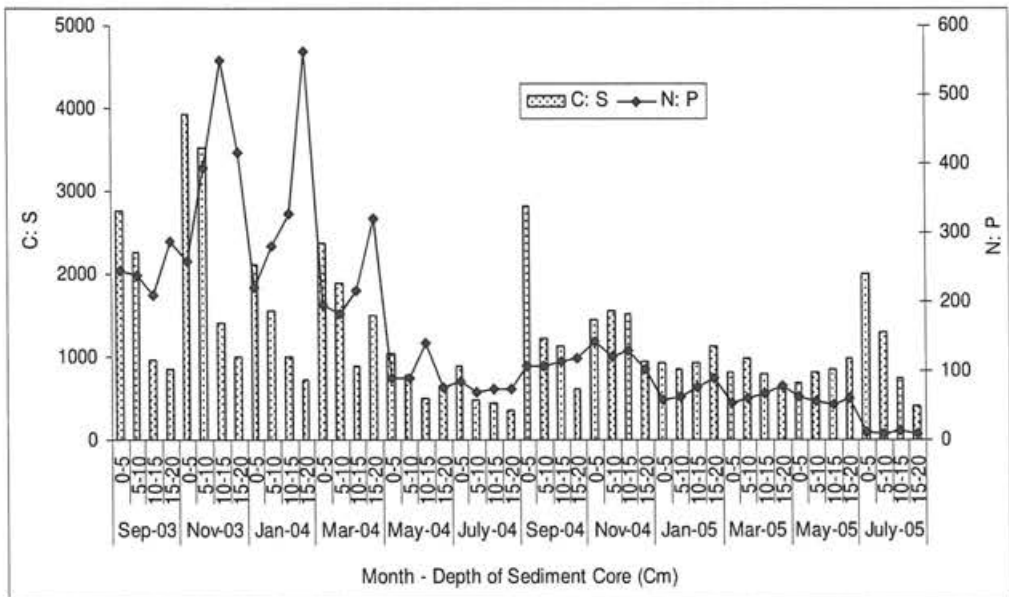


Figure 4.3.5. Variation in C: S ratio and N: P ratio

Table 4.3.1. Univariate Analysis of Variance of elements and their ratios

Parameters	Source of variation (P value)*	
	Months	Soil layers
pH	0.000	0.000
EC	0.000	0.000
TDS (water extract)	0.000	0.000
TOC	0.000	0.000
TN	0.000	NS
TAP	0.000	NS
TAS	0.000	0.013
C: N	NS	0.000
C: P	0.000	0.000
C: S	0.000	0.000
N: P	0.000	NS
*Post-Hoc test (LSD-Least Significant Difference) was performed only in the cases with $P < 0.05$; NS: Not significant		

Table 4.3.2. LSD (Post-Hoc) tests for the variables studied in the bed sediments of KNP (Source of variation: Months and Sediment layers)

pH												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	7.05	7.5	7.9	7.6	8.1	8.3	7.6	7.9	8.6	8.4	8.2	7.9
Soil layers	1	2	3	4								
Description	0-5 cm	5-10 cm	10-15 cm	15-20 cm								
Mean	7.5	7.8	8.1	8.3								
EC												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	56.8	84.0	108.7	119.5	166.3	190.7	66.6	77.2	133.5	149.9	259.9	207.1
Soil layers	1	2	3	4								
Description	0-5 cm	5-10 cm	10-15 cm	15-20 cm								
Mean	174.4	130.2	118.1	117.5								
TDS												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	28.1	41.9	54.1	59.7	83.4	95.3	64.0	50.9	102.5	110.5	167.9	116.0
Soil layers	1	2	3	4								
Description	0-5 cm	5-10 cm	10-15 cm	15-20 cm								
Mean	105.0	79.3	70.9	69.6								

TOC												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	2.9	5.3	3.2	5.6	4.6	5.03	4.4	4.5	3.4	3.3	4.3	3.3
Soil layers	1	2	3	4								
Description	0-5 cm	5-10 cm	10-15 cm	15-20 cm								
Mean	7.8	4.2	2.6	1.9								
TN												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	0.52	0.53	0.57	0.49	0.56	0.47	0.51	0.59	0.36	0.37	0.38	0.34
TAP												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	0.0022	0.0014	0.0019	0.0023	0.0062	0.0062	0.0047	0.0049	0.0052	0.0059	0.0066	0.0306
TAS												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	0.0015	0.0017	0.0022	0.0032	0.0058	0.0099	0.0029	0.0032	0.0037	0.0041	0.0055	0.0026
Soil layers	1	2	3	4								
Description	0-5 cm	5-10 cm	10-15 cm	15-20 cm								
Mean	0.0052	0.0039	0.0033	0.0029								
C: N ratio												

Soil layers	1	2	3	4								
Description	0-5 cm	5-10 cm	10-15 cm	15-20 cm								
Mean	16.2	9.7	6.1	6.03								
C: P ratio												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	1590.9	3036.6	1689.1	3167.4	778.0	849.5	1039.2	1084.8	824.7	705.0	741.0	123.2
Soil layers	1	2	3	4								
Description	0-5 cm	5-10 cm	10-15 cm	15-20 cm								
Mean	2449.5	1271.8	803.7	684.7								
C: S ratio												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	1576.2	2573.5	1359.2	1800.0	1024.4	715.9	1466.1	1615.6	1140.7	905.7	884.2	1150.7
Soil layers	1	2	3	4								
Description	0-5 cm	5-10 cm	10-15 cm	15-20 cm								
Mean	1983.1	1523.5	1014.2	883.2								
N: P ratio												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	251.6	445.03	456.7	244.0	103.0	86.1	117.8	176.9	151.0	116.7	61.5	11.2

The values with different colour shades in a same row differ significantly ($P < 0.05$)

Table 4.3.3. Correlation matrix of nutrients and their ratios

	pH	EC	TDS	TOC	TAN	TAP	TAS	C: N	C: P	C: S	N: P
pH	1.000										
EC	.254	1.000									
TDS	.304	.939	1.000								
TOC	-.411	.192	.176	1.000							
TAN	-.265	-.271	-.344	.246	1.000						
TAP	NS	.335	.317	NS	-.283	1.000					
TAS	NS	.577	.519	.299	NS	NS	1.000				
C: N	-.268	.336	.341	.750	-.294	NS	.324	1.000			
C: P	-.292	NS	-.174	.623	.213	-.277	NS	.390	1.000		
C: S	-.191	-.171	-.181	.618	.183	NS	-.216	.425	.769	1.000	
N: P	NS	-.363	-.426	NS	.340	-.504	-.350	-.298	.466	.208	1.000
144 Sample size, ± .164 critical value .05 (two-tail), NS: Not Significant											

Table 4.3.4. Factor loadings of the soil variables in the wetland system

Parameters	Principal Components		
	I TOC/C: S/C: P/C: N	II EC/TDS/TAS	III N/P/N: P
PH	-0.643	0.217	-0.156
EC	-0.0511	0.876	-0.297
TDS	-0.0780	0.842	-0.361
TOC	0.878	0.345	0.0534
TN	0.16	-0.0503	0.781
TAP	-0.0422	0.0910	-0.695
TAS	0.0222	0.850	0.0648
C: N	0.699	0.314	-0.43
C: P	0.721	-0.0556	0.328
C: S	0.813	-0.268	0.131
N: P	0.125	-0.250	0.641
Total loading*	2.905	2.610	2.062
% Variance explained	26.409	23.728	18.747

Extraction Method: Principal Component Analysis, varimax rotation with Kaiser Normalization (Rotation converged in 7 iterations). * Rotation sums of squared loadings

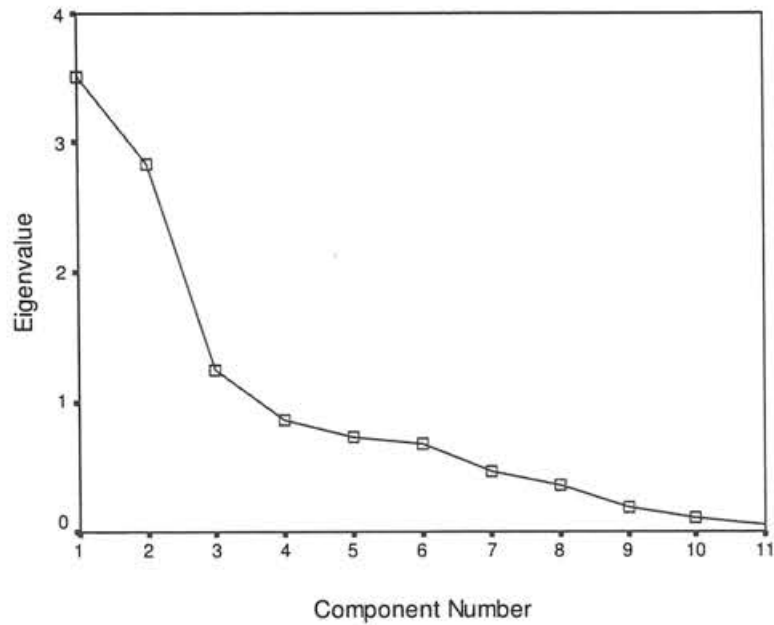


Figure 4.3.6. Scree plot of principal component analysis

PCA was done with the quantitative variables of the soil layers horizons studied, in order to synthesize the variation patterns in those elements that are potentially associated with the biogeochemical processes in the soil. Table 4.3.4 shows that the PCA resulted in three components that explained 68.9% of the total variance. These components were selected and studied based on a visual inspection of scree plots, shown in Figure 4.3.6. Table 4.3.4 provides the factor loadings of the original variables studied here and the three components generated by the PCA that permitted these components to be interpreted.

The first component that accounted for 26.4% of the variance was highly correlated with soil variables such as TOC levels, C: S, C: P, C: N. The second component that accounted for 23.7% of the variance was correlated with the total dissolved solids (EC, TDS and TAS). The third component accounting for 18.7 % of the variance was correlated only with the level of soil nitrogen, phosphorus and their ratio. Thus, the three PCA components can be characterized as 'soil organic carbon and its ratios with other elements', 'TDS/TAS' and 'the limiting nutrients such as N and P'.

4.4. DISCUSSION

The present study examines the distribution of select nutrients in the wetland sediments along the depth profile on a seasonal basis. The soil properties varied drastically based on the hydro-meteorological conditions in the Park. The factors that would influence the pattern of the nutrient distribution are water availability, quantum of water input into the Park, period of inundation and saturation, aquatic plant growth and their subsequent decomposition, and ambient temperature (Zech et al. 1997), one of the main driving forces for the detritus decomposition and mineralization of nutrients for their recirculation in the environment.

In the present study, surface layers of the sediment were slightly acidic while the lower layers slightly alkaline. The relatively acidic nature of upper layer could be associated with the production of organic acids resulting from the gradual accumulation of detritus from the overlying water column associated with the anoxic condition and slow decomposition (McBride 1994, and Batjes 1995). The presently

reported pH in KNP sediment (Table 4.4.1) was lesser than the values reported by Mathew et al. (2002) from urban wetlands of Coimbatore city, receiving runoff from an urban and semi-urban catchment area. EC and TDS showed a similar trend because of their close inter-relation. The higher values of EC and TDS at the surface might be because of the input water that carries in salts present in the agricultural runoff from the surrounding area. The significant variation ($P < 0.05$) of these basic parameters among months as well as sediment layers might be because of the seasonal pattern in the water availability in the wetland system and organic matter decomposition and mineralization.

The higher values of TOC during September-November in both the years, i.e. 2003 and 2004 could be associated with the deposition of both autochthonous materials produced in the system and allochthonous materials brought in by the incoming water from the external reservoir during July and September. The highest TOC content in the present study was about 14%. The TOC content $> 10\%$ was also been reported by Moorhead et al. (2000) from some of the Appalachian fens in North Carolina, USA. The range reported by Moorhead et al. (2000) was 0.2 to 23.9%. Bunn (1988a) has studied the importance of allochthonous detritus in the functioning of aquatic systems in detail. A major proportion of detrital input to the aquatic systems is composed of Coarse-Particulate Organic Matter (CPOM), predominantly plant parts from the surrounding vegetation, which is later reduced to Fine Particulate Organic Matter (FPOM) and Dissolved Organic Matter (DOM) by a combination of physical and biological processes. Moreover, the seasonal flooding in the terrestrial areas of the Park also contributes to the CPOM fraction in the wetland system.

Nutrient enrichment in wetlands especially lakes has often been associated with an increased likelihood of anoxic conditions (Clausnitzer et al. 2003) and accompanying lowering of reduction-oxidation potential in sediments (Qualls et al. 2001). Hence, accumulation of plant detritus on the surface layer with subsequent slow decomposition and the mechanism of soil organic matter replenishment through the detritus (Srivastava and Singh 2002) result in the gradual aggradations of organic matter. This might add on to the TOC content that decrease with the core depth. The deposited materials, which are submerged for some times, seemed to decompose faster and subsequently mineralize during the warmer months (March to June), when

the water level is very low and some parts of the wetland are completely dry. This could be the reason why the TOC and C: N ratio were high during rainy and winter months than other months of the year. The study by Miller et al. (2004) on the response of SOM, soil organic nitrogen as well as C: N ratio reports similar type of trend.

Table 4.4.1. General concentration range of nutrients Vs recorded concentration in the present study in the KNP wetland

Parameters	Present observation	Concentration range	Authors reported	Locations
pH	6.5 – 8.6	7.5 – 9.6	Mathew et al. (2002)	Urban wetlands, Coimbatore, India
EC ($\mu\text{S}/\text{cm}$)	48.0 – 473.7	34.3 – 346	Prusty et al. (2006b)	Urban wetlands (soil profile), Coimbatore, India
TDS (mg/kg water extract)	243.3 – 2890.0	240.0 – 1457.0	Prusty et al. (2006b)	Urban wetlands (soil profile), Coimbatore, India
TOC (%)	0.61 – 14.01	0.2 – 23.9	Moorhead et al. (2000)	Southern Appalachian Fens, North Carolina, USA
TN (%)	0.26 – 0.68	0.001 – 0.47	Mandal et al. (2003)	North Bihar wetlands, India [Piper (1984) & Jackson (1962) method]
TAP (%)	0.001 – 0.034	0.001 – 0.423	Mandal et al. (2003)	North Bihar wetlands, India [Jackson (1962) method]
TAS (%)	0.0008 – 0.012	0.002 – 0.016	Prusty et al. (2006b)	Urban wetlands (soil profile), Coimbatore, India
C: N	1.38 – 13.56	20 – 25	Nair et al. (2001)	Native wetland, North Florida
C: P	18.81 – 5995.83	142.1 – 872.9	Prusty et al. (2006b)	Urban wetlands (soil profile), Coimbatore, India
C: S	352.2 – 3929.5	139.2 – 878.9	Prusty et al. (2006b)	Urban wetlands (soil profile), Coimbatore, India
N: P	9.34 – 561.6	43.6 – 411.8	Prusty et al. (2006b)	Urban wetlands (soil profile), Coimbatore, India

Assuming that the input of organic materials into the wetland system is more or less constant, the seasonal variation in the sedimentary nutrient content could be due to the differential decomposition rates constrained by the water availability as Manlay et al. (2004) reported slow decomposition and the resultant immobilization of nutrients (García-Oliva et al. 2003) during the rainy season. Ostrovsky et al. (1997) also reported water availability and microbial processes as two key factors for the detritus decomposition on the upper layer of the bottom sediment. In addition, other micro environmental factors might be influencing the variations in the soil TOC and biological carbon cycling (Soto-Jiménez et al. 2003). The higher values of TOC, TAN and TAP in the surface sediments and their subsequent decline indicated that N and P could be largely associated with the SOM (Gonsiorczyk et al. 1997). The disappearance of SOM depends on the rate of decomposition. This in turn is subject to the detritus quality (Lovett et al. 2004), period of water stagnation (Zech et al. 1997, and He et al. 2003), macro invertebrates (Bunn 1988b), insects (Russell et al. 2004), microbes (Rejmánková et al. 2004, and Hossain and Othman 2005) and other abiotic properties of the study site / processes (Manlay et al. 2004). Kellman (2002) also reports the association of SOM with other major nutrients that could be taken up by plants as a function of decomposition and mineralization. The observed value of TN was higher than the range reported by Mandal et al. (2003) from North Bihar wetlands in India. However, the TAP level was lesser than that of the level reported by Mandal et al. (2003).

The prolonged water saturation was probably the reason for which N and P did not vary significantly among the sediment layers. Shallow water stagnation along with physical activities such as animal movements results in mobilization of nutrients across the sediment layers. The higher concentration of sedimentary nitrogen in the upper layer could be associated with the input from the agricultural runoff (Sheibley et al. 2003, Lucassen et al. 2004, and Webb et al. 2004). It may also be due to the accumulation of plant materials on the surface. The study of Kao et al. (2003) reports high nitrogen and phosphorous content in the plant litter in wetlands. There are also chances of absorption of atmospheric N by watersheds, by plants and microbes (Nielsen and Kahl 2007) that inhabit the area. Moreover, research suggests that initial N status of the site drives differences in N dynamics on a temporal as well spatial level (Nelson et al. 2007). However, Campbell et al. (2004) suggest that there are

multiple controls on N retention; hydrology, vegetation and land use history being important ones among them. P input by way of guano of the colonial nesting birds may also be one of the reasons of the higher concentration in surface layers. According to Doren et al (1996), the higher P concentrations might also be due to agricultural runoff. The runoff water from the surrounding area of the Park is likely to contain high P concentration, as there is high application of fertilizer in the catchment area. The nutrients from the catchments are known to accumulate in wetlands (and lakes) that are known sinks for wastewaters and runoff from adjacent areas (Mohanraj et al. 2000b, and Cooper et al. 2003). Among the nutrient elements under the study, P in particular is known to be adsorbed by soil particles and transported by erosion due to surface runoff (Sileika et al. 2005). Hence, the differential water input to this wetland system could also be one of the reasons for high variability in the sedimentary nutrient content in different months. The relatively high occurrence of organic acids in surface layer may also enhance release of P by competing for exchange sites (Maharudrappa et al. 2000). Two factors might be responsible for lowering P level in soils; one is the plant uptake of the nutrient and the other being the sorption of the nutrient element on to the mineral matrix. However, the contribution by the plant uptake seems to be a major factor in other studies also (Kellman 2002, and Schrumpp et al. 2006). This is supported by the results of the LSD among the sediment layers. Upper two layers, i.e. up to 10 cm were distinct and did differ from the rest of the layers. Many of the wetland macrophytes, the rooted ones, have their root network up to this depth only. The P level in the present case is well with in the level reported by Mandal et al. (2003).

Although a combined adsorptive/absorptive process provides a plausible explanation for the reported sedimentary nutrient content, it was not attempted to confirm in the present study. The rise in sulphur concentration with depth is probably because of its source being the weathering of the parent material. The low concentration of TAS during the time of water stagnation may be because, in anoxic conditions, most of the sulphur remains in an inorganic and reduced stage (Meier et al. 2004) the relative (bio) availability of which is low. Hence, the higher level of TAS during July 2004 could be because of the dry conditions prevailing in the wetland system resulting from late monsoon. The presently reported level of TAS is lower than the values reported elsewhere (Prusty et al. 2006b). As per Stribling (1997), sulphur shows both temporal

and spatial variations which in are affected by variation in the salinity of the incoming waters and by sulphur cycling in soil. In wetlands under anoxic conditions, sulphate serves as the primary terminal electron acceptor (Lucassen et al. 2004) in decomposition of organic matter, even in low salinity wetlands (as in the present case).

All the nutrient ratios in the present study were found to have high variability among the layers and months. Distribution pattern of most of the ratios were found to be similar. The nutrient ratios C: N, C: P and C: S exhibited a gradual decline towards the bottom of the core like the major nutrients such as TOC and TAN. C: N ratio is an indicator of an approximate state of resistance of complex mixtures of organic materials to decomposition (Wetzel 2001). The higher C: N ratio is an indication of lesser mobilization of nutrients from the decaying detritus layer. The commonly found C: N values in wetlands soils are 20-25 as reported by Nair et al. 2001 (Table 4.4.1) in his study in native wetlands in North Florida and is higher than the range seen in this study, probably because of accumulation of plant detritus in a saturated, anaerobic environment that retards decomposition (Ewing and Vepraskas 2006). The maximum-recorded value of C: N ratio during the present investigation was 13.56 only, which indicates that the deposition or the influence of autochthonous materials is more than that of their allochthonous counterparts (Wetzel 2001). The dominating autochthonous materials might be due to the high growth of wetland plants, without any comparable scale of grazing. The C: N ratio slightly higher than 10 indicates limited direct influence of SOM (Soto-Jiménez et al. 2003). Other carbon: element ratios, i.e. C: P, C: S and N: P ratios exceeded the range reported from the Coimbatore wetlands sediments (Prusty et al. 2006b, Table 4.4.1).

The positive correlation ($P < 0.05$) of TOC with TAN, TAS, C: N, C: P and C: S indicates the importance of soil organic matter in the biogeochemical process determining nutrients levels in the wetland soil. The positive correlation of TDS with TAP and TAS indicates phosphate and sulphate salts to be the potential contributors of the soluble solids / salts in the soil. The correlation of TAN and TAP with TAS was found not to be significant, could be because of the difference in their sources. Nitrogen and phosphorous enter the Park as agricultural runoff, where as sulphur has primarily a sedimentary source. The positive correlation of TOC with TAN and C: N

ratio indicates that the recently deposited detritus, with high elemental ratios, is disintegrated in the course of time, i.e. during drier periods when the situation is conducive. This results in the loss of carbon (Vejre et al. 2003) and mineralization.

The three PCA components obtained from the data set on temporal variation can be stated as representing 'soil organic carbon and its ratios with other elements', 'TDS/TAS' and 'the limiting nutrients such as N and P'. As reported in the previous chapter, the indicator variables for the assessment of spatial (vertical and horizontal) variation in the soil physico-chemical parameters are 'N: P, soil P and C', 'TDS', 'C: S ratio', and 'soil TN' respectively. The variables in this section (temporal study) appear to be different to an extent from those obtained in the case of the data set used for the spatial study perhaps for the following reasons:

- Spatial study dealt with the variation on annual basis among different habitats and samples were taken up to a depth of 100 cm from a trench made for the purpose. The site-specific geochemical factors and nutrient and / or element concentrations at the specific locations is likely to be influencing the results.
- The temporal study deals with only wetland bed sediments on bimonthly basis, wherein hydroperiod is the single most important factor determining the changes in the substrate quality. Since water is released into the system from external source, anthropurgic activities outside the Park are likely to influence the wetland more than other habitats in the Park. This also is likely to change the results from the PCA.

4.5. CONCLUSION

The present study reports the pedological characteristics of wetland sediment up to a depth of 20 cm on a temporal scale. TOC peaked in the soil during November, while other nutrients such as TN, TAP and TAS were seen high during and/or after the rain, i.e. during July and afterwards, an indication of the influence of water on their distribution. Many of the variables were found to vary significantly among the months. The nutrient content in the soil appeared to be cumulative function of plant uptake, detritus decomposition, period of inundation, evapotranspiration and ambient temperature, one of the driving forces for the detritus decomposition. However, this study on the temporal variability of nutrients in bed sediment suggest several 'easy to

measure' indicator variables for the assessment of nutrient distribution and dynamics in wetlands. These are TOC and its ratio with other nutrients such as TN and TAP; TDS and TAS; and other nutrients in the wetland system, i.e. TN and TAP.

The temporal distribution of SOM and other nutrient elements in the bed sediments (0-20 cm) of the monsoonal wetland system indicated that the input water could bring in the nutrients and sediments along with the allochthonous materials and could influence the pattern. Deposition of allochthonous materials peaked during the wet season and after the input of water to the Park during July - September. Most of the nutrients are at their maximum level during this period. Rainfall seasonality and timing of the water input affected the mineralization of nutrients and their redistribution in the sediment profile. Phosphorous, one of the limiting nutrients, seems to come to this wetland system from agricultural sources, where as S comes from runoff from the catchments. Plant uptake of nutrients seems to be a significant factor in the case of P, as it was found with in the general reported range despite its input via the agricultural runoff and guano deposit. Drier periods were characterized by the decomposition of organic materials deposited during the wet periods, as the level of TOC was low and other nutrients such as TN was high. Both the autochthonous and allochthonous materials significantly influence the nutrient distribution in the wetland.

5. SPATIAL VARIATION OF ALKALI AND ALKALINE EARTH METALS IN THE KNP HABITATS

5.1. INTRODUCTION

Slow and gradual weathering of silicate minerals is considered the principal source of alkali metals in the mineral soil (Tyler 2004). In general, the fraction of metals present in the crystal lattice of minerals is not immediately bioavailable. In soil, only metals present in water-soluble and exchangeable forms are readily bio-available and participate in the short-term nutrient cycles, while the non-exchangeable fraction is considered slowly available over a long period. The relative abundance of water soluble, exchangeable and non-exchangeable fractions of metals is governed by the dynamic equilibrium of the metals (non-exchangeable fraction = exchangeable fraction = water-soluble fraction) in soil (Mishra 2001). The equilibrium responds to any changes such as removal of the element by plants or addition into soil in the form of chemical fertilizers. Several edaphic and environmental factors and management activities affect the equilibrium that ultimately controls the bioavailability of these elements.

An understanding of the soil nutrients including alkali and alkaline earth metals are important for proper management of wetland-dominated systems, as they greatly influence the productivity (Mitsch and Gosselink 2000, and Bai et al. 2005) of the system and possible successional changes. However, studies on the alkali metal status of Indian soils are extremely scarce, except for reports such as the one by Mehta et al. (1983) on the soils from certain locations in Haryana. Their study dealt with the exchange equilibria of K versus Ca and Na. Studies on the soil characterization emphasizing nutrient distribution and mobilization in general and alkali and alkaline earth metals in particular along the depth profile in protected areas in India are wanting. The profile-wise variation in soil properties in Navegaon National Park, Maharashtra (Horkar and Totey 2002); nutrient status in soil and plants in the hill ranges of Garo, Khasi and Jantia in Meghalaya, India (Garg and Singh 2005); soil characterization in reserve forests of Kumaun in central Himalaya (Bisht and Lodhiyal 2005) are some of such studies. A search of literature failed to locate many studies on alkali (Na and K) and alkaline earth metals (Ca, Li and Mg) in different

habitat types and/or vegetation stands. Furthermore, the available studies dealt with only surface soils and provided little information about distribution of these metals in deeper layers. The impetus behind the present research was to investigate the depth wise distribution of Na, K, Li, Ca and Mg in the soil profile of three habitats (woodland, wetland and grassland) in the World Heritage site, the Keoladeo National Park, Bharatpur, India. The study examined the vertical distribution of the bioavailable and exchangeable fraction of these metals in these systems.

