

**ROLE OF DETRITUS IN TRACE METAL DYNAMICS OF A WETLAND
SYSTEM: A CASE STUDY OF KEOLADEO NATIONAL PARK,
BHARATPUR, INDIA**



Report Submitted to
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, NEW DELHI

by
B. ANJAN KUMAR PRUSTY

**DIVISION OF ENVIRONMENTAL IMPACT ASSESSMENT
SÁLIM ALI CENTRE FOR ORNITHOLOGY AND NATURAL HISTORY
COIMBATORE, TAMIL NADU**

MAY-2008



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PARK, BHARATPUR**

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FINAL REPORT (APRIL 2006 – MARCH 2008)

Submitted by
B. ANJAN KUMAR PRUSTY
Senior Research Fellow
(Award No. 9/845(4)/06/EMR - I)

Research Supervisor
DR. P. A. AZEEZ
Sr. Principal Scientist



DIVISION OF ENVIRONMENTAL IMPACT ASSESSMENT
SÁLIM ALI CENTRE FOR ORNITHOLOGY AND NATURAL HISTORY
COIMBATORE, TAMIL NADU
MARCH-2008

ANNEXURE