5.2. METHODS

The details about the sampling and preliminary processing are discussed in the section 2.2.1. The total number of soil samples collected annually from 2003 to 2005, after processing, pooling and packing in plastic bags, was 162. In these samples, a portion was analyzed for the cations namely Na, K, Li, Ca and Mg. The alkali and alkaline earth metals were estimated after element specific extraction and the protocols followed for each metal is listed in Table 2.2.1. To estimate exchangeable fractions (bioavailable portion) of the metals, soil samples were extracted with 1M neutral Ammonium Acetate solution (Jackson 1958, SubbaRao 2001, and Wang and Scott 2001). The extractions were done by shaking 5 g samples of air-dry soil with 25 ml of the extractant for 30 minutes, filtering and storing in small pre-cleaned acid-treated plastic vials until further analysis. Simultaneously blanks and internal standards were also run to verify the precision of the method and accuracy. The precision and bias was generally < 10%. For quality assurance throughout the experiments and analyses, all reagents were prepared with metal free, AnalaR grade chemicals (Qualigens Fine Chemicals Division of GlaxoSmithKline Pharmaceuticals Limited, Mumbai) in double distilled water prepared using quartz double distillation assembly. Room temperature was around 30 °C, while extractions were carried out. Polypropylene bottles and storage vials were subjected to cleaning procedures prescribed by Laxen and Harrison (1981). Na, K and Li were analyzed using a Flame Photometer (Systronics 126), and Ca and Mg were estimated using EDTA titration. Subsequently the cationic ratios such as Na: K and Mg: Ca was calculated. Cation Exchange Capacity (CEC), the ability of a soil to hold cations, was determined by summation of all the base cations after converting the mg/kg value into milliequivalents/kg (meq/kg, Darmody and Marlin 2002). The sodium or alkali hazard is determined by the

absolute and relative concentration of cations (Singh et al. 2005) and is expressed in terms of Sodium Absorption Ratio (SAR). SAR was estimated as $\text{Na} / [(\text{Ca} + \text{Mg})/2]$ where the cations were taken in meq/kg (Azeez et al. 2000). The percentage ratio of Na to the total of all the cations (pNa) was calculated as $100 * \text{Na} / (\text{Na} + \text{K} + \text{Ca} + \text{Li} + \text{Mg})$. pNa is also known as the percentage of exchangeable Na. The ratio of Ca to the total of all other cations (rCa) was calculated as $\text{Ca} / (\text{Na} + \text{K} + \text{Li} + \text{Mg})$. The above two ratios were also calculated for all other cations under study.

5.3. RESULTS

The vertical distribution of Na, K, Ca, Li and Mg is presented in Figure 5.3.1 to Figure 5.3.3 for the year 2003 to 2005 respectively. Among alkali metals, Na was found in the range of 40 to 4533 mg/kg (Table 5.3.1). The lowest value was observed at the surface layer of woodland during 2004 and highest at the bottom layer (100 cm depth) of grassland during 2005. The minimum and maximum values for K were 77 and 1802 mg/kg soil with the corresponding location being the grassland (100 cm depth) and wetland (litter layer) respectively during 2005. Na showed a trend of increase from the surface downward until 100 cm depth in all the three years. K showed a trend of decline downwards until the bottom of the profile (100 cm). During 2004 (Figure 5.3.2) and 2005 (Figure 5.3.3), the decline in K concentration was sharp from litter layer and the upper soil layers followed by a gradual decreasing trend till the bottom of the profile. GLM-ANOVA showed that the variation of Na was significant among the years, habitats and soil layers (Table 5.3.2). However, the post-hoc test (LSD) shows that, Na level during 2004 was significantly different from the other two years (Table 5.3.3, $P < 0.05$). However, as far as habitats are concerned, Na level in wetland differed significantly only from the grassland habitat. In the case of soil layers, the Na level in the lowest layer of the profile and the one immediately above (i.e. at a depth of 75 and 100 cm) was distinct from rest of the upper layers including the litter layer (Table 5.3.3, $P < 0.05$). K level in soil differed only among the habitats and soil layers (GLM-ANOVA, Table 5.3.2). Among the habitats, K level in wetland soil was distinct and differed significantly from the other two habitats (LSD, Table 5.3.3, $P < 0.05$). In the soil layers, K level in the litter layer and the upper

layer of the profile (i.e. 0 cm) was distinct and differed significantly from the rest of the layers in the soil profile.

Table 5.3.1. Concentration range for alkali metals in soils of KNP

Metals and/or ratios	Present observation
Na*	40.0 - 4533.0
K*	77.0 - 1802.0
Ca*	548.0 - 5976.0
Li*	1.74 - 15.0
Mg*	230.3 - 5653.9
CEC**	76.9 - 1222.3
C: Ca	0.32 - 204.4
Na: K	0.06 - 58.9
Ca: Mg	0.08 - 81.4
Mg: Ca	0.09 - 1.7
SAR	0.02 - 4.7
pNa	0.8 - 69.4
rCa	0.1 - 3.9
*mg/kg, **meq/kg	

Among the alkaline earth metals, Ca showed a gradual decline from the litter layer until the bottom of the profile in all the three years irrespective of the habitat type (Figure 5.3.1 to Figure 5.3.3). Mg, on the contrary, had an increasing trend in the wetland habitat and declining trend in the terrestrial areas. However, the trend was not sustaining throughout the soil profile in any of the three habitats. Ca was found in the range of 548.0 to 5976.0 mg/kg soil (Table 5.3.1). Ca level in KNP soil differed significantly among the years, habitats and soil layers (GLM-ANOVA, Table 5.3.2, $P < 0.05$). However, in the case of years, the Ca level during 2003 differed significantly from the other two years (LSD, Table 5.3.3, $P < 0.05$). In the case of habitats, Ca level in all the habitats are significantly different from each other. As far as the soil layers are concerned, Ca level in litter layers was distinctly different from the rest of the layers in the soil profile (LSD, Table 5.3.3, $P < 0.05$). The lowest and highest values of Mg were 230.26 and 5653.95 mg/kg. In woodland, the decline of Mg was rapid until 25 cm depth and afterwards the decline was gradual (Figure 5.3.1 and Figure 5.3.3). Similar to Ca, Mg level in KNP soil also differed significantly among the years, habitats and soil layers (GLM-ANOVA, Table 5.3.2, $P < 0.05$). However,

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among the years, the Mg level during 2003 differed significantly from the other two years (LSD, Table 5.3.3, $P < 0.05$). In the case of habitats, Mg level in wetland soil was significantly different from the level in other two habitats (LSD, Table 5.3.3, $P < 0.05$).

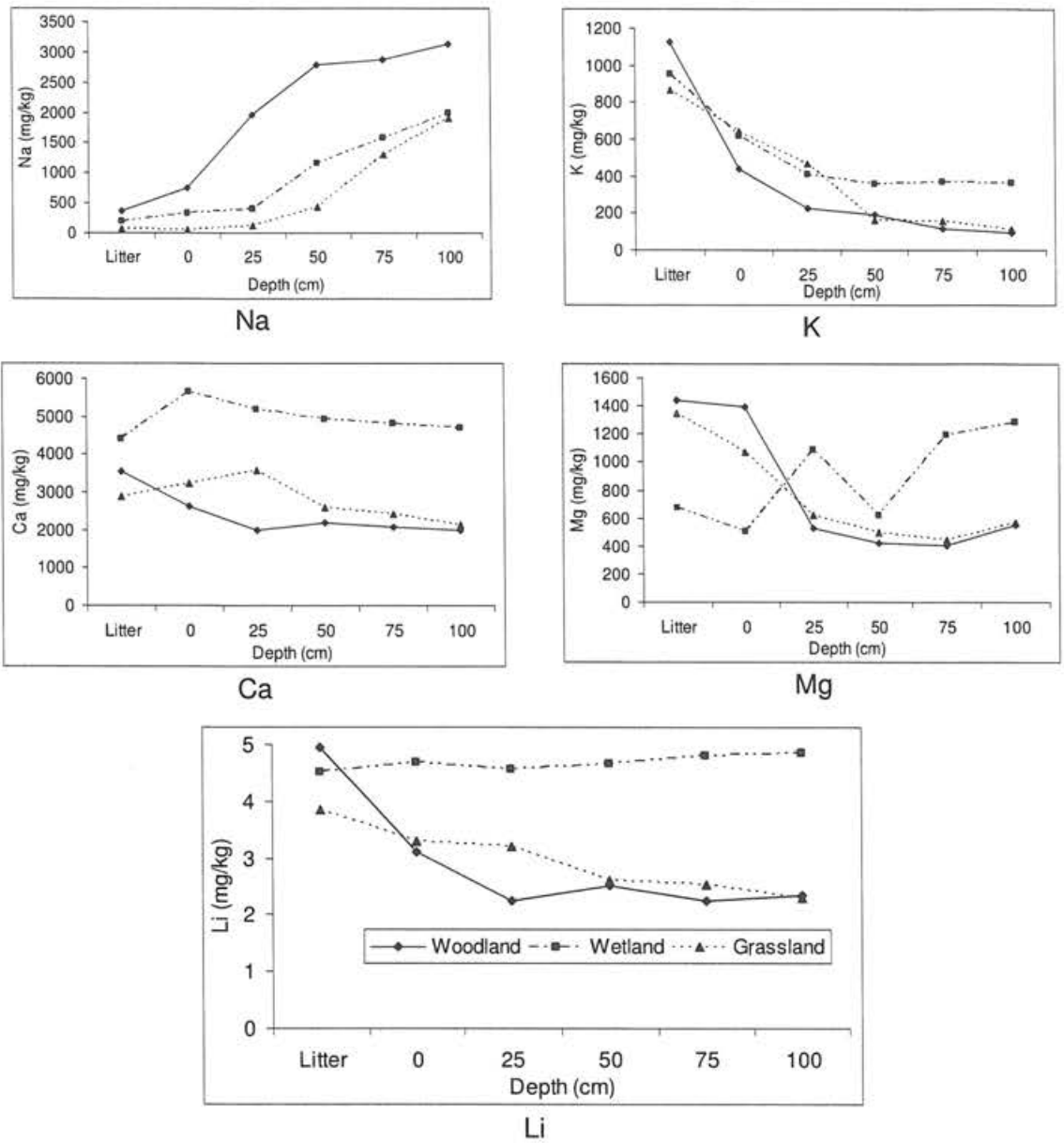


Figure 5.3.1. Depth wise variation of metals in different habitats during 2003

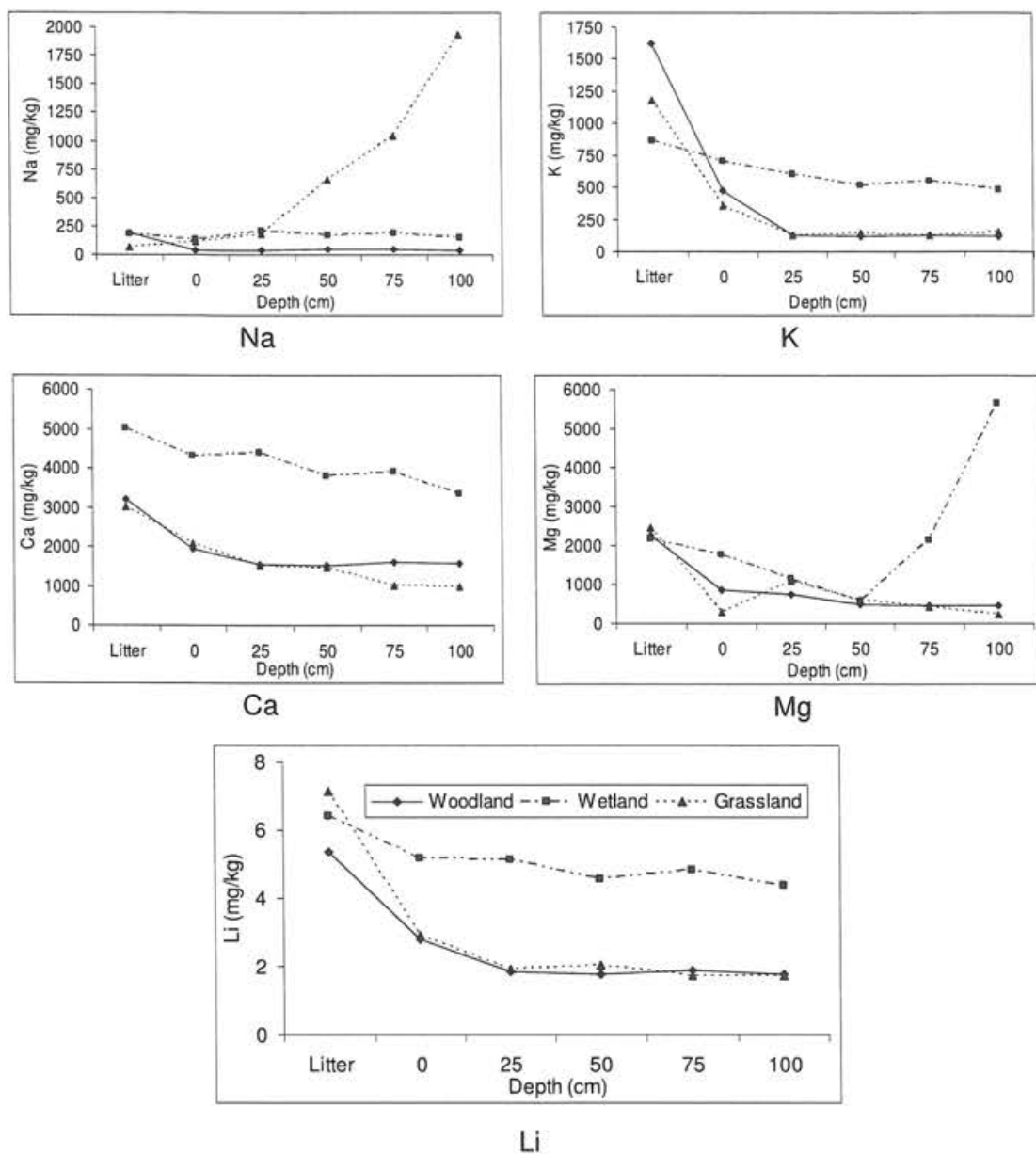


Figure 5.3.2. Depth wise variation of metals in different habitats during 2004

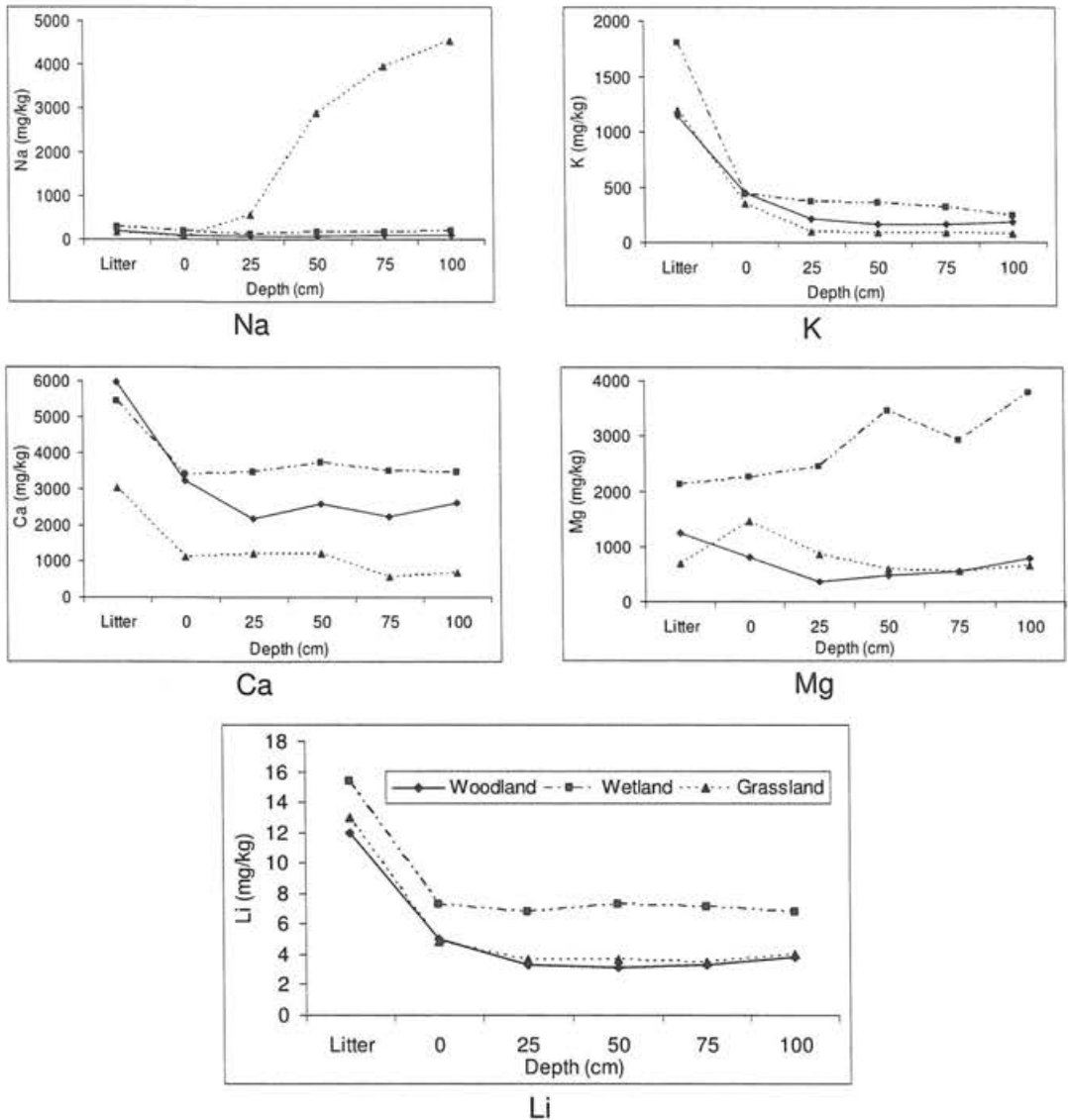


Figure 5.3.3. Depth wise variation of metals in different habitats during 2005

Li was found in the range of 1.74 to 15.00 mg/kg soil. The lowest value was recorded during 2004 in grassland at a depth of 75cm and 100 cm, while the highest value was recorded in the wetland litter layer during 2005. Li also, like K, showed a gradual trend of depth wise decrease irrespective of the habitat type during 2004. However, such decline was seen during 2005 only in terrestrial areas. In the wetland blocks, no consistency of the decline with depth was noted. The wetland surface layer during 2003 had comparatively lesser concentration of Li than the deeper layers of the profile and it had a slight increasing trend in this habitat. In the terrestrial areas, the decline was sharp from litter layer to the next layer in the soil profile and subsequently a gradual declining trend along the depth. However, during 2005 all the habitats had consistently high concentration of Li than the previous years. The variation in the Li level in KNP soil was significant among the years, habitats and soil layers (GLM-ANOVA, Table 5.3.2, $P < 0.05$). Across the years, the Li level during 2005 differed significantly from the other two years (LSD, Table 5.3.3, $P < 0.05$). In the case of habitats, Li level in wetland soil was significantly different from the level in other two habitats. As far as the soil layers are concerned, Mg level in litter layers differed significantly from the rest of the layers (LSD, Table 5.3.3, $P < 0.05$).

The CEC of KNP soil was in the range of 77.0 to 1222.3, the lowest value being in bottom layer of the woodland and the highest in the bottom layer in wetland during 2004. The carbon to element ratio, i.e. C: Ca was seen lowest (0.32) at a depth of 75 cm in woodland during 2005, and highest (204.4) in the grassland litter layer during 2005. Metal ratios such as Na: K and Mg: Ca varied widely among the habitats as well as among the soil layers. The lowest and highest values of Na: K were 0.06 and 58.89 respectively. Grassland litter layer recorded the lowest value during 2004 and the deepest layer of the profile in the same habitat recorded the highest value during 2005 (Figure 5.3.4). Ca: Mg ratio ranged between 0.08 and 81.4. The lowest value was seen in the bottom of the profile in grassland during 2005 and the highest at a depth of 50 cm in woodland during 2003. The CEC differed significantly among the years, habitats and the soil layers (GLM-ANOVA, Table 5.3.2, $P < 0.05$). The post-hoc test reveals that CEC did not differ significantly with in the years (LSD, Table 5.3.3, $P < 0.05$). However, CEC of soil in the wetland distinct and different from the other two habitats. Similar to CEC, C: Ca ratio was also significantly different among the years, habitats and the soil layers. Post-hoc test reveals that the ratio did not vary

significantly from each other or with in the years. As far as the habitats are concerned, C: Ca ratio in grassland was distinctly different from the other two habitats (LSD, Table 5.3.3, $P < 0.05$). The ratio in litter and surface layer of the profile was significantly different from the rest of the soil layers.

Among the base cationic ratios, Na: K ratio varied significantly among the years, habitats and the soil layers (GLM-ANOVA, Table 5.3.2, $P < 0.05$). In the case of Ca: Mg, no significant difference was found among the years, habitats and soil layers. However, Mg: Ca ratio differed significantly only among the years and habitats. Post-hoc test (LSD) reveals that the Na: K ratio during 2004 differed significantly from other two years (Table 5.3.3, $P < 0.05$). In the case of habitats, the ratio was found to differ significantly in wetland than the other two habitats. In contrast with the Na: K ratio, Mg: Ca ratio in year 2005 differed from the other two years. As far as the variation of this ratio within the habitats are concerned, Mg: Ca ratio in grassland habitat differed significantly from the other two habitats (LSD, Table 5.3.3, $P < 0.05$). The Mg: Ca ratio ranged between 0.09 and 1.7. The lowest value was seen in the surface layer of the wetland during 2003, while the highest value was seen at the bottom of the wetland during 2004.

SAR for the samples ranged from 0.02 to 4.7. The lowest ratio was seen in grassland litter layer during 2004 and the highest at a depth of 75 cm in the same habitat during 2005. The ratio of Na to the total of all major cations under study (Na, K, Ca, Li and Mg) was in the range of 0.8 to 69.4. The corresponding locations were the same that of the SAR. On the contrary, rCa was seen highest in the aquatic areas of KNP. SAR varied significantly among the habitats and soil layers only (GLM-ANOVA, Table 5.3.2, $P < 0.05$). As far as the variation within the habitats are concerned, SAR in grassland was distinct and differed significantly from the other two habitats (LSD, Table 5.3.3, $P < 0.05$). pNa differed significantly in all the respects, i.e. among the years, habitats and soil layers. Further examination (LSD) showed pNa in grassland, similar to SAR, differed significantly from the other two habitats. As far as the variation with in the soil layers are concerned, pNa value in the upper three layers (i.e. litter, 0 cm and 25 cm) differed significantly from the lower three layers (50, 75 and 100 cm, LSD, Table 5.3.3, $P < 0.05$). In contrast to the results seen in the case of SAR and pNa, rCa differed significantly only among habitats. As far as the variation of this

ratio within habitats is concerned, rCa in grassland (minimum among the habitats) was significantly different from the rest two habitats (LSD, Table 5.3.3, $P < 0.05$).

The Pearson's correlation of all the base cations and their ratios are given in Table 5.3.4 Na was negatively correlated with the rest of the base cations ($P < 0.05$, Table 5.3.4) reflecting their differences in distribution along the soil profile. Positive correlation of alkaline earth metals was seen with each other and with the CEC also. Na was positively correlated with the Na: K ratio, an indication of the dominating presence of Na in soil. Among the metal ratios, Na: K, SAR and pNa were positively correlated with Na, where as Ca: Mg was positively correlated with rCa (Table 5.3.4).

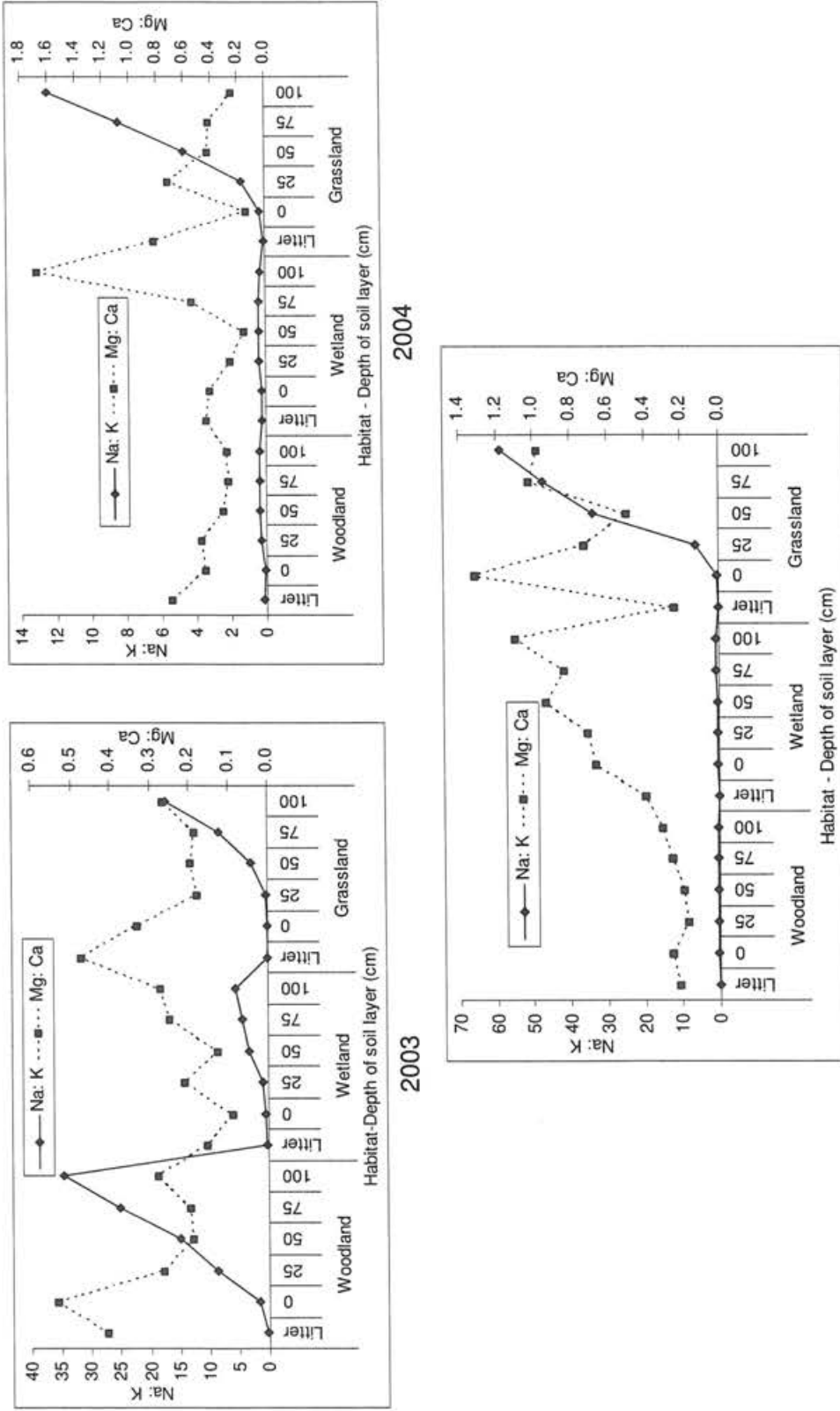


Figure 5.3.4. Depth wise variation of metal ratios during 2003 to 2005

Table 5.3.2. Univariate Analysis of Variance of metals and their ratios

Parameters	Source of variation (P value)*		
	Years	Habitats	Soil Layers
Na	0.000	0.003	0.000
K	NS	0.000	0.000
Ca	0.000	0.000	0.002
Li	0.000	0.000	0.000
Mg	0.006	0.000	0.048
CEC	0.041	0.000	*
C: Ca	0.018	0.000	0.000
Na: K	0.000	0.000	0.000
Ca: Mg	NS	NS	NS
Mg: Ca	0.000	0.004	NS
SAR	NS	0.003	0.011
pNa	0.001	0.007	0.000
rCa	NS	0.008	NS

*Post-Hoc test (LSD-Least Significant Difference) was performed only in the cases with $P < 0.05$; NS: Not Significant

Table 5.3.3. LSD (Post-Hoc) tests for the variables studied

	Year	1	2	3			
	Description	2003	2004	2005			
	Mean	1188.9	293.6	775.9			
Na	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	707.1	435.4	1116.0			
	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	175.5	197.2	407.2	932.7	1249.9	1554.6
K	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	332.3	573.5	354.0			
	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	1070.6	496.4	293.2	233.1	222.9	203.3
Ca	Year	1	2	3			

	Description	2003	2004	2005					
	Mean	3386.5	2507.4	2758.1					
	Habitat	1	2	3					
	Description	Woodland	Wetland	Grassland					
	Mean	2418.3	4307.8	1925.9					
	Soil Layers	1	2	3	4	5	6		
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm		
	Mean	3930.7	3063.9	2782.9	2670.9	2462.5	2393.1		
	Year	1	2	3					
	Description	2003	2004	2005					
	Mean	3.5	3.4	6.3					
Li	Habitat	1	2	3					
	Description	Woodland	Wetland	Grassland					
	Mean	3.4	6.1	3.7					
	Soil Layers	1	2	3	4	5	6		
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm		
	Mean	7.8	4.4	3.6	3.6	3.6	3.6		
	Year	1	2	3					
	Description	2003	2004	2005					
	Mean	814.1	1321.9	1446.5					
Mg	Habitat	1	2	3					
	Description	Woodland	Wetland	Grassland					
	Mean	789.4	1990.4	802.6					
	Soil Layers	1	2	3	4	5	6		
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm		
	Mean	1603.8	1155.4	984.1	861.8	1007.8	1551.9		
	Year	1	2	3					
	Description	2003	2004	2005					
	Mean	299.1	257.5	302.3					
CEC	Habitat	1	2	3					
	Description	Woodland	Wetland	Grassland					
	Mean	225.4	413.2	220.3					
	Soil Layers	1	2	3	4	5	6		
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm		
	Mean	364.3	269.9	245.6	251.2	266.4	320.5		
	Year	1	2	3					
	Description	2003	2004	2005					
	Mean	15.9	14.8	24.9					
C: Ca ratio	Habitat	1	2	3					
	Description	Woodland	Wetland	Grassland					
	Mean	14.8	11.5	29.4					

	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	61.9	23.5	6.8	5.01	7.4	6.8
	Year	1	2	3			
	Description	2003	2004	2005			
	Mean	10.7	1.7	8.4			
Na: K ratio	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	8.6	1.1	11.2			
	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	0.2	0.5	2.7	9.2	12.7	16.4
	Year	1	2	3			
	Description	2003	2004	2005			
	Mean	0.3	0.5	1.2			
Mg: Ca ratio	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	0.4	0.5	1.2			
	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	0.4	0.1	1.6			
SAR	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	0.1	0.1	0.2	0.8	1.04	2.2
	Year	1	2	3			
	Description	2003	2004	2005			
	Mean	17.2	7.6	13.6			
pNa	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	10.9	4.6	22.8			
	Soil Layers	1	2	3	4	5	6
	Description	Litter	0 cm	25 cm	50 cm	75 cm	100 cm
	Mean	2.3	3.04	7.6	16.5	21.7	25.7
rCa	Habitat	1	2	3			
	Description	Woodland	Wetland	Grassland			
	Mean	2.1	1.9	1.1			

The values with different colour shades in a same row differ significantly ($P < 0.05$)

Table 5.3.4. Correlation matrix of the alkali and alkaline earth metals and their ratios

	Na	K	Ca	Li	Mg	CEC	C: Ca	Na: K	Ca: Mg	Mg: Ca	SAR	pNa	rCa
Na	1.000												
K	-.342	1.000											
Ca	-.310	.651	1.000										
Li	-.200	.768	.596	1.000									
Mg	-.202	.205	.226	.322	1.000								
CEC	NS	.446	.634	.543	.824	1.000							
C: Ca	NS	.401	NS	.302	NS	NS	1.000						
Na: K	.905	-.349	-.361	-.216	-.197	NS	NS	1.000					
Ca: Mg	NS	NS	NS	NS	-.313	NS	NS	NS	1.000				
Mg: Ca	.371	NS	-.346	NS	.195	NS	.339	.353	-.204	1.000			
SAR	.597	-.196	-.309	NS	NS	NS	NS	.544	NS	.268	1.000		
pNa	.943	-.395	-.450	-.265	-.273	NS	NS	.862	NS	.393	.661	1.000	
rCa	-.305	NS	.332	NS	-.343	-.190	-.160	-.273	.658	-.286	-.180	-.313	1.000

162 Sample size, ± .154 critical value at P < 0.05 (two-tail), NS: Not Significant

Table 5.3.5. Factor loadings of the soil variables

Parameters	Principal Components			
	I Na/SAR/Na: K	II CEC/Ca/Li/K	III rCa	IV C: Ca
Na	0.96	-0.058	-0.033	-0.102
K	-0.275	0.679	0.125	0.553
Ca	-0.298	0.815	0.329	-0.049
Li	-0.109	0.761	0.011	0.462
Mg	-0.16	0.602	-0.614	-0.197
CEC	0.047	0.916	-0.298	-0.173
C: Ca	0.055	-0.003	-0.171	0.899
Na: K	0.913	-0.106	-0.037	-0.087
Ca: Mg	0.139	0.021	0.82	-0.121
Mg: Ca	0.443	-0.054	-0.447	0.306
SAR	0.732	-0.09	-0.014	0.158
pNa	0.946	-0.202	-0.034	-0.038
rCa	-0.258	0.01	0.831	-0.045
Total loading*	3.676	2.973	2.187	1.554
% Variance explained	28.280	22.866	16.820	11.955
Extraction Method: Principal Component Analysis, varimax rotation with Kaiser Normalization (Rotation converged in 6 iterations). * Sums of squared loadings				

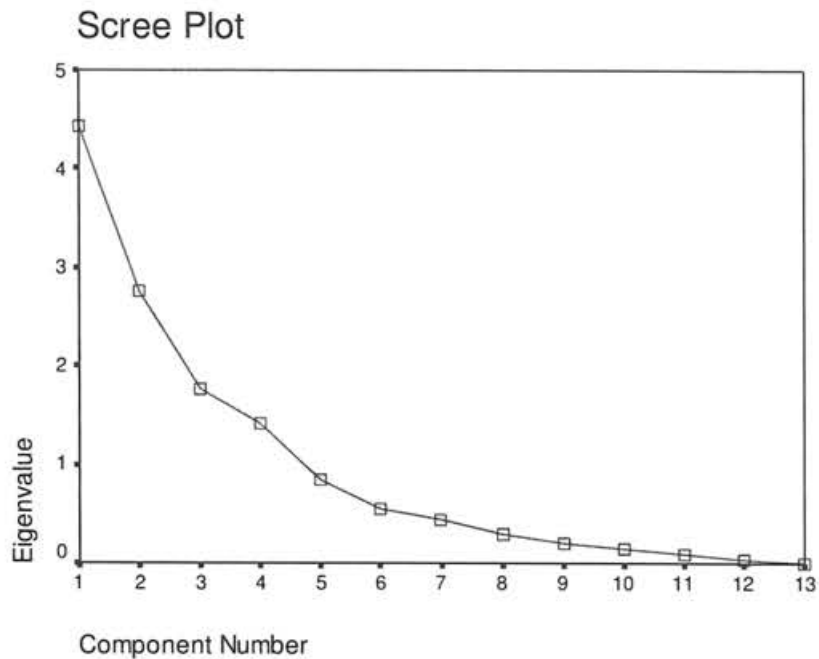


Figure 5.3.5. Scree plot of principal component analysis

PCA was performed with the alkali and alkaline earth metals and their ratios observed in KNP soil showed in total, four components to be the hidden variables (Table 5.3.5). These four components explained 68.9% of the total variance. These components were selected and studied based on a visual inspection of scree plots, shown in Figure 5.3.5. Table 5.3.5 provides the correlations between the original variables studied and the four components generated by the PCA, as well as the factor loadings based on which these components to be interpreted.

The first component accounting for 28.3% of the variance was highly correlated with Na levels in soil. It was also associated with other variables such as Na: K ratio and SAR. The second component that accounted for 22.9% of the variance was correlated with certain base cations such as Ca, Li and K and the cation exchange capacity. The third component was correlated with the rCa and accounted for 16.8% of the variance. The fourth component that accounted for 12.0% of the variance was correlated with carbon to cation ratio, i.e. C: Ca. Thus, the four PCA components can be characterized as 'Na and its associated variables', 'Base cations and exchange capacity', 'the ratio of Ca to the total of all other major cations'.

5.4. DISCUSSION

Given the influence of the hydroperiod, the extent of inundation in the wetland blocks as well as the adjacent terrestrial areas and annual variation in water input to the Park, wide dissimilarity in distribution and mobilization of alkali and alkaline earth metals was expected among the habitats. Since most of the metals (Na, K, Ca, Li and Mg) are water soluble and highly mobile, they could get distributed vertically depth wise in the soil profile either by percolation of water downwards the soil profile or the reverse way by the upward movement of water due to capillary action. Results from the geostatistical analysis showed that most of the metals analyzed here differed significantly among the habitats (ANOVA, $P < 0.05$). However, the variation of cations such as Ca and Li was not significant among the soil layers. While K varied significantly among the soil layers in all the three years, it varied significantly among the habitats only during 2005. This result is unanticipated given the difference in the type of soil and vegetation among the habitats.

Na was found distributed more in the deeper layer of the soil profile. Its concentration was always higher in the terrestrial areas, which could be associated with the type of parent material in these areas. The salts carried up by the capillary action from the underground aquifer could also substantially add to this situation. Na was found in low concentration in the surface layers than the deeper ones. The Na: K ratio also followed a similar pattern. The natural sources for dissolved ions are rock weathering, atmospheric precipitation and groundwater. Weathering of NaCl deposits are known to supply Na and Cl in equal proportions (Chakrapani 2002). Bhushan and Sharma (1987) report water in the phreatic aquifer in the KNP to be predominantly saline. A saline tract with brine of resistivity 20-30 Ohms⁻¹ and sodium chloride as major salt underneath. The phreatic aquifer is in close interaction with wetland water and may contribute to the alkalinity and chloride content (Azeez et al. 2000). Na, one of the critical elements in soil permeability (Puri 1949), deflocculates the soil (Senthilnathan and Azeez 1999) and makes the crust impermeable (UNESCO/WHO 1978). An excess of neutral salts of Na and Cl that leads to an alkaline condition is usually termed as soil salinity (Rosicky et al. 2006). Another feature of the saline-alkaline soil studied by Rosicky et al. (2006) and in the case of KNP is high pH values coinciding

with high Na content. The pH in the terrestrial sites of KNP with high Na concentration was in the range of 7.7 to 9.97. Excessive salinity should be seen as an additional variable that affects plant germination and growth negatively, particularly during dry periods. This could be one of the reasons for the saline patches in KNP harbouring sparse vegetation. The dominant species in these areas is *P. juliflora* (considered a weed in the KNP), *A. nilotica*, *Capparis*, *Salvadora* and *Zizyphus* spp.

The trend of distribution for K was just the reverse of that of Na. The input water is likely to bring in considerable amount of K as it is mixed with run off from urban and agricultural landscape. As noted earlier, silicate minerals with low weathering rates constitute the primary mineral pool of the alkali elements (Tyler 2004). K has an additional biogenic source (Chakrapani 2002). However, in the present case the application of chemical fertilizers in the catchments would have significant contribution to the observed concentration of K. Many aquatic plants such as *C. alopecuroides*, *H. verticillata*, *I. aquatica*, *N. oleracea*, *P. punctatum*, *P. distichum* and *P. spinescens* are known to have high K uptake rate (Azeez et al. 2007) and hence the litters contain higher amount of K than the surface soil. Plant uptake is considered to be more important for the reduction of such ion concentrations in the soil solution than the sorption of ions to particles in the mineral soil (Schrumpf et al. 2006). Olufemi and Ikulamberu (2004) also reported similar vertical distribution of K in Okeluse Forest Reserve in Ondo State, Africa. The observed Na and K content in soil was well above the values reported elsewhere (Table 5.4.1).

Ca, similar to K, was high in wetland surface layers and was high only in certain years, (e.g. during 2005) in woodland habitat. As the Park administration pumps out ground water at select locations to maintain the wetland during the dry periods, it adds on to the Ca content of the soil in these areas. The ground water in the KNP has high hardness (as CaCO_3 , Azeez et al. 2000). The highest concentration of Ca in wetland litter during 2004 and woodland litter during 2005 could be because of the high Ca content in the falling plant parts that form most of the litter fraction in these systems. Ca being less mobile, conservative in movement, and constituents of cell wall and/or chlorophyll (Garg and Singh 2005) can add to the total concentration in the litter considerably. Kelly and Mays (1999) also reported vertical declining trend of Ca similar to the present study in two deciduous forest soils in Great Smoky Mountains

National Park, Blount County, TN, USA. Sahu et al. (2001) also reported down ward reduction of Ca in some Vertisols of Western Orissa, India.

Lithium is present in soils mainly as a component of silicates and sandstone soils are especially rich in Li. The presently reported concentration of Li (1.74 to 7.00 mg/kg) is considerably lesser than the concentration reported elsewhere. For example, Haddadin et al. (2002) reported 10.2 to 44.9 mg/kg (Table 5.4.1) in the Jordanian soils. According to them (Haddadin et al. 2002), soils with high levels of organic matters tend to be low in lithium; the wetland surface layer in the present study during 2003 contained comparatively lesser concentration of Li than the deeper layers of the profile. However, during 2005 all the habitats had consistently high concentration of Li than the previous years, which could be due to the inputs via water, subsequently being distributed along the soil profile. Even though Li is considered as one of the most mobile elements (Rudnick et al. 2004), it did not vary consistently with depth. The distribution of Mg, similar to that of Na, followed a downward increasing trend indicating the accumulation of salts carried in by the input water and the upward movement of salts in soil moisture during the dry periods of the year (Michael 1990, Sehgal and Abrol 1994, Pachauri and Sridharan 1998, and Azeez 2000). The vertically increasing trend of Mg was also reported by Horkar and Totey (2002) in *Tectona* and *Terminalia* patches in Navegaon National Park of Maharashtra in India. Mg in the present case exceeded the generally reported levels for this element (Table 5.4.1). The lack of variation among the layers could be because of the prolonged water logging condition in the wetlands and some portions of the adjacent terrestrial blocks. During this period, there might be an admixing of nutrients and other dissolved salts among the layers.

The amount of Na, K, Ca and Mg (base cations) stored in the mineral soil fraction predetermines the status of soils as well as, in the long term, its evolution in the view of anthropogenic activities (Fichter et al. 1998). In the great majority of soils, three base cations, i.e. K, Ca and Mg stand out from all others in that they occur in important quantities in exchangeable form. Although exchangeable K is normally present in much lower concentrations than either Ca or Mg, plants utilize it in appreciably greater amounts than the two. It is also more often deficient. Not only the quantum but also the ratios of cations in the soil solution are of utmost importance in

determining their behaviour in different soils. In the present case Na: K and Mg: Ca ratio was examined as (i) Ca and Na are the major competing cations in normal and alkali soils (Mehta et al. 1983), and (ii) among the alkaline earth metals, Ca is relatively less mobile (Garg and Singh 2005). Ca and Mg are antagonistic towards soil permeability with Na. The high value of Na: K ratio indicates the dominating presence of Na salts compared to K. It is known that Na and Mg salts are more soluble than Ca salts (Sahu et al. 2001). Ca, being less mobile than other base cations, determines the type of enrichment in saline and alkaline soil. The cationic ratio above 1.0 denotes to Ca type enrichment and a ratio below 0.5 shows Na type enrichment (Azeez et al. 2000). In the present case, the lowest value of r_{Ca} , i.e. 0.124 was observed in the terrestrial areas and the highest (i.e. 3.91) in the aquatic blocks. This indicates to the Ca type enrichment in the wetland and Na type enrichment in the woodland and grassland blocks. This is supported by the higher values of pNa , rNa and SAR in these terrestrial blocks. High Na and SAR values are the indicators of an alkaline soil (Singh et al. 2005). In the present case, the highest value of pNa was 69.4. However, a pNa value of 4 would not likely have an adverse effect on plant growth (Hausenbuiller 1978). Nonetheless, the pNa value of 14 can have an adverse effect on soil properties important to plant growth. Calcite bearing sediments are likely to increase the pCa and accordingly the rCa also. Samecka-Cymerman et al. (2002) reported a high Mg: Ca ratio up to a range of 1.3 to 11 in some serpentine soils in Lower Silesia, Poland. The present study recorded very low Mg: Ca molar ratio with a range of 0.089 to 1.681.

Table 5.4.1. Reported levels of select alkali-alkaline earth elements in soil

Metals	Present observation (mg/kg)*	Concentration range (mg/kg)	Authors reported	Locations
Na	41-690	4.6 – 6.9	Aluko (1993)	<i>Terminalia superba</i> stands -Southwestern Nigeria
K	180-775	39.4 – 73.1	Olufemi and Ikulamberu (2004)	Okeluse forest reserve, Ondo State Nigeria
Ca	1247-3957	40 – 793	Aluko (1993)	<i>Terminalia superba</i> stands -Southwestern Nigeria
Li	1.4-6.9	10.2 – 44.9	Haddadin et al. (2002)	Jordanian soils
Mg	185.2-5147.7	57.12 – 167.7	Olufemi and Ikulamberu (2004)	Okeluse forest reserve, Ondo State Nigeria
CEC	111.4 – 526.9	5 – 95	Lamersdorf and Meyer (1993)	Northwest German Forest
Na: K	0.113 – 0.979	26.5 – 53.0	Rivera-Monroy et al. (2004)	Riverine mangrove forest, San Juan River, Venezuela
Ca: Mg	0.22 – 10.03	2.7 – 14.4	Kim et al. (2001)	Subalpine marshes, Lake Tahoe basin, USA
Mg: Ca	0.129-2.582	1.3-11	Samecka-Cymerman et al. (2002)	Serpentine soils in Lower Silesia, Poland

*The values of the present observation exclude the concentration observed in the litter layer

5.5. CONCLUSION

K, Ca and Li showed gradual declining trend down ward in the soil profile in all the habitats where as Na showed an increasing trend in the same direction. Mg did not have any consistency in the depth profile. Of all the base cations the level of Na and Mg were relatively higher and exceeded already reported level. Our data suggests that differences exist among the habitats in the Park not only in terms of the major vegetation types, but with respect to the type of cationic enrichment also. Na type enrichment was observed only in the terrestrial areas particularly the woodlands. On the contrary, the wetland showed Ca type enrichment. Saline underground aquifer and input water to the Park seems to contribute significantly to the elevated levels of elements such as Na, K and Ca.

6. TEMPORAL VARIATION OF ALKALI AND ALKALINE EARTH METALS IN KNP WETLAND

6.1. INTRODUCTION

Wetlands particularly lakes with their clear-cut boundary represent one of the most versatile ecosystems on the earth (Chakrapani 2002). The diversity and existence of wetland plants are very important in reducing nutrient enrichment of wetland systems (Boston and Perkins 1982, Kao et al. 2003, and Azeez et al. 2007). Quantifying the plant available forms of the nutrients in the sediment is important for the sustainable management of these natural systems. However, because of anthropogenic pressure of several types and magnitudes and inflow of wastewater from several sources wetlands gradually are enriched by nutrients exceeding their assimilation and carrying capacity. The process is speeded up in the case of seasonal or monsoonal wetlands, which depend exclusively on the external surficial input of water. Bed sediment in wetlands serves as repository for macronutrients such as nitrogen, phosphorous, sulphur, potassium and calcium from anthropogenic sources (Campbell and Tessier 1991, Mathew et al. 2002, and Shanthi et al. 2003) including those from agricultural sources. Among alkali metals, Potassium chiefly finds its way into wetlands as agricultural runoff. Sodium in KNP largely has a sedimentary origin, as the soil and the water in the phreatic aquifer in the Park are predominantly saline (Prusty et al. 2007). Among alkaline earth metals, Calcium and Magnesium are mostly of biological origin (Griffith 1980, Barbosa and Fearnside 1996, and Singh and Jha 2002), finding their way into the water bodies from animal and other municipal wastes that are dumped in. The level of all the above elements is likely high in the cases where wetlands receive domestic and municipal wastewater.

Several studies in India have dealt with the assessment of nutrient content in wetlands, lakes and other aquatic systems (Ahmad et al. 1996, Chakrapani 2002, Mathew et al. 2002, Mandal et al. 2003, and Shanthi et al. 2003). A search of literature failed to locate many studies specifically on alkali (Na and K) and alkaline earth metals (Ca and Mg) in wetland sediments in general and protected areas in particular. However, the available studies dealt with only surface sediments providing little information about mobilization and distribution of alkali and alkaline earth metals in deeper layers

from the surface downward. The present investigation was carried out to assess variations of select alkali (Na and K) and alkaline earth metals (Ca, Li and Mg) among close by deeper layers of the bed sediments in the monsoonal wetland system of Keoladeo National Park, Bharatpur, India from September 2003 to July 2005.

6.2. MATERIALS AND METHODS

The details of the sampling wetland sediment and preliminary processing are discussed in the section 2.2.2. The samples from each layer (0-5, 5-10, 10-15 and 15-20 cm) collected bimonthly were pooled and homogenized. After pooling and homogenizing the sub samples from each layer the total number of samples were 144 for the whole study period. All these samples were analyzed for several base cations and the protocols adopted for their estimation are given in Table 2.2.1. Moreover, details of the analysis are discussed in section 5.2.

6.3. RESULTS

Figure 6.3.1, Figure 6.3.2 and Figure 6.3.3 show the vertical and seasonal pattern in the distribution of alkali and alkaline earth metals in the KNP wetland soil. None of the elements showed any consistency in the pattern across the layers during all the months. Among the alkali metals, the lowest and highest concentration of Na was 41 and 690 mg/kg (Figure 6.3.1). The lowest value was seen in the surface layer during the monsoon, while the highest was seen during the summer season, i.e. in the month of May in the year 2005 (Table 6.3.1). Na had an increasing trend with depth during January and September of 2004, and July 2005. The minimum and maximum value for K was 180 and 775 mg/kg soil with the corresponding month being November (2003) and July (2004) respectively. K decreased with depth during September 2004 and May 2005. Both Na and K varied significantly only among the months (GLM-ANOVA, Table 6.3.2, $P < 0.05$). However, the post-hoc test (LSD) shows that the Na level in wetland during July 2004 and May 2005 differed significant from the rest of the months (Table 6.3.3, $P < 0.05$). In the case of K, there seems to be two groups of months as far as the variation of K level in soil is concerned. September 2003 to March 2004 and July 2005, form one group and distinct from the rest of the months (Table 6.3.3, $P < 0.05$).

Table 6.3.1. Elemental concentrations and ratios in the wetland sediment

Element	Range	Month- Year	Sediment layer (cm)	Mean	Stdev#
Na*	L = 41.0	July-05	0-5	188.32	129.55
	H = 690.0	May-05	0-5		
K*	L = 180.0	Nov-03	10-15	457.07	149.75
	H = 775.0	July-04	0-5		
Ca*	L = 1247.0	Sep-03	5-10	3058.06	647.00
	H = 3957.0	May-04	5-10		
Li*	L = 1.4	July-05	0-5, 15-20	3.07	1.20
	H = 6.9	July-04	5-10		
Mg*	L = 185.2	Sep-03	15-20	2358.39	938.25
	H = 5147.7	Nov-03	5-10		
CEC**	L =111.4	Sep-03	15-20	367.00	95.80
	H =526.9	Nov-03	5-10		
C: Ca	L =2.31	July-05	15-20	14.22	10.71
	H =59.09	Nov-03	0-5		
Na: K	L =0.113	July-05	0-5	0.41	0.24
	H =0.979	Jan-04	15-20		
Ca: Mg	L =0.224	Mar-04	15-20	1.88	1.47
	H =10.035	Sep-03	15-20		
Mg: Ca	L =0.129	Sep-03	15-20	0.80	0.42
	H =2.582	Nov-03	5-10		
SAR	L =0.008	Nov-03	5-10	0.05	0.03
	H =0.161	May-05	0-5		
pNa	L =0.404	Nov-03	5-10	2.17	1.27
	H =7.216	May-05	0-5		
rCa	L =0.223	Nov-03	5-10	0.85	0.49
	H =3.516	Sep-03	15-20		
L: Low, H: High, * mg/kg, ** meq/kg, # Standard deviation					

Li was seen lowest at the surface and highest at a depth of 5-10 cm during the monsoon of 2005 and 2004 respectively. The range for Li was 1.4 to 6.9 mg/kg. Except three months, i.e., September 2004, March 2005 and May 2005, it did not show distinguishable trend of either decrease or increase with depth (Figure 6.3.2). Li varied significantly among the months ($P < 0.05$, Table 6.3.2). The LSD test (as a post-hoc test) reveals that the Li level in soil in the month of May 2004 and July 2004 are distinctly different from the rest of the months (Table 6.3.3, $P < 0.05$). Among the alkaline earth metals, Ca concentrated least (1247 mg/kg) in the sediments during September 2003 at a depth of 5-10 cm. It concentrated highest (3957 mg/kg) in the same layer during the summer of 2004 (May). The minimum and maximum concentration of Mg in the wetland sediment was 185.2 and 5147.7 mg/kg respectively. The lowest concentration was at the bottom layer during September 03 and the highest at a depth 5-10 cm during November 2003. Although Mg did not show any consistent pattern along the depth, it showed a decreasing trend during September 2003 and an increasing trend during January 2005 (Figure 6.3.3). Similar to the alkali metals, both the alkaline earth metals (i.e. Ca and Mg) also varied significantly only among the months (GLM-ANOVA, $P < 0.05$, Table 6.3.2). LSD results shows that in the case of Ca, the level in soil in the month of September and November 2003 is distinct from the rest. For Mg, it was only September 2003 (Table 6.3.3, $P < 0.05$). The variation was not significant among the soil layers in case of any of these metals. Based on the highest concentration, the base cations follow the sequence $Mg > Ca > K > Na > Li$.

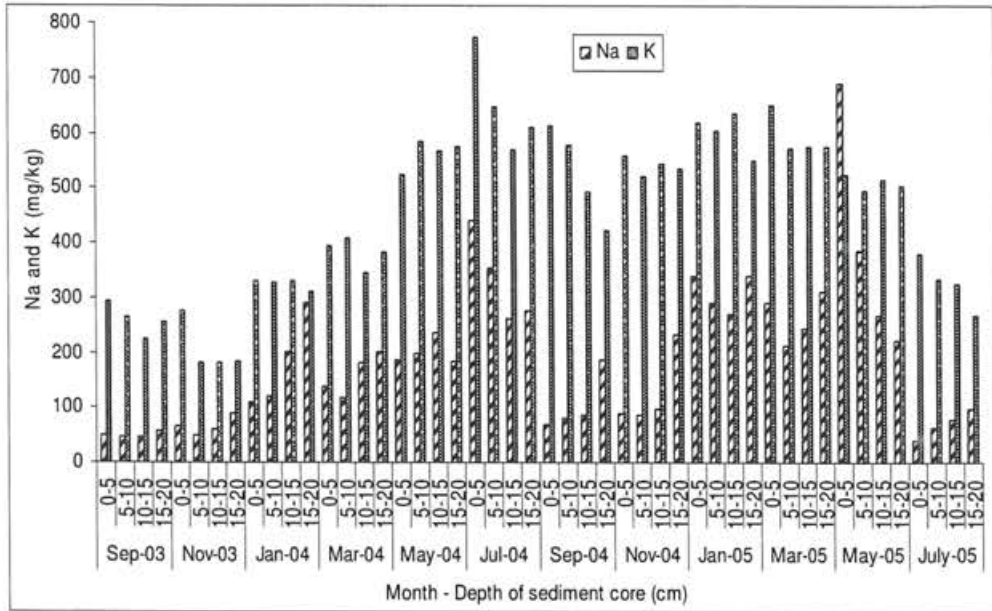


Figure 6.3.1. Temporal variation in Sodium and Potassium

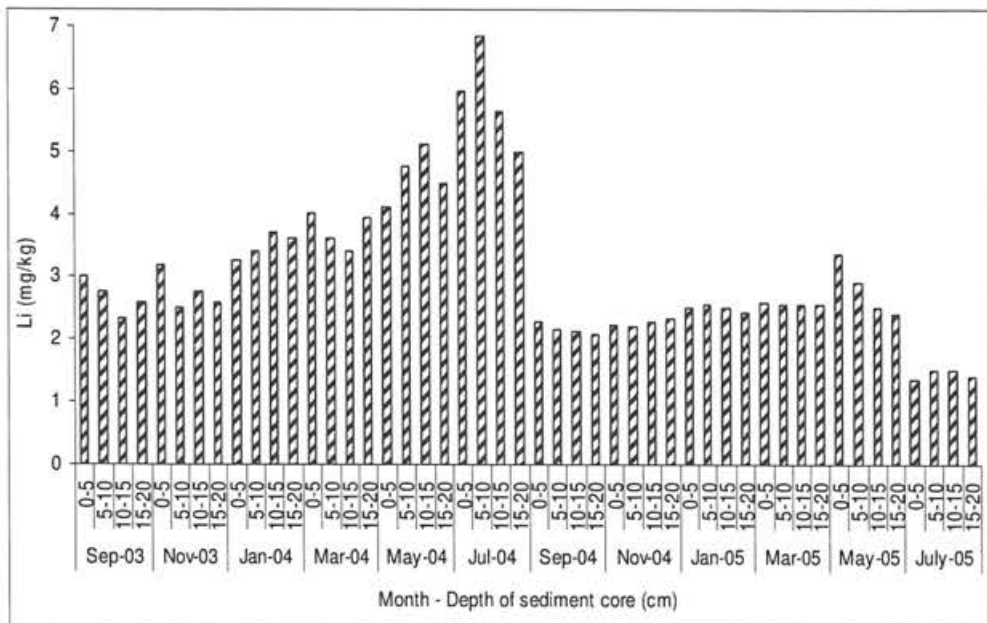


Figure 6.3.2. Temporal variation in Lithium

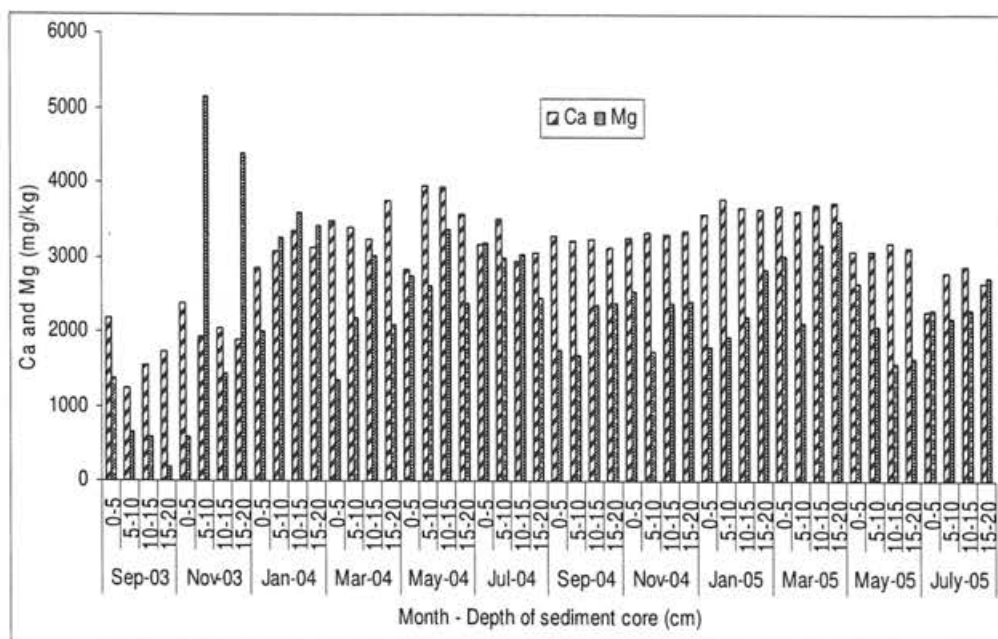


Figure 6.3.3. Temporal variation in Calcium and Magnesium

The CEC varied widely among the months as well as soil layers. The lowest and highest values of CEC are 111.4 and 526.9 meq/kg (Table 6.3.1). The lowest value was recorded at the bottom layer of the sediment core during September 2003 and the highest at a depth 5-10 cm during November 2003. The variation of CEC was significant only among the months only (GLM-ANOVA, Table 6.3.2, $P < 0.05$) and the post-hoc test results showed that, similar to Ca and Mg, the CEC of sediments were distinct in the month of September 2003 and significantly different from the other months (Table 6.3.3, $P < 0.05$). The carbon: element ratio (i.e. C: Ca) ranged between 2.3 and 59.1. The ratio was high at the surface of the core and low at the bottom layer. The ratio varied significantly among the months as well as soil layers (GLM-ANOVA, Table 6.3.2, $P < 0.05$). The post-hoc test revealed that the ratio in November 2003, January 2005 and March 2005 did differ significantly from the rest of the months (Table 6.3.3, $P < 0.05$). As far as the variation of C: Ca ration in soil among layers are concerned, the value of the ratio in upper two layers, i.e. 0-5 cm and 5-10 cm were significantly different from the rest of the layers. The minimum and maximum value of Na: K was 0.113 and 0.979 with their corresponding locations being bottom of the core and surface layer respectively. Ca: Mg was in the range of 0.2 to 10.03, while Mg: Ca was in the range of 0.1 to 2.6. Although both the values of

Ca: Mg were observed at the bottom layer of the core, the minimum value was recorded during March 2004 and the maximum during September 2003. The minimum value for Mg: Ca was also observed during September 2003 and at the bottom layer.

The metal ratios such as Na: K, Ca: Mg and Mg: Ca varied significantly among the months (ANOVA, $P < 0.05$) only. However, Na: K ratio in the sediment during May 2005 was significantly different from the rest of the months. Ca: Mg ratio in the sediment was distinct during September 2003 and different from rest of the months, where as Mg: Ca ratio during November 2005 did differ significantly from the rest of the months (Table 6.3.3, $P < 0.05$). The value of SAR and pNa in the May 2005, July 2004 and January 2005 were different from the rest of the months. However, in the case of rCa, it was only September 2003, i.e. rCa level in the soil during this month was significantly different from rest of the months during the study period.

SAR in the samples ranged between 0.008 and 0.161. The ratio of Na to the total of all major cations under study (Na, K, Ca, Li and Mg), i.e. pNa ranged between 0.4 and 7.2. Both SAR and pNa were seen the lowest during November 2003 at a depth of 5-10 cm and the highest in the surface layer during May 2005. The variation of SAR was significant only among the months (ANOVA, Table 6.3.2, $p < 0.05$). pNa also varied significantly among the months. The range of values for all other major cationic ratios and metals with their corresponding locations are given in Table 6.3.1. pK and pCa were highest during September 2003, where as pLi and pMg were highest during July 2004 and November 2003 respectively. The ratio of Na to other major base cations, i.e. rNa was in the range of 0.004 to 0.08. The ratio of Ca to other major cations, i.e. rCa ranged between 0.2 and 3.5. The lowest value was seen during November 2003 at a depth of 5-10 cm, and the highest value during September 2003 at the bottom layer of the core. The variation of rCa was significant among the months as observed in the case of SAR and pNa. SAR was positively correlated only with pNa and rNa.

The Pearson's correlation matrix (Table 6.3.4) shows that of the cations and their ratios studied, Na was positively correlated with all other cations, CEC, Na: K ratio, SAR and pNa, while negatively correlated with rCa (Table 6.3.4, $P < 0.05$). K was

also positively correlated with other cations and CEC. CEC was positively correlated with all the cations. As far as the cation ratios are concerned, K was negatively correlated with Mg: Ca ratio (Table 6.3.4, $P < 0.05$). CEC was positively correlated with metal ratios such as Na: K and Mg: Ca, where as negatively correlated with cationic ratios such as Ca: Mg, rCa and C: Ca ($P < 0.05$). As expected Na: K was positively correlated with SAR and pNa.

Table 6.3.2. Univariate Analysis of Variance of metals and their ratios

Parameters	Source of variation (P value)*	
	Months	Soil layers
Na	0.000	NS
K	0.000	NS
Ca	0.000	NS
Li	0.000	NS
Mg	0.011	NS
CEC	0.000	NS
C: Ca	0.001	0.000
Na: K	0.000	NS
Ca: Mg	0.002	NS
Mg: Ca	0.039	NS
SAR	0.000	NS
pNa	0.000	NS
rCa	0.001	NS
*Post-Hoc test (LSD-Least Significant Difference) was performed only in the cases with $P < 0.05$; NS: Not Significant		

Table 6.3.3. LSD (Post-Hoc) tests for the alkali metals and ratios studied

		Na											
Months	1	2	3	4	5	6	7	8	9	10	11	12	
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05	
Mean	50.0	66.0	180.5	160.5	201.4	333.2	106.0	126.2	310.2	264.8	391.5	69.5	
		K											
Months	1	2	3	4	5	6	7	8	9	10	11	12	
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05	
Mean	260.0	205.5	324.8	383.3	562.9	650.5	526.8	539.3	602.3	593.8	509.0	327.0	
		Ca											
Months	1	2	3	4	5	6	7	8	9	10	11	12	
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05	
Mean	1675.5	2059.8	3107.5	3462.0	3577.8	3170.0	3221.0	3308.5	3663.8	3686.3	3124.0	2640.8	
		Li											
Months	1	2	3	4	5	6	7	8	9	10	11	12	
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05	
Mean	2.7	2.8	3.5	3.7	4.6	5.9	2.2	2.3	2.5	2.6	2.8	1.4	
		Mg											
Months	1	2	3	4	5	6	7	8	9	10	11	12	
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05	
Mean	693.8	2887.7	3062.7	2497.8	2769.9	2915.1	2048.6	2269.1	2194.5	2945.0	1986.3	2373.6	
		CEC											
Months	1	2	3	4	5	6	7	8	9	10	11	12	
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05	
Mean	149.9	348.9	423.8	408.3	430.3	430.0	347.7	371.4	392.7	453.4	349.8	338.7	
		C: Ca ratio											
Months	1	2	3	4	5	6	7	8	9	10	11	12	
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05	
Mean	16.9	24.8	10.9	17.1	14.5	16.2	14.2	15.3	9.4	8.9	13.9	13.2	

Soil layers	1	2	3	4
Description	0-5 cm	5-10 cm	10-15 cm	15-20 cm
Mean	28.7	15.6	8.5	6.2

Na: K ratio												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	0.2	0.3	0.6	0.4	0.4	0.5	0.2	0.2	0.5	0.5	0.8	0.2

Ca: Mg ratio												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	4.2	1.9	1.2	1.7	1.5	1.4	1.7	1.8	2.9	1.4	2.0	1.2

Mg: Ca Ratio												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	0.5	1.5	1.0	0.7	0.8	0.9	0.7	0.7	0.6	0.8	0.6	0.9

SAR												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	0.04	0.02	0.04	0.04	0.04	0.07	0.03	0.03	0.08	0.05	0.1	0.01

pNa												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	1.7	1.1	1.9	1.7	2.1	3.3	1.3	1.4	3.6	2.6	4.8	0.9

rCa												
Months	1	2	3	4	5	6	7	8	9	10	11	12
Description	Sep-03	Nov-03	Jan-04	Mar-04	May-04	Jul-04	Sep-04	Nov-04	Jan-05	Mar-05	May-05	Jul-05
Mean	1.7	0.9	0.7	0.9	0.8	0.7	0.9	0.9	1.2	0.7	0.9	0.7

The values with different colour shades in a same row differ significantly (P < 0.05)

Table 6.3.4. Pearson's correlation matrix of alkali and alkaline earth metals and their ratios in sediments

	Na	K	Ca	Li	Mg	CEC	C: Ca	Na: K	Ca: Mg	Mg: Ca	SAR	pNa	rCa
Na	1.000												
K	.454	1.000											
Ca	.404	.730	1.000										
Li	.258	.342	.317	1.000									
Mg	.261	.063	.240	.171	1.000								
CEC	.400	.314	.540	.265	.941	1.000							
C: Ca	NS	NS	-.281	NS	-.225	-.290	1.000						
Na: K	.811	NS	NS	NS	.314	.336	-.172	1.000					
Ca: Mg	NS	NS	NS	NS	-.523	-.473	NS	-.185	1.000				
Mg: Ca	NS	-.214	NS	NS	.888	.709	NS	.228	-.431	1.000			
SAR	.880	.327	.179	NS	NS	NS	NS	.762	NS	NS	1.000		
pNa	.888	.325	.185	NS	NS	NS	NS	.773	NS	NS	.996	1.000	
rCa	-.204	NS	NS	NS	-.617	-.562	NS	-.245	.972	-.519	NS	NS	1.000

144 Sample size, ± .164 critical value of Correlation coefficient r at P < 0.05 (two-tail), NS: Significant

Table 6.3.5. PCA Factor loadings of the alkali and alkaline earth metals in the bed sediment

Parameters	Principal Components			
	I Alkaline earth metals	II Na/SAR	III K/Ca/ Li	IV C: Ca
Na	0.172	0.902	0.335	0.087
K	-0.079	0.167	0.885	0.056
Ca	0.050	0.096	0.856	0.343
Li	0.151	0.102	0.608	-0.289
Mg	0.884	0.047	0.125	0.322
CEC	0.782	0.112	0.400	0.385
C: Ca	-0.090	-0.057	-0.057	-0.829
Na: K	0.285	0.893	-0.106	0.125
Ca: Mg	-0.834	0.011	-0.041	0.230
Mg: Ca	0.827	-0.024	-0.224	0.201
SAR	-0.149	0.965	0.140	-0.040
pNa	-0.139	0.969	0.145	-0.032
rCa	-0.885	-0.038	-0.042	0.146
Total loading*	3.747	3.549	2.283	1.283
% Variance explained	28.825	27.299	17.560	9.872
Extraction method: Principal Component Analysis, varimax rotation with Kaiser normalization (Rotation converged in 5 iterations). *Sums of squared loadings				

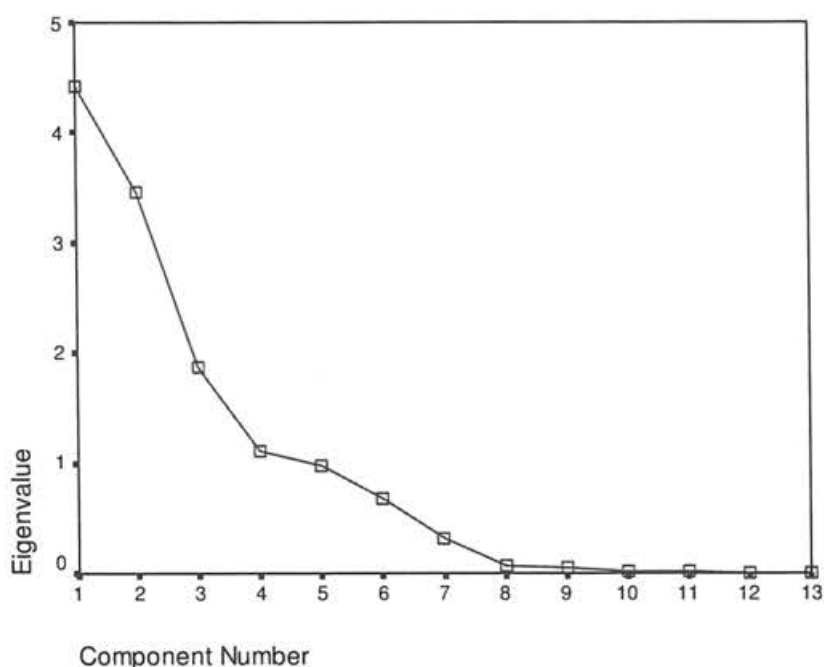


Figure 6.3.4. Scree plot of principal component analysis

PCA was performed on the analytical data in order to synthesize the variation patterns in those elements that are potentially associated with the saline and alkaline nature of the soil. The Table 6.3.5 shows that the PCA resulted in four principal components that explained 83.6% of the total variance. These components were determined based on a visual inspection of scree plots, shown in Figure 6.3.4. Table 6.3.5 provides the factor loadings based on which these components are to be interpreted.

The first component accounting for 28.8% of the variance was highly correlated with soil variables related to the alkaline earth metals (i.e., rCa, Mg, Ca: Mg and Mg: Ca). The second component accounted for 27.3% of the variance and was correlated with specific alkali metals (i.e., pNa, SAR, Na and Na: K). The third component accounted for 17.5 % of the variance and was correlated with rest of the alkali and alkaline earth metals (i.e., K, Ca and Li). The fourth component that accounted for 9.9% of the variance was correlated with carbon to metal ratio (i.e., C: Ca). Thus the four PCA components can be characterized as 'soil alkaline earth metals', 'soil Na/SAR', 'soil K/Ca/ Li', and 'soil C: Ca' respectively.

6.4. DISCUSSION

Wide variations in the distribution of the alkali and alkaline earth metals in the wetland soil were expected since the hydroperiod is known to have significant influence in the system. The time, duration and quantum of water release also have crucial roles as far as the cationic distribution is concerned. Statistical analysis showed that the variation of metals is significant only among the months (ANOVA, Table 6.3.2, $p < 0.05$). No significant variation was observed among the soil layers. All the metals / base cations studied here are water soluble and highly mobile. Since the wetland system in KNP remains inundated for most part of the years, it is expected to result in high mobility of the cations among the soil layers.

Of the cations, Na and Ca concentrated highest during the summer months. This might be because during the dry period accumulation of salts on the soil surface is a common phenomenon in aquatic bodies. Moreover, the salts carried up by the capillary action from the underground aquifer may substantially add to this. The existence of a saline phreatic aquifer underneath is probably a reason for Na increasing along the depth of the core during certain months, although no consistency in the pattern was seen. Na is known to be one of the critical elements that make the crust impermeable by deflocculating the soil. An excess of neutral salts of Na and Cl that leads to alkaline condition is usually termed as soil salinity (Rosicky et al. 2006). The increasing pattern of Na downward could also be associated with geochemical processes (Cox et al. 2002).

Similar to Na, Ca also likely to have a significant source underground. The higher levels of Ca during the dry periods in the Park could be due to two reasons; 1) The Park management pumps out ground water at select locations to overcome the dry period and it adds on to the Ca concentration in soil in the aquatic areas, and 2) during the dry periods, the death and decay of aquatic vegetation might also contribute to the Ca content. Ca being a structural constituent of plant (cell wall and/or chlorophyll) and animal tissue can add to the total concentration in the litter and ultimately in soil considerably. The input water also contributes Ca to the system. The release of marl from surface of macrophytes after their death adds to the Ca level in bottom soil (Singh and Jha 2002). Cox et al. (2002) opines that Ca level in soil could more be

attributed to the geochemical processes rather than the biological. In wetland soil/sediments, Ca remains in the form of CaCO_3 . The presently recorded values of the base cations and their ratios were compared with the published values from other similar environments across the globe. In the present case, Na exceeded the values reported elsewhere, while Ca was well within the reported value (Table 6.4.1).

K and Li concentrated highest during the monsoon season, i.e. July. The higher values in the surface layer during this time are an indication that these elements mostly find their way into the KNP wetland system through the input water. The input water to KNP is the surface water, and runoff of a vast agricultural landscape outside the KNP. K has an additional biogenic source also (Chakrapani 2002). In the present case, the chemical fertilizers extensively used in the catchment areas might have contributed to the K concentration in soil. However, the concentration of K was lower than certain urban wetlands of Coimbatore (Prusty et al. 2006c) that also receive runoff water from their respective catchments. In KNP, many aquatic plants such as *C. alopecuroides*, *H. verticillata*, *I. aquatica*, *N. oleracea*, *P. distichum*, *P. punctatum*, *P. spinescens*, are known to have high K uptake rate (Azeez et al. 2007) and helping in lowering the K level in the wetland system. This is probably the reason why K was seen minimum during November. All the above-cited plants were found to have peak growth in the same period, which results in high uptake of nutrients from soil.

Li (1.4 to 6.9 mg/kg) is considerably low in concentration compared to the values recorded by Haddadin et al. (2002, 10.2 to 44.9 mg/kg). High organic matter content in soil tends to show lower Li levels in soil. The organic matter content in the wetland soils in KNP was found to be up to 24.15%. Li did not show any consistent pattern along the depth. Mg, as in the case of K and Li was also concentrated least at the bottom of the core. It concentrated highest at a depth of 5-10 cm. The surface accumulation of the salts could have resulted in the trend observed in the present case (Michael 1990, Sehgal and Abrol 1994, Pachauri and Sridharan 1998, and Azeez 2000). Mg in the present case exceeded the values reported elsewhere (Table 6.4.1). Most of the cations concentrated least in soil during or immediately after monsoon could be associated with the washing up off the salts from the soil and its subsequent percolation down the soil column.

CEC ranged from 111.4 to 526.9 and exceeded the earlier reported values elsewhere (Table 6.4.1). Higher CEC in this case is a good indication for the mobility and bioavailability of inorganic contaminants in the wetland system. The attenuation of inorganic contaminants in wetlands is a function of CEC of the bottom soil (Taha and Kabir 2005). The behaviour, mobility and bioavailability of base cations are determined by their concentration as well as of the ratios of the base cations in soil solution. Since Ca and Na are the major competing cations in soil (Mehta et al. 1983) and Ca is relatively less mobile (Garg and Singh 2005), we examined Na: K, Ca: Mg and Mg: Ca. Higher values of Na: K and Ca: Mg indicate the dominance of Na and Ca in the soil. The percentage of exchangeable Na, i.e. pNa, in the present case, was at maximum of 7.2. However, as per Hausenbuiller (1978) a pNa value in soil up to 4 is not likely to have any adverse implications on plant growth. Excess exchangeable Na is harmful to plants because it induces undesirable physical and chemical conditions in soils. It causes dispersion of clay leading to breakdown of aggregates and lowers the permeability of the soil to air and water. Dispersion also results in the formation of dense, impenetrable surface crusts that greatly hinder the emergence of seedlings.

Since Ca salts are less soluble in water than Na and Mg, its lesser mobility than other base cations determines the type of cationic enrichment in soil. The cationic ratio < 0.05 denotes to Na type enrichment and > 1.0 refers to Ca type enrichment (Azeez et al. 2000). The highest value for rCa in the present case was found to be 3.516, indicating Ca type enrichment in the wetland system. This is also evident from the highest factor loadings in the case of first component of pCa (Table 6.3.5). In the present study, rCa had the highest factor loading (-0.885). This is also supported by a very low SAR. The highest value of SAR was 0.161. Generally, freshwater wetlands have molar ratio of Mg: Ca < 3 and higher molar ratio indicates the predominance of CaCO₃ rocks as the major source (Chakrapani 2002). The presently recorded molar ratio is below this level (ranging between 0.1 and 2.6). All the three cationic ratios, Na: K, Ca: Mg and Mg: Ca were within the range reported elsewhere (Table 6.4.1). Uniform Ca concentration and Ca: Mg ratio in the soil/sediment core indicates relatively constant input of Ca. However, in the present study, the wide variation in the ratio (0.22 to 10.03) suggests anthropurgic influences to a certain extent as inferred by kim et al. (2001) elsewhere. The C: Ca in the present study also indicates net mineralization (Wesemael 1993).

Table 6.4.1. General concentration range for alkali metals in wetland sediments Vs recorded concentration in the present study

Metals	Present observation (mg/kg)	Concentration range (mg/kg)	Authors reported	Locations
Na	41-690	21 - 649	Prusty et al. (2006c)	Urban wetlands, Coimbatore, India
K	180-775	110 - 1042	Prusty et al. (2006c)	Urban wetlands, Coimbatore, India
Ca	1247-3957	2560 – 4350	Mandal et al. (2003)	North Bihar wetlands, India
Li	1.4-6.9	10.2 – 44.9	Haddadin et al. (2002)	Jordanian soils
Mg	185.2-5147.7	1242 - 4920	Prusty et al. (2006c)	Urban wetlands, Coimbatore, India
CEC	111.4 – 526.9	14 - 145	Nair et al. (2001)	Native wetlands, North Florida
Na: K	0.113 – 0.979	26.5 – 53.0	Rivera-Monroy et al. (2004)	Riverine mangrove forest, San Juan River, Venezuela
Ca: Mg	0.22 – 10.03	2.7 – 14.4	Kim et al. (2001)	Subalpine marshes, Lake Tahoe basin, USA
Mg: Ca	0.129-2.582	2.7 – 3.8	Rivera-Monroy et al. (2004)	Riverine mangrove forest, San Juan River, Venezuela

6.5. CONCLUSION

Our findings suggest that similar approaches may be used in examining the alkali and alkaline earth metal enrichment in the wetland bed sediment. The qualitative predictions using a relative scale may be based on the results of PCA of the soil variables as described in this chapter. The alkaline earth metals, rCa, Na and/or SAR, K, CEC, and C: Ca ratios are “relatively easy-to-measure” indicator variables that are expected to predict the nutrient-enrichment rates as well. However, this assumption need to be further tested and confirmed with wider data set on nutrients availability and distribution in different types across geographic regions.

7. TRACE METALS: DISTRIBUTION AND CHEMICAL PARTITIONING IN THE KNP HABITATS

7.1. INTRODUCTION

Soil contamination with heavy metals that comes chiefly from industrial activities, atmospheric deposition and agricultural usage of chemical fertilizers has received much attention in recent years. Several heavy metals are known to accumulate in water, soil, sediments and tissues of organisms (Lambou and Williams 1980, Chaphekar 1991, and Ramadan 2003) and cause chronic to acute toxicity in the course of time. Biogeochemical particularities of natural systems may increase or decrease the chances of a pollutant reaching toxic levels, irrespective of the original quantity of input. Wetland environments concentrate the elements, but in most cases biogeochemical reactions alter their chemical form, mobilization and bioavailability (Lacerda and Fitzgerald 2001). The heavy metals from anthropogenic sources are easily accumulated in the top soil (Baker 1990, Samsøe-Peterson et al. 2002, and Lu et al. 2005), which results in toxicity to plants and animals, accumulation in food chain, perturbation of the ecosystem and adverse health effects even if it is a point contamination (Borůvka et al. 1997). It assumes significance in the case of protected areas such as Keoladeo National Park that is visited by large number of migratory birds.

Although the total trace metal concentrations in soil and sediment give a somewhat convenient measure of metal pollution, many studies have highlighted that such measures do not predict the toxicity of these pollutants (Louma 1983, Louma 1989, and Di Toro et al. 1990). The mobility and bioavailability of trace metals depend mostly on their physical and chemical forms. Thus quantifying the geochemical phases of metals associated with soil is an important step in predicting the ultimate fate, bioavailability, and toxicity of metals (Salomons and Förstner 1984, Prusty et al. 1994, and Lu et al. 2005). Many studies have reported the relationships between the metal bioavailability and its partitioning in different geochemical phases (Tessier and Campbell 1987, Bryan and Langston 1992, Babukutty and Chacko 1995, Fan and Wang 2001, and Fan et al. 2002).

Sequential extraction, although operationally defined, can give information about the association of heavy metals with geochemical phases of soil, hence helps to reveal the distribution of trace metals in fractions and to assess their mobility and toxicity in soils (Quevauiller et al. 1993, and Ahnstrom and Parker 1999). Several Sequential Chemical Extraction procedures are in practice in chemical fractionation studies to assess metals in different environmental matrices (Tessier et al. 1979, Pickering 1981, Badri and Aston 1983, Kersten and Förstner 1986, and Young et al. 1992). Element specific methods have also been developed as that of Poulton and Canfield (2005) for iron partitioning. Of these, the five-step extraction method by Tessier et al. (1979) is a widely used one, although the disadvantages of this extraction scheme have been well recognized (e.g., non-specificity of extraction and re-sorption, Nirel and Morel 1990, and Reuther 1999). According to this protocol, metals in soil were fractionated into five geochemical pools, viz., exchangeable (EXC), carbonate- (CA), multiple hydroxide (Fe-Mn oxide), organic matter and sulphide bound (oxidizable, OM-S) and lithogenic or residual fractions (RES). The mobility and bioavailability of metals decrease approximately in the order of extraction sequence (Prusty et al. 1994) and hence the strength of the chemical reagent increases with the sequence. Generally, exchangeable form is considered readily mobile and easily bioavailable, while lithogenic or residual form is considered as incorporated into crystalline lattice of soil minerals and the most inactive. The carbonate, Fe-Mn oxide and organic matter-bound fractions could be relatively active depending on the physical and chemical properties of the medium. Metals bound to sulphides and organic matters are more stable and hard to take part in the geochemical cycle and mostly act as a sink and reservoir for pollutants (Prusty et al. 1994, and Yuan et al. 2004).

During the recent years studies of heavy metals distribution and contamination in ecosystem has received global prominence. Although numerous studies have highlighted heavy metal contamination in agricultural, lake and sewage soils, studies of their distribution in natural forest ecosystems are limited. Moreover, there are rare studies in multihabitat Protected Areas as that of KNP. The Keoladeo National Park, in spite of being an early Ramsar sites in the country is lacking studies on soil characterization and assessment of metal distribution in the soil from a viewpoint of mobility and bioavailability. Hence, the present study investigated the chemical partitioning of select metals in the soil profile of the Park. The objectives were to 1)

examine the distribution of Cu, Pb and Zn among different operationally defined geochemical pools, 2) assess the variation of the metal attachment amongst different habitats, and 3) assess the variation of metal distribution on a temporal scale, i.e. among different years.

7.2. MATERIALS AND METHODS

7.2.1. Soil Sampling, Processing and Analysis

The details of soil sampling and processing is discussed in the earlier chapter dealing with general sampling strategy under section 2.2.1. The samples were collected in mid June of the year up to a depth of 100 cm, from a trench of 1 m³ was dug for the purpose. Excluding the uppermost litter layer, samples from layers at 0, 25, 50, 75 and 100 cm depths were collected and processed for chemical partitioning study. Equal proportion of air dried samples from all the three sites was thoroughly mixed to get a representative sample of the habitat. It is recognized that vital information on distribution of trace metals may be lost when soil samples are dried (Tokalioğlu et al. 2003). However, drying is the best compromise to achieve stability of samples since moist soils are more difficult to homogenise, and microbial and chemical reactions may lead to transformations of the fractionation pattern, when immediate extraction is not possible (Rauret et al. 2000).

Soil pH and TOC (%) were measured following standard protocols as given in Table 2.2.1. The TOC values were later converted to the Total Organic Matter (TOM) by multiplying with 1.724 assuming that TOM contains 58% TOC. The carbonate content in the soil (CO₃-C, %) was estimated following rapid titration method of Allen (1989), wherein the dilute Hydrochloric Acid reacts with soil carbonates. The unspent acid gives an approximate measure of the carbonate content. The unspent acid is determined by titration against sodium hydroxide.

Sequential Extraction Technique (SET) of Tessier et al. (1979) was followed to extract the operationally defined geochemical pools and examine the distribution of the metals among these fractions and their relative mobility and bioavailability. Simultaneously blanks and internal standards were also run to verify the precision of the method and accuracy. The precision was generally more than 90%. For quality

assurance throughout the experiments and analyses, all extracting reagents were prepared using metal free, AnalaR grade chemicals procured from Qualigens Fine Chemicals Division of GlaxoSmithKline Pharmaceuticals Limited, Mumbai. The reagents were made in double distilled water, prepared using quartz double distillation assembly. Room temperature was about 30 °C, while extractions were carried out. Polypropylene centrifuge tubes and bottles were subjected to cleaning procedures prescribed by Laxen and Harrison (1981). The extracts were analyzed for the metals using Atomic Absorption Spectrometer (Perkin Elmer AAnalyst 800). The metals bound to five geochemical pools were identified, viz. Exchangeable (EXC), Carbonate bound (CA), Fe-Mn hydroxide bound (Fe-Mn), Organic matter and sulphides bound (OM-S) and Residual (Res). Aquaregia digestion was adopted to estimate the total metal content (Pseudototal). The details of the extraction process and the chemical reagents used are given in Table 7.2.1.

Table 7.2.1. Details of the sequential extraction process followed in the present study

Fraction	Details of the extraction procedure
F-1: Exchangeable (EXC)	1 gm soil + 8 ml of 1M Magnesium Chloride (pH 7.0) → 1 hour continuous agitation → Supernatant collected by centrifugation process.
F-2: Bound to Carbonates (CA)	Residue from step-1 + 8 ml of 1 M Sodium Acetate (pH 5.0). → 5 hours continuous agitation → Supernatant collected.
F-3: Bound to Fe-Mn oxides (Fe-Mn)	Residue from step-2 + 20 ml of 0.04 M Hydroxylamine Hydrochloric Acid → digestion at 96 °C for 6 hours with occasional shaking → Supernatant collected.
F-4: Bound to organic matter and sulphides (OM-S)	Residue from step-3 + 3 ml of 0.02 M Nitric Acid + 8 ml of 30% hydrogen peroxide → digestion at 85 °C for 5 hours with occasional shaking + 5 ml of 3.2-M Ammonium Acetate → agitation for 30 minutes → Supernatant collected.
F-5: Residual (RES)	Residue from step-4 → Aqua Regia digestion for 2 hours.
The quantity of chemical reagents as mentioned in the table is for 1 gm soil.	
Source: Tessier et al. 1979 (F1 to F4) and Tokalioglu et al. (2003) for F-5	

7.3. RESULTS AND DISCUSSION

7.3.1. Cu

The variation of Cu concentration in the soil profile among different years and habitats is given in Figure 7.3.1. Overall, the concentration of Cu in the Park ranged from 17.4 to 50.5 mg/kg. The presently reported Cu level is higher than the level reported by Mohanraj et al. (2000a) from a natural forest site in Siruvani Hills, Southern India. The level reported by them ranged between 5.0 and 28 mg/kg. The total Cu content in uncontaminated soil ranges from 6 to 60 mg/kg (Altaher 2001). Of the three habitats, the highest concentration of Cu was seen in wetland and the least concentration in woodland habitats. In wetland Cu concentration ranged from 36.7 to 49.2 mg/kg soil, and in woodland, it was from 17.4 to 28.7 mg/kg soil. Cu in grassland ranged between 23.6 and 46.4 mg/kg soil. However, the presently recorded values are well within that reported from Doon Valley soils, outer Himalaya, India (Purohit et al. 2001, i.e. 8.0 to 107 mg/kg). In wetland, Cu was seen least at the bottom of the trench during 2005 and highest in the surface layer during 2004. In woodland, Cu concentrated was lowest at the surface layer of the trench during 2005 and highest at the bottom of the trench during 2003. Grassland was found to have lowest Cu at a depth of 25 cm during 2003 and highest in the surface layer during 2004. No consistent pattern of Cu along the soil profile was seen in any of the habitats during the whole duration of the study. The level of Cu in soil showed significant variation only among the habitats (ANOVA, $P < 0.05$). No significant variation was observed among the years and soil layers. The Post-Hoc test, i.e. LSD carried out revealed that all the habitats are distinct and significant from each other regarding the Cu level in soil (Table 7.3.1). The Cu levels higher in the surface layers than the subsequent layers in certain habitats as in the case of wetland and grassland might be because of the contribution from the plant litters during the process of decomposition. The results of the earlier works by the authors in the KNP reports several species of plants showing notable uptake rates for elements such as Cu, Pb and Zn from the soil (Azeez et al. 2007, and Prusty et al. 2007). The runoff entering the KNP from the agricultural field outside the Park also might be bringing in the metal considerably. Thuy et al. (2005) also opines that agrochemicals such as fertilizers and pesticides are a major source of metals such as Cu.

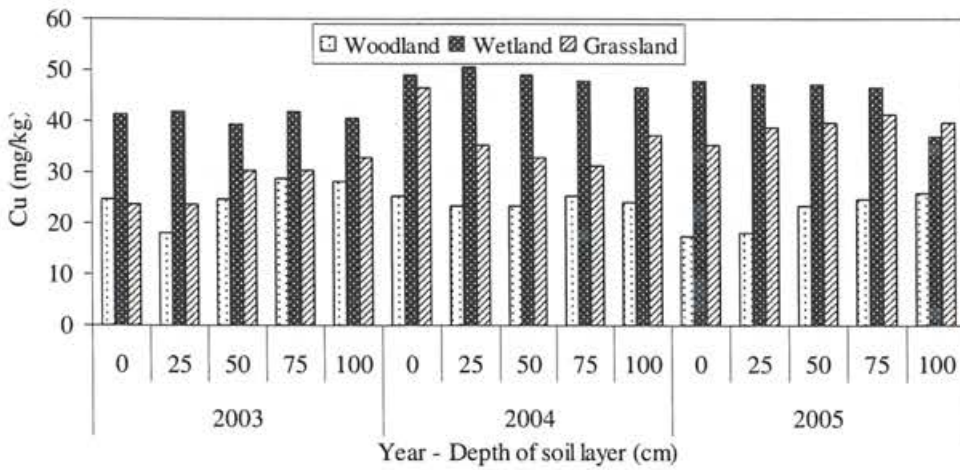


Figure 7.3.1. Habitat – Depth wise Variation of Cu in soil

Table 7.3.1. LSD of Cu (Habitats)

Multiple Comparisons

Dependent Variable: CU

LSD

(I) HABITAT	(J) HABITAT	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Woodland	Wetland	-21.1587*	1.75052	.000	-24.6913	-17.6260
	Grassland	-10.8491*	1.75052	.000	-14.3818	-7.3164
Wetland	Woodland	21.1587*	1.75052	.000	17.6260	24.6913
	Grassland	10.3096*	1.75052	.000	6.7769	13.8423
Grassland	Woodland	10.8491*	1.75052	.000	7.3164	14.3818
	Wetland	-10.3096*	1.75052	.000	-13.8423	-6.7769

*. The mean difference is significant at the .05 level.

The association of Cu to various geochemical phases was presented in Figure 7.3.2 to Figure 7.3.4. Of the habitats studied, Cu was mostly attached with Fe-Mn phase in woodland and wetland habitats while in grassland it was RES phase. Nevertheless, Cu was least contained in the EXC phase in all the habitats. In woodland, Cu was seen in the range of 2.1 to 99.4% in the Fe-Mn phase and 0.01 to 1.5% in the EXC phase (Figure 7.3.2). In this habitat, fractions in terms of Cu concentration was in the order Fe-Mn > RES > OM-S > CA > EXC. In wetland also the order of the fractions in terms of Cu concentration was Fe-Mn > RES > OM-S > CA > EXC. Cu was seen in the range of 5.8 to 78.4% in the Fe-Mn phase and 0.01 to 0.7% in the EXC phase

(Figure 7.3.3). In contrast, in grassland soil, in terms of Cu concentration the order of the fractions was RES > Fe-Mn > OM-S > CA > EXC. Cu was seen in the range of 30.4 to 76.2% in the residual phase and 0.01 to 0.7% in the EXC phase (Figure 7.3.4). Invariably all the metals were seen in lowest concentration in the EXC pool followed by CA phase.

The results indicate two major points: (1) Fe-Mn phase is the important binding site for Cu in both woodland and wetland soil and the reducible Fe and Mn plays a major role in binding these metals. (2) RES phase is the important binding site in the grassland soil indicating that the major proportion of Cu is incorporated in the silicate mineral matrix. This may indicate that this element was derived from natural geological sources. RES phase represents the second most significant sink for woodland and wetland after Fe-Mn phase.

It has been shown that in Saline - alkaline soils, as in the case of KNP, the second extraction step (CA phase) may not be effective in removing all the carbonate minerals into solution. Metals extracted in step 3 (Fe-Mn phase) therefore may contain a proportion of the carbonate forms in addition to those bound to Fe-Mn oxides (Maskall and Thronton 1998). Of these three habitats, Cu had higher preferences to the CA phase in woodland followed by wetland and grassland. Cu was seen in the range of 0.01 to 3.38% in the CA phase in woodland, while in wetland, it was 0.01 to 2.8% and in grassland, it was 0.01 to 1.9%. The observed higher attachment of Cu to the Fe-Mn phase is consistent with observations of Saha et al. (1991). However, the presently reported values are higher than reported by Saha et al. (1991). This may be due to the higher content of amorphous Fe and Mn oxide in soils. The contents, however, recorded a decrease with depth in all the habitats.

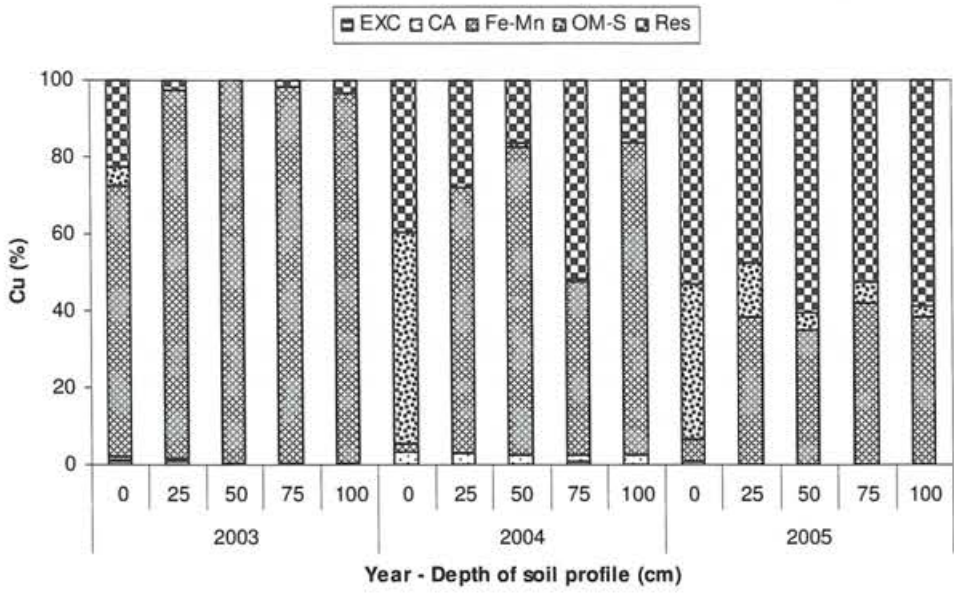


Figure 7.3.2. Cu fractionation in woodland

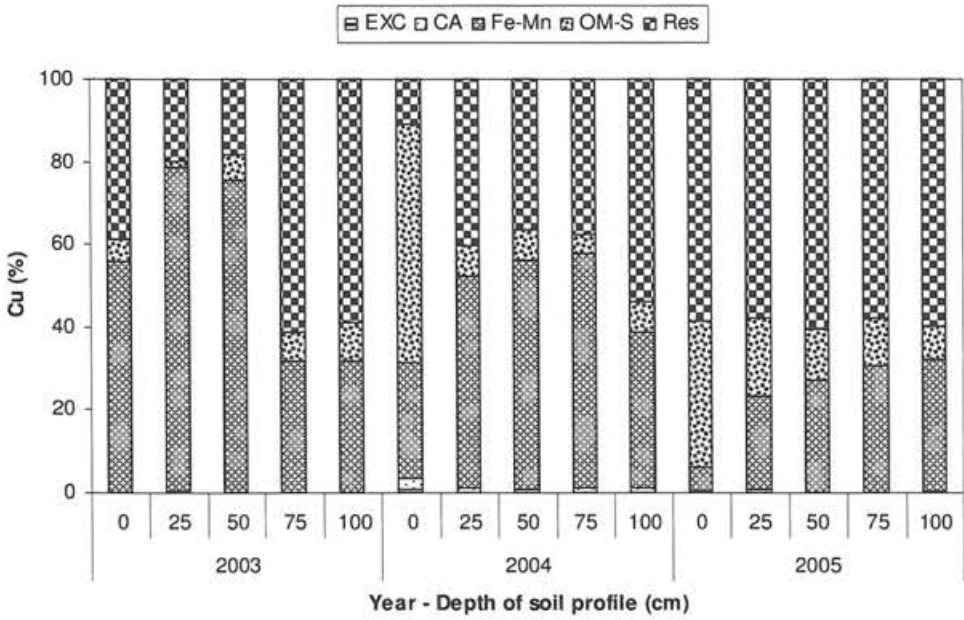


Figure 7.3.3. Cu fractionation in wetland

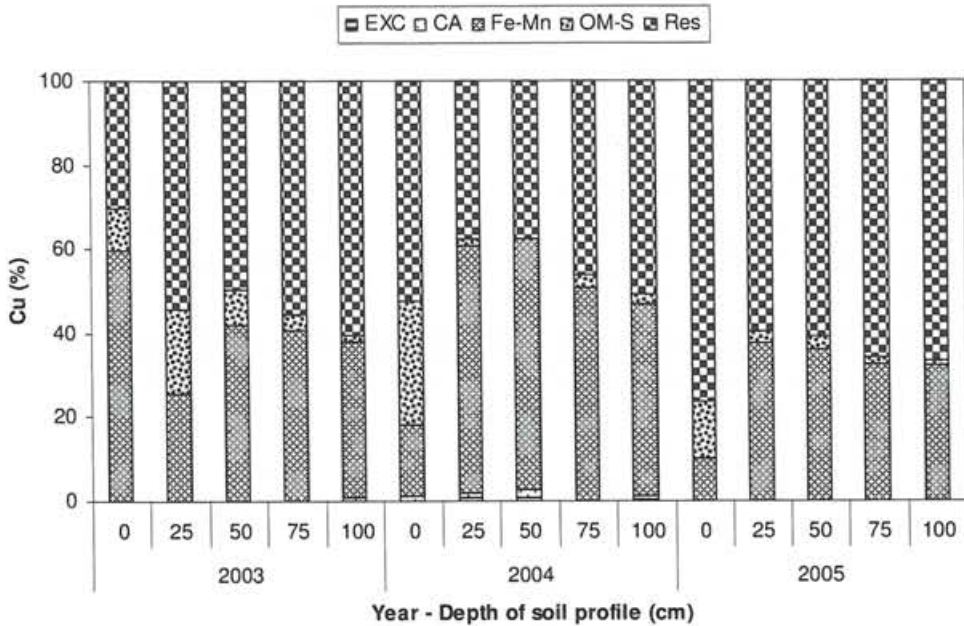


Figure 7.3.4. Cu fractionation in grassland

The extent of association among different fractions, and with TOM (%) and $\text{CO}_3\text{-C}$ (%) is shown in Table 7.3.2. Irrespective of the habitat, only among the non-residual fractions only Fe-Mn was negatively correlated with the OM-S and RES fraction. Two important results were reasonably expected during the present investigation: (1) Total organic matter content of the soil (TOM, %) is very likely to show positive correlation with the OM-S fraction and (2) $\text{CO}_3\text{-C}$ content of soil is positively correlated with the CA phase in the case of all the metals. However, in the wetland soil, the OM-S was found not significantly positively correlated ($P < 0.05$) with the TOM (%) in soil and it is felt that this needs to be further investigated. Similarly no significant correlation between CA fraction and $\text{CO}_3\text{-C}$ content in soil was seen in any of the habitats ($P < 0.05$), requiring further investigation.

The Univariate test performed following the General Linear Model (GLM) showed that the distribution of metals was significant only among different fractions ($P < 0.05$) and hence the Post-hoc analysis (One-Way ANOVA - LSD) was performed on the fractions. The results are shown in Table 7.3.3 to Table 7.3.5. Of the habitats studied, Fe-Mn and RES phase were distinct from the other fractions and found to contribute significantly to the reported variability in the case of terrestrial habitats, i.e. woodland

and grassland. However, in the case of wetland it was only OM-S fraction (Table 7.3.4). The findings in the case of terrestrial habitats indicate the lithogenic nature of the metals. Hence, Fe-Mn hydrous oxides can be regarded as a common scavenger of Cu in the terrestrial blocks of the Park. Although the attachment of metals to Fe-Mn oxides indicates their relative immobilization, the situation is largely dependent on the micro environmental conditions.

Table 7.3.2. Correlation matrix of Cu fractions in the soil

Woodland								
	EXC	CA	Fe-Mn	OM-S	Res	Total metal	TOM (%)	CO ₃ -C (%)
EXC	1.000							
CA	-.316	1.000						
Fe-Mn	.234	-.116	1.000					
OM-S	-.060	.241	-.772*	1.000				
Res	-.299	-.056	-.878*	.375	1.000			
Total metal	-.334	.175	.304	-.288	-.231	1.000		
TOM (%)	.434	.038	-.471	.661*	.186	-.277	1.000	
CO ₃ -C (%)	.187	.299	.370	-.017	-.541*	.075	.037	1.000
Wetland								
	EXC	CA	Fe-Mn	OM-S	Res	Total metal	TOM (%)	CO ₃ -C (%)
EXC	1.000							
CA	.789*	1.000						
Fe-Mn	-.189	-.078	1.000					
OM-S	.839*	.638*	-.569*	1.000				
Res	-.535*	-.501	-.676*	-.221	1.000			
Total metal	.280	.582*	-.257	.408	-.074	1.000		
TOM (%)	.338	.121	-.048	.366	-.262	-.010	1.000	
CO ₃ -C (%)	-.105	-.216	-.202	-.019	.262	-.096	-.191	1.000
Grassland								
	EXC	CA	Fe-Mn	OM-S	Res	Total metal	TOM (%)	CO ₃ -C (%)
EXC	1.000							
CA	.787*	1.000						
Fe-Mn	.570*	.366	1.000					
OM-S	-.344	-.055	-.592*	1.000				
Res	-.509	-.466	-.826*	.038	1.000			
Total metal	.021	.166	-.396	.018	.455	1.000		
TOM (%)	-.275	-.069	-.617*	.673*	.289	.176	1.000	
CO ₃ -C (%)	-.393	-.110	-.107	-.250	.312	.157	-.070	1.000

45 Sample size, ± .514 critical value, P < 0.05 (two-tail), * Significant

EXC = Exchangeable metal, CA = Carbonate bound metal, Fe-Mn = Iron – Manganese bound metal, OM-S = Bound to organic matter and sulphur, Total metal = Pseudototal metal, TOM = Total Organic Matter, CO₃-C = Carbonate carbon

Table 7.3.3. LSD of Cu – fractions (Woodland)

Multiple Comparisons

Dependent Variable: CU
LSD

(I) FRACTION	(J) FRACTION	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
EXC	CA	-.5853	7.05596	.934	-14.6579	13.4874
	Fe-Mn	-59.3975*	7.05596	.000	-73.4701	-45.3248
	OM-S	-8.2695	7.05596	.245	-22.3421	5.8032
	RES	-29.8655*	7.05596	.000	-43.9382	-15.7929
CA	EXC	.5853	7.05596	.934	-13.4874	14.6579
	Fe-Mn	-58.8122*	7.05596	.000	-72.8849	-44.7395
	OM-S	-7.6842	7.05596	.280	-21.7569	6.3885
	RES	-29.2803*	7.05596	.000	-43.3529	-15.2076
Fe-Mn	EXC	59.3975*	7.05596	.000	45.3248	73.4701
	CA	58.8122*	7.05596	.000	44.7395	72.8849
	OM-S	51.1280*	7.05596	.000	37.0553	65.2007
	RES	29.5319*	7.05596	.000	15.4593	43.6046
OM-S	EXC	8.2695	7.05596	.245	-5.8032	22.3421
	CA	7.6842	7.05596	.280	-6.3885	21.7569
	Fe-Mn	-51.1280*	7.05596	.000	-65.2007	-37.0553
	RES	-21.5961*	7.05596	.003	-35.6687	-7.5234
RES	EXC	29.8655*	7.05596	.000	15.7929	43.9382
	CA	29.2803*	7.05596	.000	15.2076	43.3529
	Fe-Mn	-29.5319*	7.05596	.000	-43.6046	-15.4593
	OM-S	21.5961*	7.05596	.003	7.5234	35.6687

*. The mean difference is significant at the .05 level.

Table 7.3.4. LSD of Cu – fractions (Wetland)

Multiple Comparisons

Dependent Variable: CU
LSD

(I) FRACTION	(J) FRACTION	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
EXC	CA	-.5568	4.95178	.911	-10.4328	9.3193
	Fe-Mn	-41.2802*	4.95178	.000	-51.1563	-31.4042
	OM-S	-13.2447*	4.95178	.009	-23.1208	-3.3687
	RES	-44.6378*	4.95178	.000	-54.5138	-34.7618
CA	EXC	.5568	4.95178	.911	-9.3193	10.4328
	Fe-Mn	-40.7235*	4.95178	.000	-50.5995	-30.8475
	OM-S	-12.6880*	4.95178	.013	-22.5640	-2.8120
	RES	-44.0810*	4.95178	.000	-53.9570	-34.2050
Fe-Mn	EXC	41.2802*	4.95178	.000	31.4042	51.1563
	CA	40.7235*	4.95178	.000	30.8475	50.5995
	OM-S	28.0355*	4.95178	.000	18.1595	37.9115
	RES	-3.3575	4.95178	.500	-13.2335	6.5185
OM-S	EXC	13.2447*	4.95178	.009	3.3687	23.1208
	CA	12.6880*	4.95178	.013	2.8120	22.5640
	Fe-Mn	-28.0355*	4.95178	.000	-37.9115	-18.1595
	RES	-31.3930*	4.95178	.000	-41.2690	-21.5170
RES	EXC	44.6378*	4.95178	.000	34.7618	54.5138
	CA	44.0810*	4.95178	.000	34.2050	53.9570
	Fe-Mn	3.3575	4.95178	.500	-6.5185	13.2335
	OM-S	31.3930*	4.95178	.000	21.5170	41.2690

*. The mean difference is significant at the .05 level.

Table 7.3.5. LSD of Cu – fractions (Grassland)

Multiple Comparisons

Dependent Variable: CU
LSD

(I) FRACTION	(J) FRACTION	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
EXC	CA	-.2417	3.42211	.944	-7.0669	6.5835
	Fe-Mn	-38.8850*	3.42211	.000	-45.7102	-32.0598
	OM-S	-6.7867	3.42211	.051	-13.6119	.0385
	RES	-53.4141*	3.42211	.000	-60.2393	-46.5889
CA	EXC	.2417	3.42211	.944	-6.5835	7.0669
	Fe-Mn	-38.6433*	3.42211	.000	-45.4685	-31.8181
	OM-S	-6.5450	3.42211	.060	-13.3702	.2802
	RES	-53.1724*	3.42211	.000	-59.9976	-46.3472
Fe-Mn	EXC	38.8850*	3.42211	.000	32.0598	45.7102
	CA	38.6433*	3.42211	.000	31.8181	45.4685
	OM-S	32.0983*	3.42211	.000	25.2731	38.9235
	RES	-14.5291*	3.42211	.000	-21.3543	-7.7039
OM-S	EXC	6.7867	3.42211	.051	-.0385	13.6119
	CA	6.5450	3.42211	.060	-.2802	13.3702
	Fe-Mn	-32.0983*	3.42211	.000	-38.9235	-25.2731
	RES	-46.6274*	3.42211	.000	-53.4526	-39.8022
RES	EXC	53.4141*	3.42211	.000	46.5889	60.2393
	CA	53.1724*	3.42211	.000	46.3472	59.9976
	Fe-Mn	14.5291*	3.42211	.000	7.7039	21.3543
	OM-S	46.6274*	3.42211	.000	39.8022	53.4526

*. The mean difference is significant at the .05 level.

7.3.2. Pb

The distribution and variation of Pb concentration in the soil profile among different years and habitats is given in Figure 7.3.5. Overall, the concentration of Pb in soil of the multihabitat system of the Park ranged from 5.8 to 32.1 mg/kg. Of the three habitats, Pb concentrated highest in wetland and least in woodland. In wetland, Pb level in soil was seen in the range of 8.7 to 32.1 mg/kg soil, and in woodland, it was from 5.8 to 11.7 mg/kg soil. In grassland soil, Pb concentration ranged between 8.7 and 13.1 mg/kg soil. The values are lower than that reported by Mohanraj et al (2000a), i.e. 4.0 to 376.0 mg/kg. In the wetland system of the Park, Pb was seen least at the bottom layer of the trench during 2005 and highest in the surface layer during 2004. In the woodland habitat, Pb was seen least at the surface layer and highest at the bottom of the trench during 2003. In grassland, Pb level was found minimum at the bottom of the soil profile, while maximum concentration was seen at a depth of 50 cm

during 2005. The level of Pb in soil had a gradual declining trend only in the case of wetland during 2003. In woodland, the level initially decreased from the surface layer to the following layer followed by an increase and subsequently reading steady level (Figure 7.3.5). Univariate test of variance showed that Pb concentration varied significantly only among habitats ($P < 0.05$). Therefore, the Post-Hoc test (i.e. LSD) carried out revealed that aquatic area of the KNP is distinctly different from its terrestrial counterparts (Table 7.3.6). This variation in this metal level among habitat is suggestive of different source of the metal and a significant level of input from the exterior sources through the input water. The higher Pb levels in the surface layers compared to the subsequent layers in certain habitats as in the case of wetland might be because of any of the following causes:

- The contribution from the plant litters during the process of decomposition [The results of the earlier works by the authors in the KNP reports several species of plants showing notable uptake rates for elements such as Pb the soil (Azeez et al. 2007, and Prusty et al. 2007)].
- Automobile exhausts also could be one of the substantial sources for metals such as Pb (Baker 1990, and Prusty and Azeez 2007). KNP has one of the major and busy National Highway (Delhi-Jaipur) traversing beside its immediate boundary. Moreover, its proximity to Bharatpur city might add substantially to the cause.
- Higher level of Pb associated with the suspended particulate matter arising from various sources including automobiles in the atmosphere also could contribute to the cause considerably (Mohanraj et al. 2000a).

Atmospheric deposition has been a significant source of metals in soil. Long-range atmospheric transport of certain heavy metals and its subsequent deposition in Norwegian forest soil (Steinnes et al. 1997) and lakes (Steinnes and Henriksen 1993) are well-studied examples. The first evidence of significant surface soil contamination with heavy metals from long-range transport was reported from north-eastern United States (Reiners et al. 1975, and Siccama and Smith 1978) in the case of Pb and later shown also for Cu and Zn (Friendland et al. 1984).

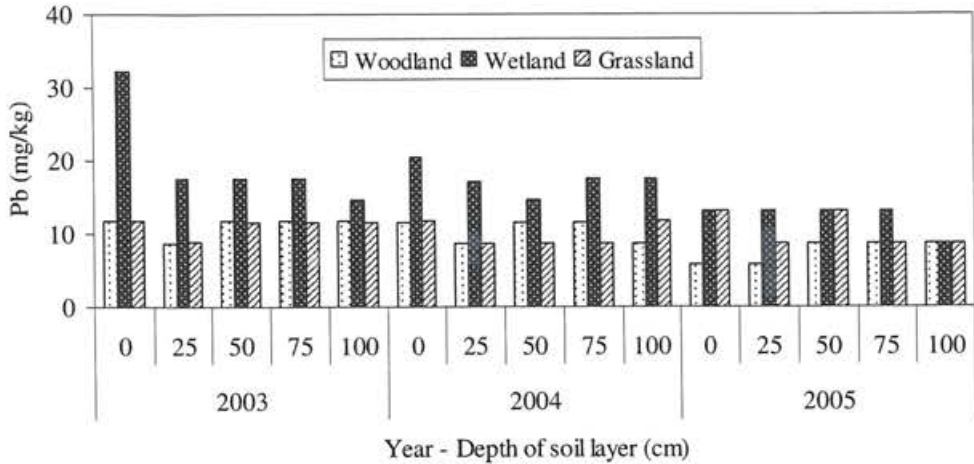


Figure 7.3.5. Habitat – Depth wise Variation of Pb in soil

Table 7.3.6. LSD of Pb (Habitats)

Multiple Comparisons

Dependent Variable: PB
LSD

(I) HABITAT	(J) HABITAT	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Woodland	Wetland	-6.8091*	1.23967	.000	-9.3108	-4.3073
	Grassland	-.7885	1.23967	.528	-3.2903	1.7132
Wetland	Woodland	6.8091*	1.23967	.000	4.3073	9.3108
	Grassland	6.0205*	1.23967	.000	3.5188	8.5223
Grassland	Woodland	.7885	1.23967	.528	-1.7132	3.2903
	Wetland	-6.0205*	1.23967	.000	-8.5223	-3.5188

*. The mean difference is significant at the .05 level.

Invariably in all the habitats, Pb was mostly associated with Fe-Mn phase while it was seen lowest in the EXC phase (Figure 7.3.6 to Figure 7.3.8). However, along the depth profile the higher level of Pb gradually become higher in RES phase. In contrast, the percentage preferences towards the OM-S phase also showed a slim rise slightly from 2003 to the year 2004 (Figure 7.3.6, Figure 7.3.7 and Figure 7.3.8). In woodland soil, Pb was mostly contained in the multiple hydroxides fraction during 2003 and the association shifted slightly towards the RES phase towards the end of the study, i.e. during 2005. Overall Pb was mostly associated with the Fe-Mn pool and associated the least attached with the EXC phase (Figure 7.3.6). Pb was seen in the

range of 37.9 to 81.03% in the Fe-Mn oxide phase and 0.02 to 8.6% in the EXC phase. In wetland soil, Pb was seen in the range of 33.5 to 88.5% in the Fe-Mn oxide phase and 0.01 to 7.6% in the EXC phase. In grassland soil, Pb was seen in the range of 36.6 to 74.0 % in the Fe-Mn oxide phase and 0.02 to 7.5% in the EXC phase. In all the three habitats, the order of fraction in terms of Pb concentration was Fe-Mn > RES > OM-S > CA > EXC.

As noted earlier, among the non-residual phases, Fe-Mn oxide fraction was the most important one for Pb in all the habitats followed by CA phase. The results indicate that Fe-Mn phase is an important binding site for Pb and the reducible Fe and Mn plays a major role in binding these metals. RES phase was seen as the second highest scavenger of the metal. This may indicate that this element was derived from natural geological sources. As the sampling was done in the summer month that experiences less soil organic matter in the KNP soil, as evidenced by our earlier reports, the metals mostly remain attached with the Fe-Mn oxides phase and that bound to organic matter (OM-S) phase was less. Fan et al. (2002) and Li et al. (2000a) have also reported similar findings. The apparently greater proportion of Pb in Fe-Mn (hydroxylamine hydrochloride-extractable) fraction compared to Cu and Zn was reported from other environments (Jones 1987). In KNP, a considerable part of the metals is contained in CA phase. In the woodland, the proportion ranges between 0.02 and 16.6%, in wetland soil the range was from 0.01 to 20.4% and in grassland soil from 3.6 to 23.06%. Of these three habitats, Pb had higher preferences to the CA phase in grassland than in wetland and woodland. Although Pb in all the habitats showed lowest presence in the exchangeable pool, the order of the habitats with average percentage of Pb bound in the EXC pool (in parenthesis) was grassland ($2.4 \pm 3.4\%$) < wetland ($1.8 \pm 2.8\%$) < woodland ($1.4 \pm 3.0\%$). This is an indication of higher anthropogenic input of Pb and its relatively higher likely mobility in grassland habitats than in wetland and woodland habitats.

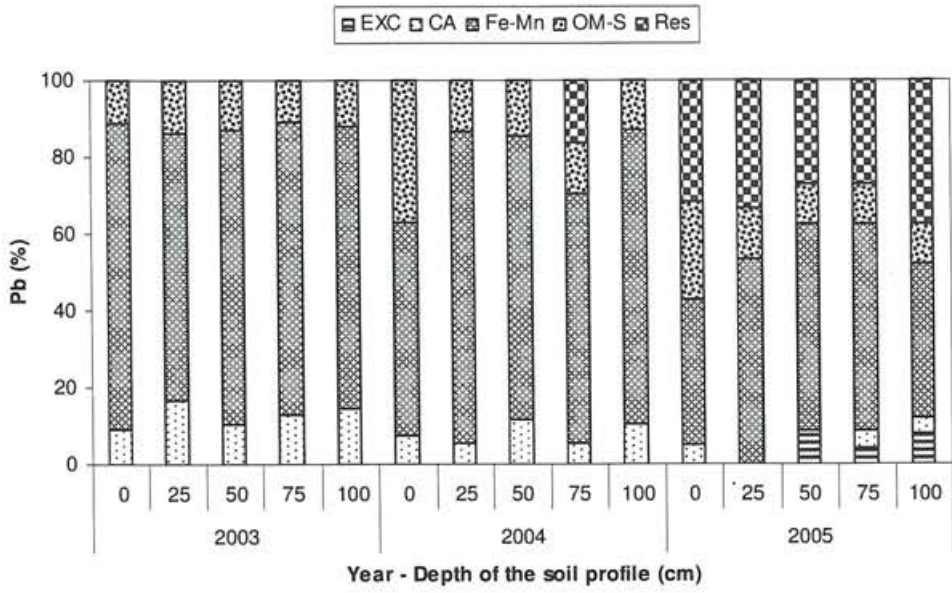


Figure 7.3.6. Pb fractionation in woodland

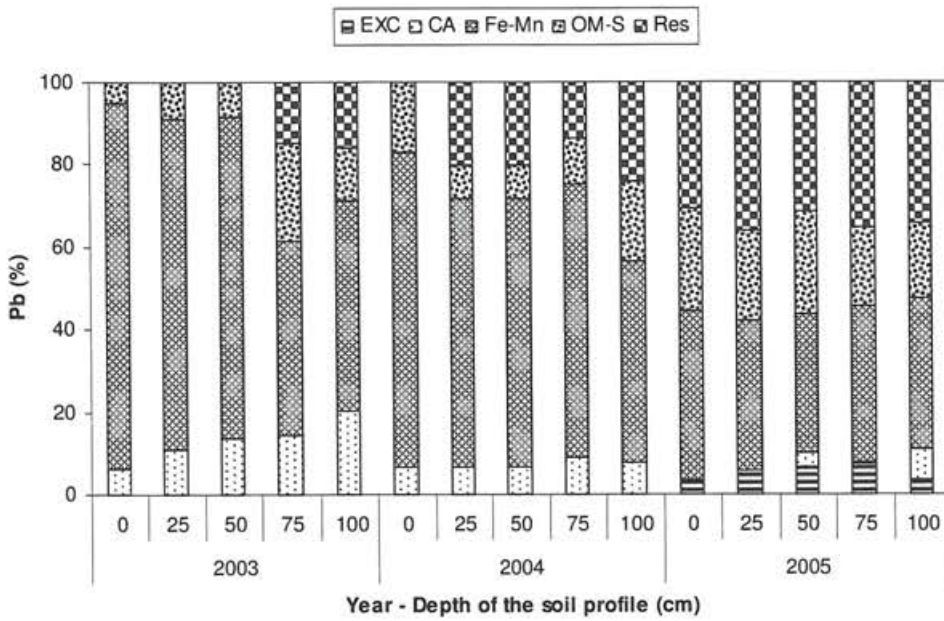


Figure 7.3.7. Pb fractionation in wetland

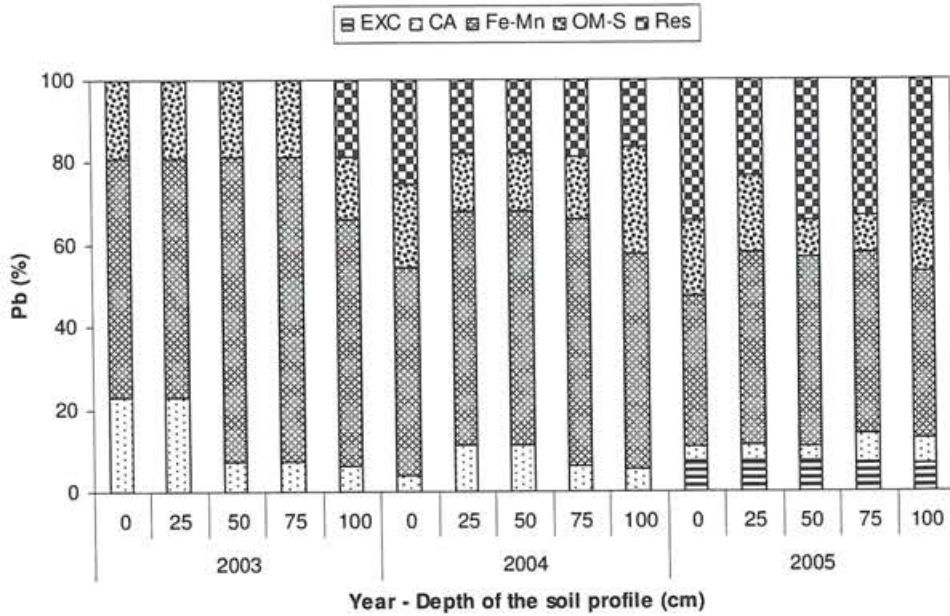


Figure 7.3.8. Pb fractionation in grassland

The extent of association among different fractions, and with TOM (%) and CO₃-C (%) is shown in Table 7.3.7. In all the habitats, Fe-Mn fraction was negatively correlated with RES fraction. However, positive correlation of Fe-Mn fraction with the total metal content was seen only in woodland and wetland soils ($p < 0.05$, Table 7.3.7). Two important and significant observations expected during the present investigation were (1) Total organic matter content of the soil (TOM, %) is likely to be positively correlated with the OM-S fraction and (2) CO₃-C content of soil is likely to be positively correlated with the CA phase in the case of all the metals. However, only in woodland, TOM (%) and OM-S were positively correlated and in other habitats, no significant correlation could be seen. Moreover, in wetland it was a negative correlation. The absence of any significant positive correlation between CA phase and the CO₃-C content in soil requires further investigation.

Table 7.3.7. Correlation matrix of Pb fractions in the soil

Woodland								
	EXC	CA	Fe-Mn	OM-S	Res	Total metal	TOM (%)	CO ₃ -C (%)
EXC	1.000							
CA	-.533*	1.000						
Fe-Mn	-.550*	.614*	1.000					
OM-S	-.301	-.032	-.321	1.000				
Res	.633*	-.783*	-.879*	-.096	1.000			
Total metal	-.224	.543*	.598*	-.017	-.686*	1.000		
TOM (%)	-.230	-.088	-.228	.558*	.027	-.091	1.000	
CO ₃ -C (%)	-.690*	.415	.571*	.139	-.600*	.330	.037	1.000
Wetland								
	EXC	CA	Fe-Mn	OM-S	Res	Total metal	TOM (%)	CO ₃ -C (%)
EXC	1.000							
CA	-.682*	1.000						
Fe-Mn	-.745*	.355	1.000					
OM-S	.626*	-.379	-.834*	1.000				
Res	.770*	-.565*	-.927*	.655*	1.000			
Total metal	-.526*	.156	.769*	-.533*	-.729*	1.000		
TOM (%)	-.173	-.220	.490	-.234	-.418	.791*	1.000	
CO ₃ -C (%)	.451	-.120	-.321	.105	.338	-.430	-.191	1.000
Grassland								
	EXC	CA	Fe-Mn	OM-S	Res	Total metal	TOM (%)	CO ₃ -C (%)
EXC	1.000							
CA	-.435	1.000						
Fe-Mn	-.773*	.281	1.000					
OM-S	-.423	.126	.204	1.000				
Res	.744*	-.659*	-.847*	-.461	1.000			
Total metal	.017	-.247	.037	.218	.012	1.000		
TOM (%)	.228	-.070	-.445	.219	.276	.490	1.000	
CO ₃ -C (%)	.446	-.160	-.203	-.780*	.396	-.359	-.070	1.000

45 Sample size, ± .514 critical value, P < 0.05 (two-tail), *: Significant

EXC = Exchangeable metal, CA = Carbonate bound metal, Fe-Mn = Iron – Manganese bound metal, OM-S = Bound to organic matter and sulphur, Total metal = Pseudototal metal, TOM = Total Organic Matter, CO₃-C = Carbonate carbon

The Univariate test performed following the General Linear Model (GLM) showed that the distribution of metals was significant only among different fractions ($P < 0.05$). Therefore, the Post-hoc analysis (One-Way ANOVA - LSD) was performed on the fractions and the results are given in Table 7.3.8 to Table 7.3.10. In all the habitats, Fe-Mn has emerged to be the singly most dominating fraction contributing to the reported variability. In woodland and in the wetland habitats, Fe-Mn is the only fraction that is significantly distinct from the rest, while in the grassland soil, the fractions that appear important are non-residual; Fe-Mn, CA and EXC. Next to the Fe-Mn phase, Pb was seen in RES phase. However, detailed analysis revealed the importance of the non-residual phases as the scavenger of the metal. Hence, Fe-Mn hydrous oxides can be regarded as a common scavenger for all metals under study. Although the attachment of metals to Fe-Mn oxides indicates their relative immobilization, the situation is more or less dependent on the micro environmental conditions. The exchangeability of metals on soils can be greatly affected by pH. Low soil pH greatly enhances solubility of metals, which in turn increases their bio-accessibility concurrently reducing the capability of soils to sorb metals (Kuo et al. 1983). Solubility of heavy metals can be by orders of magnitude different between near-neutral and higher pH (Wang et al. 2004). The terrestrial habitats in KNP have a relatively higher pH. The highest pH in the terrestrial areas of KNP was reported to be 9.97. The $\text{CO}_3\text{-C}$ content in the soil of the woodland system in KNP ranged from 1.97 to 24.5%. Maskall and Thornton (1998) reported similar observations and ascribe these to the release of Ca from soil. It can be explained by specific adsorption, which is more important for Pb than other two metals (Borůvka et al. 1997). It is felt to assess realistically the mobility of the metals, especially when most fractions of metals are in non-residual fractions such as Fe-Mn, it is imperative to have knowledge on the other associated soil parameters.

Chapter 7. Trace Metals: Distribution and Partitioning

Table 7.3.8. LSD of Pb – fractions (Woodland)

Multiple Comparisons

Dependent Variable: PB
LSD

(I) FRACTION	(J) FRACTION	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
EXC	CA	-6.3900	3.72452	.091	-13.8183	1.0383
	Fe-Mn	-62.9951*	3.72452	.000	-70.4235	-55.5668
	OM-S	-13.4070*	3.72452	.001	-20.8353	-5.9787
	RES	-10.1138*	3.72452	.008	-17.5421	-2.6855
CA	EXC	6.3900	3.72452	.091	-1.0383	13.8183
	Fe-Mn	-56.6051*	3.72452	.000	-64.0335	-49.1768
	OM-S	-7.0170	3.72452	.064	-14.4453	.4113
	RES	-3.7238	3.72452	.321	-11.1521	3.7045
Fe-Mn	EXC	62.9951*	3.72452	.000	55.5668	70.4235
	CA	56.6051*	3.72452	.000	49.1768	64.0335
	OM-S	49.5881*	3.72452	.000	42.1598	57.0165
	RES	52.8813*	3.72452	.000	45.4530	60.3097
OM-S	EXC	13.4070*	3.72452	.001	5.9787	20.8353
	CA	7.0170	3.72452	.064	-.4113	14.4453
	Fe-Mn	-49.5881*	3.72452	.000	-57.0165	-42.1598
	RES	3.2932	3.72452	.380	-4.1351	10.7215
RES	EXC	10.1138*	3.72452	.008	2.6855	17.5421
	CA	3.7238	3.72452	.321	-3.7045	11.1521
	Fe-Mn	-52.8813*	3.72452	.000	-60.3097	-45.4530
	OM-S	-3.2932	3.72452	.380	-10.7215	4.1351

*. The mean difference is significant at the .05 level.

Table 7.3.9. LSD of Pb – fractions (Wetland)

Multiple Comparisons

Dependent Variable: PB
LSD

(I) FRACTION	(J) FRACTION	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
EXC	CA	-5.6799	4.04755	.165	-13.7525	2.3927
	Fe-Mn	-54.9238*	4.04755	.000	-62.9964	-46.8512
	OM-S	-13.6226*	4.04755	.001	-21.6952	-5.5500
	RES	-16.7020*	4.04755	.000	-24.7745	-8.6294
CA	EXC	5.6799	4.04755	.165	-2.3927	13.7525
	Fe-Mn	-49.2439*	4.04755	.000	-57.3165	-41.1713
	OM-S	-7.9427	4.04755	.054	-16.0153	.1299
	RES	-11.0221*	4.04755	.008	-19.0946	-2.9495
Fe-Mn	EXC	54.9238*	4.04755	.000	46.8512	62.9964
	CA	49.2439*	4.04755	.000	41.1713	57.3165
	OM-S	41.3012*	4.04755	.000	33.2286	49.3737
	RES	38.2218*	4.04755	.000	30.1493	46.2944
OM-S	EXC	13.6226*	4.04755	.001	5.5500	21.6952
	CA	7.9427	4.04755	.054	-.1299	16.0153
	Fe-Mn	-41.3012*	4.04755	.000	-49.3737	-33.2286
	RES	-3.0793	4.04755	.449	-11.1519	4.9932
RES	EXC	16.7020*	4.04755	.000	8.6294	24.7745
	CA	11.0221*	4.04755	.008	2.9495	19.0946
	Fe-Mn	-38.2218*	4.04755	.000	-46.2944	-30.1493
	OM-S	3.0793	4.04755	.449	-4.9932	11.1519

*. The mean difference is significant at the .05 level.

Table 7.3.10. LSD of Pb – Fractions (Grassland)

Multiple Comparisons

Dependent Variable: PB
LSD

(I) FRACTION	(J) FRACTION	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
EXC	CA	-6.2347*	3.06070	.045	-12.3390	-.1303
	Fe-Mn	-51.8199*	3.06070	.000	-57.9242	-45.7155
	OM-S	-14.3561*	3.06070	.000	-20.4604	-8.2517
	RES	-15.6058*	3.06070	.000	-21.7102	-9.5014
CA	EXC	6.2347*	3.06070	.045	.1303	12.3390
	Fe-Mn	-45.5852*	3.06070	.000	-51.6896	-39.4808
	OM-S	-8.1214*	3.06070	.010	-14.2258	-2.0170
	RES	-9.3711*	3.06070	.003	-15.4755	-3.2668
Fe-Mn	EXC	51.8199*	3.06070	.000	45.7155	57.9242
	CA	45.5852*	3.06070	.000	39.4808	51.6896
	OM-S	37.4638*	3.06070	.000	31.3594	43.5682
	RES	36.2141*	3.06070	.000	30.1097	42.3184
OM-S	EXC	14.3561*	3.06070	.000	8.2517	20.4604
	CA	8.1214*	3.06070	.010	2.0170	14.2258
	Fe-Mn	-37.4638*	3.06070	.000	-43.5682	-31.3594
	RES	-1.2497	3.06070	.684	-7.3541	4.8546
RES	EXC	15.6058*	3.06070	.000	9.5014	21.7102
	CA	9.3711*	3.06070	.003	3.2668	15.4755
	Fe-Mn	-36.2141*	3.06070	.000	-42.3184	-30.1097
	OM-S	1.2497	3.06070	.684	-4.8546	7.3541

*. The mean difference is significant at the .05 level.

7.3.3. Zn

The variation in the level of Zn in the soil profile among different years is presented in Figure 7.3.9. Of all the habitats studied, Zn was seen in high level in wetland soil followed by grassland and woodland. In the wetland, Zn was seen in the range of 56.4 to 66.9 mg/kg and in grassland, it was 35.9 to 63.2 mg/kg soil. In woodland, Zn ranged between 38.6 and 56.5 mg/kg. In the wetland, Zn concentrated least at a depth of 25 cm during 2003 and the highest in the same layer during the next year, i.e. 2004. In contrast, in grassland soil, lowest concentration of Zn was seen at a depth of 25 cm and the highest at the bottom of the profile during 2003. In woodland, Zn was found least at a depth of 25 cm during 2003 and 2005, while it concentrated highest at the bottom of the trench during 2005 (Figure 7.3.9).

Irrespective of habitats, Zn showed a trend of gradual increase trend towards the bottom of the profile. In woodland, the total metal content in the soil fell immediately from the surface layer to the next layer, i.e. to a depth of 25 cm followed by a trend of

rise (Figure 7.3.9). The trend was quiet prominent during 2005. In wetland, a sustained pattern of increase through out the depth profile was observed during 2005 only (Figure 7.3.9). However, in grassland, Zn showed an increasing trend along the depth in the soil profile during all the years (Figure 7.3.9). Irrespective of the habitats, the metal level decreased from surface layer to the immediate next layer (i.e. to a depth of 25 cm) and then gradually increased until the bottom of the soil profile. The depth wise trend of increase of metals could be related with their lithogenic nature. The extent of the lithogenic nature is discussed in the subsequent paragraphs. Univariate test of Variance showed that Zn level varied significantly only among habitats ($P < 0.05$) and the Post-Hoc test (i.e. LSD) carried out revealed that all the habitats are significantly distinct from each other as far as the Zn level in soil is concerned (Table 7.3.11).

The variation in this metal level among habitats is suggestive of its source and a significant input from the exterior sources most likely through the input water. The higher metal levels in the surface layers compared to the subsequent layer might be because of two reasons, of which the first being the contribution from plant litter during its decomposition. The results of the earlier works by the authors in the KNP reports several species of plants showing notable uptake rates for elements such as Cu, Pb and Zn from the medium (Azeez et al. 2007, and Prusty et al. 2007). The agricultural runoff entering the KNP must also be contributing to the level of the metal in soil.

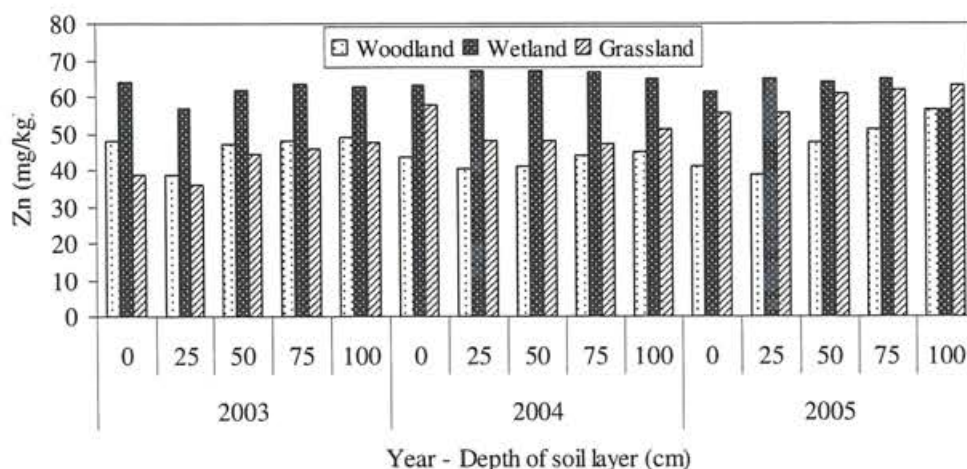


Figure 7.3.9. Habitat – Depth wise Variation of Zn in soil

Table 7.3.11. LSD of Zn (Habitats)

Multiple Comparisons

Dependent Variable: ZN
LSD

(I) HABITAT	(J) HABITAT	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Woodland	Wetland	-17.9469*	2.13150	.000	-22.2484	-13.6453
	Grassland	-5.4963*	2.13150	.014	-9.7978	-1.1947
Wetland	Woodland	17.9469*	2.13150	.000	13.6453	22.2484
	Grassland	12.4506*	2.13150	.000	8.1490	16.7521
Grassland	Woodland	5.4963*	2.13150	.014	1.1947	9.7978
	Wetland	-12.4506*	2.13150	.000	-16.7521	-8.1490

*. The mean difference is significant at the .05 level.

The association of the three metals to various geochemical phases is presented in Figure 7.3.10 to Figure 7.3.12. In all the habitats studied, Zn was mainly present in the RES phase. It was present least in CA phase in terrestrial habitats and in EXC phase in the wetland habitat (Figure 7.3.11). In woodland soil, Zn was seen in the range of 17.77 to 85.65% in the RES phase, and 0.08 to 4.9% was seen in the EXC phase. Highest proportion of the metal was seen in the Fe-Mn phase during the 1st year of the study, while the highest proportion was seen in RES phase during the 3rd year of the study (Figure 7.3.10). This is similar to the case observed in the case other two metals also. In grassland, similar to woodland, Zn had higher preferences towards RES phase and least preferences towards EXC phase (Figure 7.3.12). Zn was seen in the range of 60.7 to 88.9% in the RES phase, while 0.1 to 1.6% was seen in the EXC phase. In the wetland soil also Zn had high preferences towards RES phase and least preferences towards CA phase (Figure 7.3.11). Zn was seen in the range of 31.02 to 79.03% in the RES phase, while 0.051 to 1.1% was seen in the EXC phase. Tokalioğlu et al. (2003) have reported 82.8% Zn in the RES phase. Of the three habitats, in grassland and wetland soil, the order of fractions in terms of concentration was Res > Fe-Mn > OM-S > CA > EXC, and in woodland the order was slightly different and was Res > Fe-Mn > OM-S > EXC > CA.

For Zn, among the non-residual phases, Fe-Mn oxide fraction was the most important phase and Zn concentration ranged between 11.7 and 76.4% in woodland. The

proportion of Zn contained in the Fe-Mn phase in wetland soil 14.5 to 56.8%, and in grassland soil, it was 1.9 to 29.4%. Among the non-residual pools, Fe-Mn oxide fraction is the important scavenger for most of the metals level in all the habitats. In general, RES phase is the important binding site for Zn indicating that the major proportion of the metal is incorporated in the silicate mineral matrix. This may indicate that this element was derived from natural geological sources. Fe-Mn phase represents the second most significant sink for Zn in all the habitats and is followed by OM-S. This is an indication of the abundance of hydrous oxide of Fe and Mn in KNP soil. As the sampling was done in the summer that experiences less soil organic matter in thorny woodlands, where saline soil patches are common, the metals mostly remain attached with the RES and Fe-Mn oxides phase and the attachment to organic matter (OM-S) phase was less. The observed higher attachment of Zn to the RES phase is consistent with observations of Li et al. (2000a). The highest affinity of Zn towards RES phase was also reported by Svete et al. (2001) in a study on the chemical partitioning of Zn from a mine area. The greater contribution made by the hydroxylamine hydrochloride-extractable (Fe-Mn) fraction to the Zn was also reported from other environments (Jones 1987).

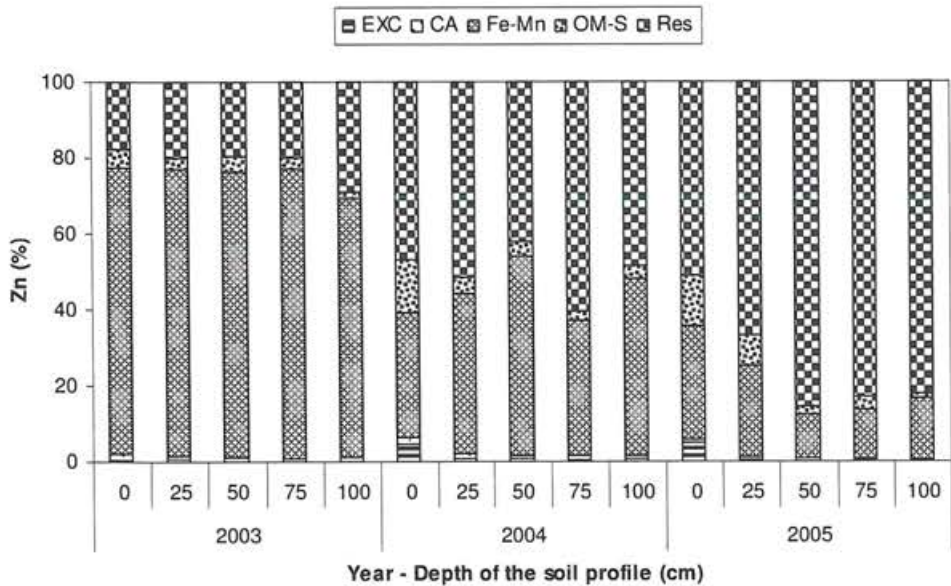


Figure 7.3.10. Fractionation of Zn in woodland

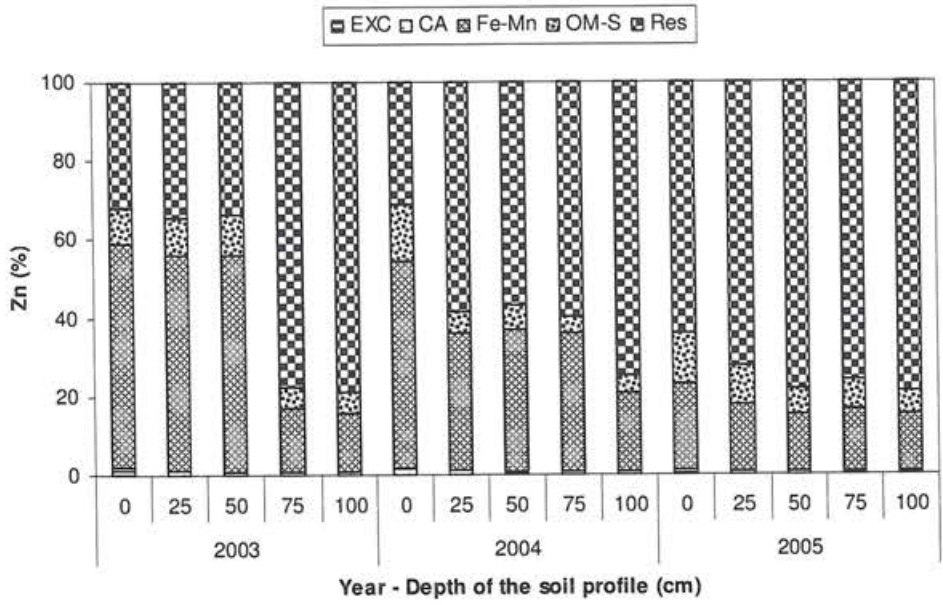


Figure 7.3.11. Fractionation of Zn in wetland

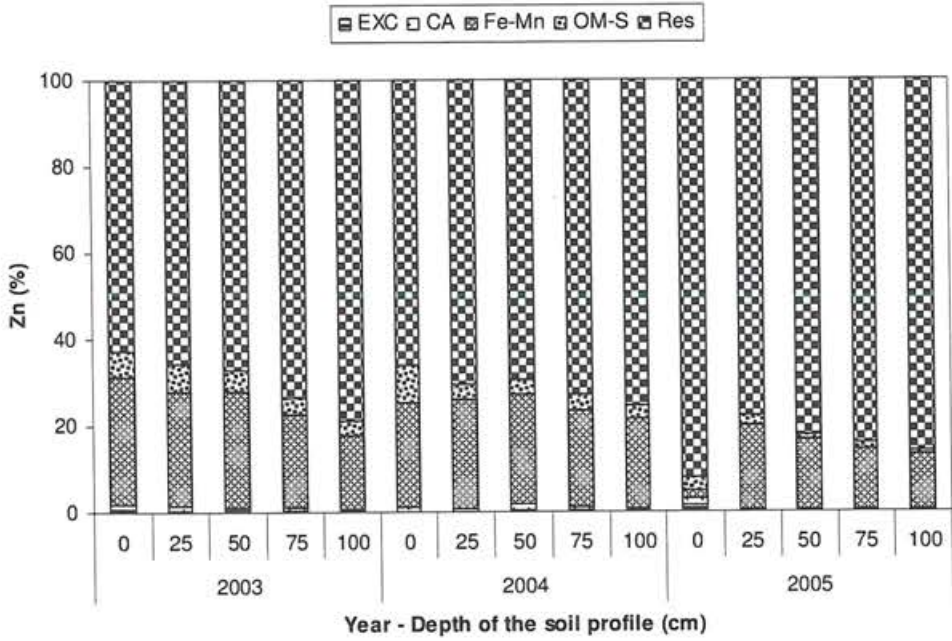


Figure 7.3.12. Fractionation of Zn in grassland

The extent of association among different fractions, and with TOM (%) and CO₃-C (%) is shown in Table 7.3.12. For Zn, among the non-residual fractions only Fe-Mn was negatively correlated with the RES fraction in all the habitats. The TOM (%) was significantly correlated (negative) with the RES fraction only in wetland soil. As expected, TOM (%) in soil was positively correlated ($P < 0.05$) with OM-S fraction only in woodland and wetland habitats. Considering the saline and alkaline nature of soil in the Park, in all the habitats, CA fraction was expected to show a positive correlation with CO₃-C content in soil. However, in contrast, a significant positive correlation between CA fraction and CO₃-C content in soil was seen only in the case of woodland ($r = 0.542$, $P < 0.05$). There was no significant correlation observed between CA and CO₃-C in the case of wetland and grassland, which requires further investigation and/or examination.

Similar to the finding in the case of Cu and Pb, the GLM-ANOVA results showed that the distribution of Zn was significant only among different fractions ($P < 0.05$) and the results of the Post-hoc analysis (One-Way ANOVA - LSD) performed on the fractions and the results are shown in Table 7.3.13 to Table 7.3.15. In the woodland soil, RES, OM-S and Fe-Mn phase was found to be the significant carrier for the metal and were distinct from the rest (Table 7.3.13). In the case of wetland soil, only RES and Fe-Mn (Table 7.3.14) were distinct from the rest. In this case RES and Fe-Mn phase were found to be distinct from others (Table 7.3.15). Hence, irrespective of the habitat types, RES and Fe-Mn phase could be regarded as the common scavenger and/or sink for Zn. Since, much of the metals are contained in the silicate mineral matrix, the likelihood of its release and subsequent availability to the biota is less. Although the attachment of metals to Fe-Mn oxides indicates their relative immobilization, the situation is largely dependent on the micro environmental conditions. Chemical changes such as pH and redox in the ambient conditions could lead to their likely mobilization and uptake by plants.

Table 7.3.12. Zn - Correlation matrix of metals fractions in the soil

Woodland								
	EXC	CA	Fe-Mn	OM-S	Res	Total metal	TOM (%)	CO ₃ -C (%)
EXC	1.000							
CA	.480	1.000						
Fe-Mn	-.242	.541*	1.000					
OM-S	.912*	.507	-.207	1.000				
Res	.021	-.680*	-.973*	-.024	1.000			
Total metal	-.358	-.411	-.157	-.446	.264	1.000		
TOM (%)	.680*	.684*	.049	.698*	-.222	-.132	1.000	
CO ₃ -C (%)	.060	.542*	.577*	.091	-.612*	-.497	.037	1.000
Wetland.								
	EXC	CA	Fe-Mn	OM-S	Res	Total metal	TOM (%)	CO ₃ -C (%)
EXC	1.000							
CA	.108	1.000						
Fe-Mn	.273	.659*	1.000					
OM-S	.178	.559*	.451	1.000				
Res	-.291	-.703*	-.988*	-.582*	1.000			
Total metal	-.014	.030	-.079	-.283	.117	1.000		
TOM (%)	.845*	.546*	.511	.527*	-.568*	.024	1.000	
CO ₃ -C (%)	-.007	-.301	-.304	-.084	.292	-.094	-.191	1.000
Grassland								
	EXC	CA	Fe-Mn	OM-S	Res	Total metal	TOM (%)	CO ₃ -C (%)
EXC	1.000							
CA	.593*	1.000						
Fe-Mn	-.395	.238	1.000					
OM-S	.098	.650*	.612*	1.000				
Res	.218	-.441	-.964*	-.791*	1.000			
Total metal	-.216	-.538*	-.683*	-.583*	.743*	1.000		
TOM (%)	.664*	.594*	-.408	.352	.180	.160	1.000	
CO ₃ -C (%)	-.129	-.250	-.326	-.382	.381	.362	-.070	1.000

45 Sample size, ± .514 critical value, P < 0.05 (two-tail), *: Significant

EXC = Exchangeable metal, CA = Carbonate bound metal, Fe-Mn = Iron – Manganese bound metal, OM-S = Bound to organic matter and sulphur, Total metal = Pseudototal metal, TOM = Total Organic Matter, CO₃-C = Carbonate carbon

Chapter 7. Trace Metals: Distribution and Partitioning

Table 7.3.13. LSD of Zn – fractions (Woodland)

Multiple Comparisons

Dependent Variable: ZN
LSD

(I) FRACTION	(J) FRACTION	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
EXC	CA	.1191	5.60673	.983	-11.0631	11.3014
	Fe-Mn	-43.9401*	5.60673	.000	-55.1223	-32.7578
	OM-S	-3.7594	5.60673	.505	-14.9417	7.4229
	RES	-47.2219*	5.60673	.000	-58.4041	-36.0396
CA	EXC	-.1191	5.60673	.983	-11.3014	11.0631
	Fe-Mn	-44.0592*	5.60673	.000	-55.2415	-32.8769
	OM-S	-3.8785	5.60673	.491	-15.0608	7.3037
	RES	-47.3410*	5.60673	.000	-58.5233	-36.1587
Fe-Mn	EXC	43.9401*	5.60673	.000	32.7578	55.1223
	CA	44.0592*	5.60673	.000	32.8769	55.2415
	OM-S	40.1807*	5.60673	.000	28.9984	51.3629
	RES	-3.2818	5.60673	.560	-14.4641	7.9005
OM-S	EXC	3.7594	5.60673	.505	-7.4229	14.9417
	CA	3.8785	5.60673	.491	-7.3037	15.0608
	Fe-Mn	-40.1807*	5.60673	.000	-51.3629	-28.9984
	RES	-43.4625*	5.60673	.000	-54.6447	-32.2802
RES	EXC	47.2219*	5.60673	.000	36.0396	58.4041
	CA	47.3410*	5.60673	.000	36.1587	58.5233
	Fe-Mn	3.2818	5.60673	.560	-7.9005	14.4641
	OM-S	43.4625*	5.60673	.000	32.2802	54.6447

*. The mean difference is significant at the .05 level.

Table 7.3.14. LSD of Zn – fractions (Wetland)

Multiple Comparisons

Dependent Variable: ZN
LSD

(I) FRACTION	(J) FRACTION	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
EXC	CA	-.6357	4.16188	.879	-8.9363	7.6649
	Fe-Mn	-30.4976*	4.16188	.000	-38.7982	-22.1970
	OM-S	-7.5751	4.16188	.073	-15.8757	.7255
	RES	-60.2539*	4.16188	.000	-68.5545	-51.9533
CA	EXC	.6357	4.16188	.879	-7.6649	8.9363
	Fe-Mn	-29.8619*	4.16188	.000	-38.1625	-21.5613
	OM-S	-6.9394	4.16188	.100	-15.2400	1.3612
	RES	-59.6182*	4.16188	.000	-67.9188	-51.3176
Fe-Mn	EXC	30.4976*	4.16188	.000	22.1970	38.7982
	CA	29.8619*	4.16188	.000	21.5613	38.1625
	OM-S	22.9225*	4.16188	.000	14.6219	31.2231
	RES	-29.7563*	4.16188	.000	-38.0569	-21.4557
OM-S	EXC	7.5751	4.16188	.073	-.7255	15.8757
	CA	6.9394	4.16188	.100	-1.3612	15.2400
	Fe-Mn	-22.9225*	4.16188	.000	-31.2231	-14.6219
	RES	-52.6788*	4.16188	.000	-60.9794	-44.3782
RES	EXC	60.2539*	4.16188	.000	51.9533	68.5545
	CA	59.6182*	4.16188	.000	51.3176	67.9188
	Fe-Mn	29.7563*	4.16188	.000	21.4557	38.0569
	OM-S	52.6788*	4.16188	.000	44.3782	60.9794

*. The mean difference is significant at the .05 level.

Table 7.3.15. LSD of Zn – Fractions (Grassland)

Multiple Comparisons

Dependent Variable: ZN
LSD

(I) FRACTION	(J) FRACTION	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
EXC	CA	-.5969	1.80145	.741	-4.1898	2.9959
	Fe-Mn	-20.8475*	1.80145	.000	-24.4403	-17.2546
	OM-S	-4.2336*	1.80145	.022	-7.8265	-.6407
	RES	-72.2304*	1.80145	.000	-75.8233	-68.6375
CA	EXC	.5969	1.80145	.741	-2.9959	4.1898
	Fe-Mn	-20.2505*	1.80145	.000	-23.8434	-16.6577
	OM-S	-3.6367*	1.80145	.047	-7.2295	-.0438
	RES	-71.6335*	1.80145	.000	-75.2263	-68.0406
Fe-Mn	EXC	20.8475*	1.80145	.000	17.2546	24.4403
	CA	20.2505*	1.80145	.000	16.6577	23.8434
	OM-S	16.6139*	1.80145	.000	13.0210	20.2067
	RES	-51.3829*	1.80145	.000	-54.9758	-47.7901
OM-S	EXC	4.2336*	1.80145	.022	.6407	7.8265
	CA	3.6367*	1.80145	.047	.0438	7.2295
	Fe-Mn	-16.6139*	1.80145	.000	-20.2067	-13.0210
	RES	-67.9968*	1.80145	.000	-71.5897	-64.4039
RES	EXC	72.2304*	1.80145	.000	68.6375	75.8233
	CA	71.6335*	1.80145	.000	68.0406	75.2263
	Fe-Mn	51.3829*	1.80145	.000	47.7901	54.9758
	OM-S	67.9968*	1.80145	.000	64.4039	71.5897

*. The mean difference is significant at the .05 level.

7.4. GENERAL DISCUSSION

The heavy metal partitioning in soil could be used to determine their mobility and possible sources. Fractionation of total metal contents might give indications about the origin of the metals. The EXC, CA and Fe-Mn fraction are relatively mobile fractions and may indicate pollution from anthropogenic origin, while the OM-S and RES fraction are relatively immobile. The metal in the EXC fraction usually includes the weakly sorbed metal species, particularly those retained on the soil surface by relatively weakly electrostatic interactions. Förstner and Wittmann (1979) also states that the metal levels in EXC fraction play a very important role in the evaluation of environment and always act as a pollution indicator. The results from the present study indicate that the habitats of KNP are not of much concern in terms of metal pollution according to this measure. Metals occurred in the second fraction (i.e. CA) may be thought to have been present as co-precipitated with carbonate minerals and sensitive to pH changes and metal release is achieved through dissolution of the fraction of the solid material at a lower pH. Since, all the habitats have a pH towards

the higher side; the likely release of the metals from this fraction is also negligible. Moreover, carbonates are regarded as insufficient metal carrier phases (Sigg 1987) especially in aquatic systems.

The Fe-Mn phase being the highest scavenger in most of the cases needs further attention from the point of view of metal mobility and bioavailability. Due to their high scavenging capacity, Fe and Mn oxides have been recorded as significant heavy metal sink in soil. Yuan et al. (2004) reports that Fe and Mn oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles, these oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions. Although the dynamics of metal scavenging by Fe and Mn oxides is still poorly understood, assuming that the extraction using Hydroxylamine hydrochloride with acetic acid is an appropriate indicator of metals associated with amorphous iron and manganese oxides, this process seems to exert a significant control on the metals studied in this grassland system.

The scavenging potential of OM-S also cannot be ignored in the present study. It appears to play a significant role in scavenging Zn in woodland and Cu in wetland soil. In soil, trace metals may be associated with the organic matters, such as living organisms, organic coatings on inorganic particles and biotic detritus (Prusty and Azeez 2007). Under the oxidizing conditions, the organic materials may be destroyed and the trace metals associated with them may be released into the environment. Metals in this fraction are more stable and difficult to take part in the geochemical cycle, and the metals in this fraction largely act as a sink and reservoir for pollution, but it is not to say that, metals in this fraction do not pose threat to environment. Tokalioğlu et al. (2000 and 2003) and Jagadeesh et al. (2006) opine that Cu occurs in forms of the stable organic complexes and metal sulphides.

Metals in the RES fraction are safer to environment for their lowest mobility and bioavailability. Primary and secondary mineral containing metals in the crystalline lattice constitute bulk of this fraction. In almost all the cases in the present study, RES phase was a significant scavenger for metals. Given that the stability of metals in all fractions, other than the residual, is likely to be affected by changes in pH and redox potential, the results of extractions such as those presented here have important

implications for management of wetland-dominated systems. Metal behaviour cannot be entirely predicted by sequential extraction studies alone (or by geochemical modelling) given the complexity of ligand availability, geochemistry, and kinetics.

Identification and estimation of operationally defined species of metals and relating them to interactions, biogeochemical process in soils, effects on biota, and processes like transportation and transformations have remained a challenge to researchers. It requires further intensive studies, as the metal species identified by the fractionation schemes are operationally defined and likely to be distinct from the forms that naturally exist in natural ecosystems. The extraction and the preconcentration procedures are likely to change the forms that actually occur in nature. Since, the operationally defined methods can give only an approximation of species distribution, simultaneous computer based modelling based on theoretical consideration can provide a better realistic understanding.

8. SUMMARY

The present study reports the pedological characteristics along the soil profile in a mixed habitat system (woodland, wetland and grassland) with emphasis on selected nutrient elements, alkali and alkaline earth metals, and heavy metals. The main purpose of this study was to examine the distribution pattern of nutrients, alkali and alkaline earth metals and heavy metals on a spatio-temporal scale. Soil samples collected at depths of 0, 25, 50, 75 and 100 cm were examined with respect to certain select physico-chemical parameters following standard methods and was found to differ considerably in their nutrient contents. Variations were also found on a temporal scale for the soils collected on bimonthly basis up to a depth of 20 cm. The aspects specific findings are as given below:

- Irrespective of the habitat type and year, most of the parameters, such as TOC, TN, TAP and TAS, were highest in the litter layer gradually declining through the depth in the soil profile. The major elemental ratios such as C: N, C: P and C: S also followed a similar trend. In contrast N: P ratio increased downwards along the soil profile. The higher values of the elemental ratios in the litter layer indicate the relatively protracted mobilization of nutrients from the decaying detritus layer. In the case of most of the variables, litter and surface layer of the soil profile was distinct and differed from the rest of the layers.
- The variations of the nutrients and their respective ratios were significantly different among soil layers considering the entire period of study. However, in several cases among habitats, it was not significant. This is suggestive of the sources of these nutrient elements and the distribution of some species of plants across the different habitats.
- Among the layers litter layer and the surface layer of the profile stand distinct and different from the rest of the layers in the soil profile with reference to several soil variables. Plant litters seemed to be the deciding factor for the reported variability.

- The temporal distribution of organic matter and other nutrient elements in the wetland soils (0-20 cm) of the monsoonal wetland system indicated that although the input water could bring in the nutrients and sediments along with the allochthonous materials, the nutrient content in soil appeared to be a function of plant uptake, decomposition, period of inundation and ambient temperature. Moreover, the initial status of the soil variables in the site determines the differences in their dynamics on a temporal as well spatial level.
- Deposition of allochthonous materials peaked during the wet season and after the input of water to the Park during July - September. Most of the nutrients are at their maximum level during this period. Rainfall seasonality and water input timing affected the mineralization of nutrients and their redistribution in the sediment profile. Drier periods were characterized by the decomposition of organic materials deposited during the wet periods, as the level of TOC was low and other nutrients such as TAN was high. Both the autochthonous and allochthonous materials significantly influence the nutrient distribution in the wetland.
- As far as the variation of nutrients among the months is concerned, May was the month where, EC and TDS were distinct from the rest of the months. For major nutrients such as TAP and TAS, the month of July was distinct. For most of the ratios, November was distinct. Among the sediment layers, two upper layers of the core (i.e. 0-5 cm and 5-10 cm) remained distinct and different from the two lower cores. These two layers were more prone to seasonal as well as other physical influence such as plant growth.
- K, Ca and Li showed gradual declining trend down ward in the soil profile in all the habitats where as Na had a downward increasing trend. Mg did not show any consistency in its pattern along the depth profile. It is inferred that differences exist among the habitats in the Park not only in terms of the major vegetation types, but with respect to the type of cationic enrichment also. In summary, Na type enrichment was observed only in the terrestrial areas

particularly the woodlands where saline patches were seen on the ground. On the contrary, the wetland showed Ca type enrichment. Saline underground aquifer and input water to the Park seems to contribute significantly to the elevated levels of certain elements such as Na, K and Ca.

- In the present study, soil parameters related to the geochemical processes and ecological and biological processes seems to vary on a spatio-temporal scale. Parameters such as Na and Li appear related more with the geochemical processes. Although geo-chemical processes are critical to parameters such as C, N, P, S, K, Ca and Mg, they seem to be more influenced by biological and ecological processes / factors including water input and availability. However, specific soil parameters could not be distinguished in terms of they being influenced primarily by any single type of processes since the level of a parameter (element) is a combined function of all the relevant processes as discussed earlier.
- Of the metals under study, Cu and Pb, in most of the cases, concentrated least in the bottom of the profile and highest in the surface layer. However, the reverse was seen in the case of Zn, i.e. least in the surface layer and highest in the bottom of the profile.
- Invariably in all the habitats, for all the metals, Fe-Mn oxides stand to be the single most important binding site. However, in certain cases, RES was also found high regarding metals levels in the fraction. The stability of metals in all fractions, other than the residual, is likely to be affected by changes in pH and redox potential. Sequential extraction studies alone cannot predict metal behaviour given the complexity of ligand availability, geochemistry, and kinetics. Moreover, the analytical procedures involved may alter the original forms of the ligands. The fractions determined by analytical procedures are highly operationally defined. In view of the limitations, better realistic understanding of the dynamic situation is possible through advanced modelling of organic, natural and biotic, ligands, and metals supported and

supplemented with analytical data. An array of computer based programs are available that can be used to predict the actual situation.

- Both quality and quantity of plant residues incorporated in the soil determines the rate of decomposition, and dynamics and plant uptake of nutrients. Hence, understanding the litter and organic matter decomposition in soil along the depth profile influenced by biotic and abiotic factors would facilitate formulating long-term management practices in ecosystems within a given and confined geographical realm. In order to get a better insight into the nutrient and heavy metal availability and input and usage by plants, biogeochemical studies in the natural systems such as that of KNP should also include analyses of belowground water. Because of the independency of the transport medium: water, nutrient fluxes assume higher importance than the concentrations for studying internal nutrient transfers within ecosystems.

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Appendix I. List of plants species recorded in KNP

- 1 *Abelmoschus ficulneus* (L.) Wt. & Arn.
- 2 *Abrus precatorius* L.
- 3 *Abutilon indicum* (L.) Sweet
- 4 *Abutilon ramosum* Guill. & Perr.
- 5 *Acacia leucophloea* (Roxb.) Willd.
- 6 *Acacia nilotica* (L.) Del. Sub sp. *Indica* (Benth.) Brenan
- 7 *Acalypha anacea* Forsk.
- 8 *Acalypha indica* L.
- 9 *Achranthes aspera* L. var. *porphyristachya* Hook. F.
- 10 *Achyranthes aspera* L. var. *argentea* Hook. F.
- 11 *Acrachne racemosa* (Heyne) Ohwi
- 12 *Adhatoda zeylanica* Medic.
- 13 *Aeschynomene indica* L.
- 14 *Ageratum conyzoides* L.
- 15 *Albizza lebbeck* (L.) Benth.
- 16 *Alghai pseudalhagi* (M. Bieb.) Desv.
- 17 *Alloteropsis cimicina* (L.) Stapf
- 18 *Alternanthera paronychioides* St. Hil.
- 19 *Alternanthera pungens* H. B. & K.
- 20 *Alternanthera sessilis* (L.) R. Br.
- 21 *Althaea ludwigii* L.
- 22 *Alysicarpus longifolius* (Roth.) Wt. & Arn.
- 23 *Alysicarpus vaginalis* DC.
- 24 *Amaranthus anacea* t L.
- 25 *Amaranthus spinosus* L.
- 26 *Amaranthus viridis* L.
- 27 *Ammannia auriculata* Willd.
- 28 *Ammannia baccifera* L.
- 29 *Anagallis arvensis* L.
- 30 *Antigonon leptopus* Hook. & Arn.
- 31 *Aponogeton natans* (L.) Engl. & Krause
- 32 *Argemone anacea* L.
- 33 *Argemone ochroleuca*
- 34 *Aristida adscensionis* L.
- 35 *Arundo donax* L.
- 36 *Asparagus racemosus* Willd.

- 37 *Azadirachta indica* A. Juss.
- 38 *Balanites aegyptiaca* (L.) Del.
- 39 *Barleria cristata* L.
- 40 *Basella alba* L.
- 41 *Bergia ammannioides* Roxb.
- 42 *Bidens biternata* (Lour.) Merr. & Sherff
- 43 *Blepharis maderaspatensis* (L.) Heyne ex Roth
- 44 *Blumea anacea* (L.) Druce
- 45 *Blumea eriantha* DC.
- 46 *Blumea laciniata* (Roxb.) DC.
- 47 *Blumea membranacea* DC.
- 48 *Blumea mollis* (D. Don) Merr.
- 49 *Boerhavia diffusa* L.
- 50 *Bombax ceiba* L.
- 51 *Bougainvillea glabra* Choisy.
- 52 *Brachiaria anace* (L.) Stapf
- 53 *Brachiaria distachya* (L.) Stapf
- 54 *Brachiaria reptans* (L.) Gard. & Hubb.
- 55 *Butomopsis latifolia* (D. Don) Kunth
- 56 *Caesulia axillaris* Roxb.
- 57 *Callistemon lanceolatus* DC.
- 58 *Calotropis procera* (Ait.) R. Br.
- 59 *Cannabis sativa* L.
- 60 *Capparis merican* (Forsk.) Edgew.
- 61 *Capparis sepiaria* L.
- 62 *Cardiospermum halicacabum* L.
- 63 *Cassia fistula* L.
- 64 *Cassia occidentalis* L.
- 65 *Cassia pumila* Lamk.
- 66 *Cassia siamea* Lamk.
- 67 *Cassia surattensis* Burm. F.
- 68 *Cassia tora* L.
- 69 *Catunaregam spinosa* (Thunb.) Tiruv.
- 70 *Cayratia trifolia* (L.) Domin
- 71 *Celosia argentea* L.
- 72 *Cenchrus ciliaris* L.
- 73 *Cenchrus setigerus* Vahl
- 74 *Centaurium centaurioides* (Roxb.) Rao & Hem.

- 75 *Ceratophyllum demersum* L.
- 76 *Ceropegia bulbosa* Roxb. Var. *Lushii* (Grah.) Hook. F.
- 77 *Chenopodium album* L.
- 78 *Chenopodium murale* L.
- 79 *Chloris dolichostachya* Lagasca
- 80 *Chloris quinquesetica* Bhide
- 81 *Chrozophora rottleri* (Geir.) Juss. Ex Spreng.
- 82 *Cleome merica* L.
- 83 *Cleome gynandra* L.
- 84 *Clerodendrum phlomidis* L. f.
- 85 *Clitoria ternatea* L.
- 86 *Coccinia grandis* (L.) J. O. Voigh.
- 87 *Cocculus hirsutus* (L.) Diels
- 88 *Cochlearia cochlearioides* (Roth)
- 89 *Coix lacryma-jobi* L.
- 90 *Coldenia procumbens* L.
- 91 *Commelina benghalensis* L.
- 92 *Commelina forskalei* Vahl
- 93 *Commelina hasskarlii* Clarke
- 94 *Commicarpus chinensis* (L.) Heimerl.
- 95 *Commicarpus helenae* (Schultes) Meikle.
- 96 *Convolvulus microphyllus* Sieb. Ex Spreng.
- 97 *Conyza bonariensis* (L.) Cronq.
- 98 *Corchorus aestuans* L.
- 99 *Corchorus capsularis* L.
- 100 *Corchorus fascicularis* Lamk.
- 101 *Corchorus olitorius* L.
- 102 *Corchorus tridens* L.
- 103 *Cordia dichotoma* Forst. F.
- 104 *Coronopus didymus* (L.) Sm.
- 105 *Cotula anthemoides* L.
- 106 *Crataeva magna* (Lour.) DC.
- 107 *Crotalaria medicaginea* Lamk.
- 108 *Croton bonplandianum* Baill.
- 109 *Crypsis schoenoides* (L.) lamk.
- 110 *Cryptostegia grandiflora* R. Br.
- 111 *Cucumis melo* L.
- 112 *Cuscuta reflexa* Roxb.

- 113 *Cynodon dactylon* (L.) Pers.
 114 *Cyperus alopecuroides* Rottb.
 115 *Cyperus alulatus* Kern
 116 *Cyperus bulbosus* Vahl
 117 *Cyperus compressus* L.
 118 *Cyperus difformis* L.
 119 *Cyperus iria* L.
 120 *Cyperus pygmaeus* Rottb.
 121 *Cyperus rotundus* L.
 122 *Cyperus triceps* (Rottb.) Endl.
 123 *Dactyloctenium aegyptium* (L.) P. Beauv.
 124 *Dalbergia sissoo* Roxb.
 125 *Datura innoxia* Mill.
 126 *Datura metel* L.
 127 *Delonix regia* (Boj.) Raf.
 128 *Dentella repens* (L.) Forst.
 129 *Desmostachya bipinnata* (L.) Stapf
 130 *Dichanthium annulatum* (Forssk.) Stapf
 131 *Dichrostachys cinerea* (L.) Wt. & Arn.
 132 *Dicliptera verticillata* (Forsk.) Christen
 133 *Digera muuricata* (L.) Mart.
 134 *Digitaria ciliaris* (Retz.) Koel.
 135 *Diospyros cordifolia* Roxb.
 136 *Diplachne fusca* (L.) P. Beauv.
 137 *Dipteracanthus anacea* te (Poir.) Nees
 138 *Echinochloa colonum* (L.) Link
 139 *Echinochloa crusgalli* (L.) P. Beauv. Var. *brevisetata* (Doell.) Niels.
 140 *Echinochloa crusgalli* (L.) P. Beauv. Var. *crusgalli*
 141 *Echinops echinatus* Roxb.
 142 *Eclipta anacea* (L.) L.
 143 *Ehretia aspera* Roxb.
 144 *Eichhornia crassipes* (Mart.) Solms.
 145 *Elatine triandra* Schk.
 146 *Eleocharis acutangula* (Roxb.) Schult.
 147 *Eleocharis atropurpurea* (Retz.) Kunth
 148 *Eleocharis dulcis* (Burm. F.) Henschel
 149 *Eleocharis palustris* R. Br.
 150 *Elytraria acaulis* (L. f.) Kuntze

- 151 *Eragrostis cilianensis* (All.) Vignolo-Lutati
 152 *Eragrostis ciliaris* (L.) R. Br.
 153 *Eragrostis gangetica* (Roxb.) Steud.
 154 *Eragrostis japonica* (Thunb.) Trin.
 155 *Eragrostis minor* Host
 156 *Eragrostis tenella*(L.) P. Beauv.
 157 *Erianthus ravennae* (L.) P. Beauv.
 158 *Eriochloa fatmensis* (Hochst. & Steud.) Clayton
 159 *Eriochloa procera* (Retz.) Hubb.
 160 *Euphorbia hirta* L.
 161 *Euphorbia orbiculata* H. B. & K.
 162 *Euphorbia parviflora* L.
 163 *Euphorbia thymifolia* L.
 164 *Evolvulus alsinoides* (L.) L.
 165 *Evolvulus nummularius* (L.) L.
 166 *Ficus benghalensis* L.
 167 *Ficus racemosa* L.
 168 *Ficus religiosa* L.
 169 *Fimbristylis anacea* (Vahl) Kunth
 170 *Fimbristylis bisumbellata* (Forssk.) Bubani
 171 *Fimbristylis ferruginea* (L.) Vahl
 172 *Fimbristylis miliacea* (L.) Vahl
 173 *Giniogyna hirta* (Willd.) Ali
 174 *Glinus lotoides* L.
 175 *Glinus oppositifolia* (L.) A. DC.
 176 *Glossostigma diandrum* Wt. & Arn.
 177 *Gnaphalium luteo-album* L. subsp. *Affine* (D. Don) Koster
 178 *Gnaphalium polycaulon* Pers.
 179 *Gnaphalium pulvinatum* Del.
 180 *Gnaphalium purpureum* L.
 181 *Gomphrena serrata* L.
 182 *Gossypium anacea* t L.
 183 *Grangea maderaspatana* (L.) Poir.
 184 *Grewia tenax* (Forsk.) Fiori
 185 *Heliotropium indicum* L.
 186 *Heliotropium ovalifolium* Forsk.
 187 *Heliotropium strigosum* Willd.
 188 *Hemarthria compressa* (L. f.) R. Br.

- 189 *Hemiadelphis polyspermus* (Roxb.) Nees
 190 *Hibiscus amblyocarpus* Hochst
 191 *Hibiscus caesius* Gracke
 192 *Hibiscus ovalifolius* (Forsk.) Vahl
 193 *Holoptelea integrifolia* (Roxb.) Planch.
 194 *Hrdrolea zeylanica* (L.) Vahl
 195 *Hydrilla verticillata* (L. F.) Royle
 196 *Hygrophila auriculata* (Schum.) Heine
 197 *Indigofera cordifolia* Heyne ex Roth
 198 *Indigofera tinctoria* L.
 199 *Indigofera trita* L. f.
 200 *Ipomoea aquatica* Forsk.
 201 *Ipomoea carnea* Jacq. Sub sp. *Fistulosa* (Mart. Ex Choisy) Austin
 202 *Ipomoea dichroa* (Roem. & Schult.) Choisy
 203 *Ipomoea hederifolia* L.
 204 *Ipomoea nil* (L.) Roth
 205 *Ipomoea pes-tigridis* L.
 206 *Ipomoea sindica* Stapf
 207 *Iseilema laxum* Hack.
 208 *Jatropha gossypifolia* L.
 209 *Justicia heterocarpa* T. Anders.
 210 *Kirganelia anacea te* (Poir.) Baill.
 211 *Laggera aurita* (Willd.) Sch.-Bip. Ex Cl.
 212 *Lantana camara* L. Var. *Aculeata* (L.) Mold.
 213 *Lathyrus aphaca* L.
 214 *Launaea procumbens* (Roxb.) Ramayya & Rajagopal
 215 *Lawsonia inermis* L.
 216 *Lemna perpusilla* Torrey
 217 *Leptochloa anacea* (Retz.) Ohwi
 218 *Leucaena latisiliqua* (L.) Gillis
 219 *Leucas urticaefolia* (Vahl) R. Br.
 220 *Limnophila indica* (L.) Druce
 221 *Limnophyton obtusifolium* (L.) Miq.
 222 *Lindernia anacea* (Colsm.) Penn.
 223 *Lindernia anacea te* (L.) F. Muell.
 224 *Lindernia parviflora* (Roxb.) Haines
 225 *Ludwigia perennis* L.
 226 *Luffa acutangula* (L.) Roxb. Var. *Amara* (Roxb.) Clarke

- 227 *Luffa echinata* Roxb.
 228 *Lycopersicon esculentum* Mill.
 229 *Maerua oblongifolia* (Forsk.) A. Rich.
 230 *Malva parviflora* L.
 231 *Malvastrum coromandelianum* (L.) Gracke
 232 *Medicago polymorpha* L.
 233 *Melia azedarach* L.
 234 *Melilotus indica* All.
 235 *Melochia corchorifolia* L.
 236 *Merremia emarginata* Hall. F.
 237 *Millingtonia hortensis* L. f.
 238 *Mitragyna parvifolia* (Roxb.) Korth.
 239 *Momordica charantia* L. var. *muricata* (Willd.) Chakravarty
 240 *Monochoria vaginalis* (Burm. F.) Presl.
 241 *Morus alba* L.
 242 *Mukia maderaspatana* (L.) M. Roem.
 243 *Murdannia nudiflora* (L.) Brenan
 244 *Najas graminea* Del.
 245 *Najas minor* All.
 246 *Neptunia oleracea* Lour.
 247 *Nicotiana alata* Link & Otto
 248 *Nicotiana plumbaginifolia* Viv.
 249 *Nothosaerva brachiata* (L.) Wt.
 250 *Nymphaea nouchali* Burm. F.
 251 *Nymphaea pubescens* Willd.
 252 *Nymphoides cristata* (Roxb.) Kuntze
 253 *Nymphoides indica* (L.) Kuntze
 254 *Ocimum basilicum* L.
 255 *Oldenlandia corymbosa* L.
 256 *Oldenlandia pseudocorymbosa* (Bakh. F.) C. R. Babu
 257 *Oligochaeta anace* (Roxb.) Wagen.
 258 *Oplismenus burmanii* (Retz.) P. Beauv.
 259 *Opuntia elatior* Mill.
 260 *Oryza rufipogon* Griff.
 261 *Oxalis corniculata* L.
 262 *Oxystelma secamone* (L.) Karst.
 263 *Panicum antidotale* Retz.
 264 *Panicum paludosum* Roxb.

- 265 *Panicum psilopodium* Trin.
 266 *Parkinsonia anacea* L.
 267 *Parthenium hysterophorus* L.
 268 *Paspalidium punctatum* (Burm.) A. Camus
 269 *Paspalum distichum* L.
 270 *Paspalum scrobiculatum* L.
 271 *Pedaliium murex* L.
 272 *Pentatropis nivalis* (Gmel.) Field & Wood
 273 *Peplidium maritimum* (L. F.) Asch.
 274 *Pergularia daemia* (Forsk.) Chiov.
 275 *Peristrophe paniculata* (Forssk.) Brummitt
 276 *Phalaris minor* Retz.
 277 *Phoenix sylvestris* (L.) Roxb.
 278 *Phyla nodiflora* (L.) Greene
 279 *Phyllanthus amarus* Schum. & Thonn.
 280 *Phyllanthus fraternus* Webster
 281 *Phyllanthus maderaspatensis* L.
 282 *Phyllanthus virgatus* Forst. F.
 283 *Physalis minima* L.
 284 *Pithecellobium dulce* (Roxb.) Benth.
 285 *Pluchea lanceolata* (DC.) Cl.
 286 *Pluchea wallichiana* DC.
 287 *Plumbago zeylanica* L.
 288 *Polygonum barbatum* L.
 289 *Polygonum glabrum* Willd.
 290 *Polygonum limbatum* Meissn.
 291 *Polygonum plebeium* R. Br.
 292 *Polypogon monospeliensis* (L.) Desf.
 293 *Pongamia pinnata* (L.) Pierre
 294 *Portulaca anacea* Roxb.
 295 *Portulaca oleracea* L.
 296 *Portulaca quadrifida* L.
 297 *Potamogeton crispus* L.
 298 *Potamogeton nodosus* Poir.
 299 *Potamogeton pectinatus* L.
 300 *Potentilla anace* L.
 301 *Prosopis cineraria* (L.) Druce
 302 *Prosopis juliflora* (Sw.) DC.

- 303 *Pseudoraphis spinescens* (R. Br.) Vickery
 304 *Pulicaria crispa* Sch.-Bip.
 305 *Pupalia lappacea* (L.) Juss.
 306 *Rhynchosia minima* (L.) DC.
 307 *Rorippa indica* (L.) Hiern
 308 *Rostellularia quinqueangularis* (Koen.) Nees var. *peploides* (Nees) Raizada
 309 *Rotala densiflora* (Roth. Ex Roem. & Schult.) Koehne
 310 *Rotala indica* (Willd.) Koehne
 311 *Ruellia anacea* L.
 312 *Rumex dentatus* L.
 313 *Rungia pectinata* (L.) Nees
 314 *Rungia repens* (L.) Nees
 315 *Saavadora persica* L.
 316 *Saccharum spontaneum* L.
 317 *Sacciolepis indica* (L.) A. Chase
 318 *Sagittaria guayanensis* H. B. & K.
 319 *Salsola baryosma* (Roem. & Schult.) Dandy
 320 *Salvadora oleoides* Dence.
 321 *Salvia anacea* R. Br.
 322 *Scirpus articulatus* L.
 323 *Scirpus lateriflorus* Gmel.
 324 *Scirpus littoralis* Schrad.
 325 *Scirpus roylei* (Nees) Parker
 326 *Scirpus supinus* L.
 327 *Scirpus tuberosus* Desf.
 328 *Sesbania bispinosa* (Jacq.) W. F. Wight
 329 *Seseli diffusum* (Roxb. Ex Sm.) Santapu & Wagh
 330 *Setaria intermedia* Roem. & Schult.
 331 *Setaria verticillata* (L.) P. Beauv.
 332 *Sida cordata* (Burm. F.) Borss.
 333 *Sida rhombifolia* L.
 334 *Sida spinosa* L.
 335 *Solanum nigrum* L.
 336 *Solanum surattense* Burm. F.
 337 *Sonchus asper* (L.) Hill.
 338 *Sonchus oleraceus* L.
 339 *Spergula arvensis* L.
 340 *Sphaeranthus indicus* L.

- 341 *Sphenoclea zeylanica* Gaertn.
 342 *Spirodela polyrhiza* (L.) Schleid.
 343 *Sporobolus coromandelianus* (Retz.) Kunth
 344 *Sporobolus helvolus* (Trin.) Th. Dur. & Schinz
 345 *Sporobolus ioclados* (Nees ex Trin.) Nees
 346 *Stellaria media* L.
 347 *Suaeda fructicosa* (L.) Forsk.
 348 *Syzygium cumini* (L.) Skeels
 349 *Tamarindus indica* L.
 350 *Tamarix aphylla* (L.) Karst.
 351 *Teramnus labialis* (L.) Spreng.
 352 *Thespesia populnea* (L.) Soland. Ex Corr.
 353 *Tinospora cordifolia* (Willd.) Miers
 354 *Tonningia axillaris* (L.) Kuntze
 355 *Tragus roxburghii* Panigrahi
 356 *Trapa natans* L. Var. *Bispinosa* (Roxb.) Makino
 357 *Trianthema portulacastrum* L.
 358 *Trianthema triquetra* Rottl. & Willd.
 359 *Tribulus terrestris* L.
 360 *Trichodesma amplexicaule* Roth
 361 *Trichosanthes cucumerina* L.
 362 *Tridax procumbens* L.
 363 *Trigonella hamosa* L. Subsp. *Uncata* (Boiss. & Noe) Townsend
 364 *Trigonella occulta* Del.
 365 *Typha angustata* Bory & Chaub.
 366 *Utricularia aurea* Lour.
 367 *Utricularia exoleta* R. Br.
 368 *Utricularia stellaris* L. f.
 369 *Vallisneria natans* (Lour.) Hara
 370 *Verbascum chinense* (L.) Santapau
 371 *Vernonia cinerea* (L.) Less.
 372 *Vetiveria zizanioides* (L.) Nash
 373 *Vicia sativa* L.
 374 *Vicoa indica* (L.) DC.
 375 *Vigna trilobata* (L.) Verdcourt
 376 *Vitex negunda* L.
 377 *Wahlenbergia marginata* (Thunb.) DC.
 378 *Wattakaka volubilis* (L. F.) Stapf

- 379 *Withania somnifera* (L.) Dunal
380 *Wolffia globosa* (Roxb.) Hartog & Plas
381 *Xanthium strumarium* L.
382 *Zaleya govindia* (Buch.-Ham. Ex G. Don) N. C. Nair
383 *Ziziphus mauritiana* Lamk.
384 *Ziziphus nummularia* (Burm. F.) Wt. & Arn.

Appendix II. List of papers In Press / Published / Accepted / Under revision /
Submitted (Communicated) during the study duration

In Journals / Periodicals / News Letters

1. **In Press) Prusty BAK** and Azeez PA. Alkali and alkaline earth metals in the soil profile of a wetland-terrestrial ecosystem complex in India. *Australian Journal of Soil Research*. 45 (7).
2. **In Press) Azeez PA** and **Prusty BAK**. Transition metals in decomposing macrophytes in a wetland system. *Asian Journal of Water, Environment and Pollution*.
3. **In Press) Chandra R, Prusty BAK** and Azeez PA. Additions to the flora of Keoladeo National Park. *Tiger paper*.
4. **In Press) Prusty BAK, Chandra R** and Azeez PA. Biodiesel: freedom from dependence on fossil fuels and a step towards sustainable development. *Journal of Environment and Energy*.
5. **2007) Prusty BAK, Chandra R, Azeez PA** and Sharma LL. New additions to the ichthyofauna of Keoladeo National Park, a World Heritage Site in India. *Zoo's Print Journal*. 22 (10): 2848-2852 (October 2007).
6. **2007) Chandra R, Prusty BAK, Maithily D, Sarimol SR** and Azeez PA. Nutrients and alkali metal distribution in the top soil of bauxite rich hillocks in Araku Valley, Andhra Pradesh, India. *Environmental Science: An Indian Journal*. 2(3): 145-153 (September 2007).
7. **2007) Prusty BAK** and Azeez PA. Role of detritus on trace metals in wetland-terrestrial systems: A review. *Environmental Science: An Indian Journal*. 2 (2): 109-129 (June 2007).
8. **2007) Prusty BAK, Azeez PA** and Jagadeesh EP. Alkali and transition metals in macrophytes of a wetland system. *Bulletin of Environmental Contamination and Toxicology*. 78 (5): 405-410 (May 2007).
9. **2007) Prusty BAK**. The eclipsed link between aboveground and belowground biota. *Malabar Trogon*. 5 (1): 15.
10. **2006) Azeez PA, Prusty BAK** and Jagadeesh EP. Chemical speciation of metals in environment, its relevancy to ecotoxicological studies and the need for

- biosensor development. *Journal of Food, Agriculture and Environment*. 4 (3&4): 235-239.
11. **2005) Prusty BAK** and Azeez PA. Humus: The Natural Organic Matter in the Soil System. *Journal of Agricultural Research and Development*. 1: 1-12.
 12. **Revised and Submitted) Prusty BAK** and Azeez PA. C-N-P-S distribution in the soil system at Keoladeo National Park, Bharatpur, India. *Acta Ecologica Sinica*.
 13. **Revised and Submitted) Prusty BAK**, Jayalakshmi V and Azeez PA. Distribution of select transition metals in monsoon fed urban wetland sediments. *Journal of Environmental Science and Health*.
 14. **Submitted) Prusty BAK**, Chandra R and Azeez PA. Macronutrients along the sediment core in a semitropical monsoonal wetland in India. *Wetlands*.
 15. **Submitted) Prusty BAK**, Chandra R and Azeez PA. Vertical and temporal variation of Zn in the soils of a multiple habitat system. *Journal of Food, Agriculture and Environment*.
 16. **Submitted) Prusty BAK**, Jayalakshmi V and Azeez PA. Alkali and alkaline earth metals in monsoon fed urban wetland sediments. *Biogeochemistry*.
 17. **Submitted) Azeez PA** and **Prusty BAK**. Select alkali and alkaline earth metals in decomposing macrophytes in a wetland system. *Acta Ecologica Sinica*.
 18. **Submitted) Chandra R**, **Prusty BAK** and Azeez PA. *Rasbora daniconius*, a new record for Keoladeo National Park, Bharatpur, India. *Tiger Paper*.
 19. **Submitted) Prusty BAK**, Chandra R and Azeez PA. Day-night variation in the movement of fry in a feeder canal of a monsoonal wetland, Keoladeo National Park (KNP), Bharatpur, India. *Journal of Fish Biology*.
 20. **Submitted) Prusty BAK**, Chandra R, Shah Hussain M and Azeez PA. Catchment geography influences the arrival pattern of fishes into a semitropical monsoonal wetland system. *The Scientific World Journal*.

In Books

1. **In Press) Prusty BAK**, Chandra R and Azeez PA. Cu, Pb and Zn fractionation in a savannah type grassland soil. Environment and Sustainable Development.
2. **In Press) Prusty BAK** and Azeez PA. Wetlands: Efficient systems for waste water treatment. Edited book on Environmental Studies. Atlantic Publishers and Distributors, New Delhi, India.

3. **In Press)** Prusty **BAK** and Azeez PA. Sustainable Development: A key environmental debate. Edited book on Environmental Studies. Atlantic Publishers and Distributors, New Delhi, India.
4. **2007)** Azeez PA, Nadarajan NR and Prusty **BAK**. Macrophyte decomposition and its impact on the water quality. In: Environmental Degradation and Protection (Eds. KK Singh, A Juwarkar and AK Singh), Volume – II, MD Publications, New Delhi. Pp. 115-156.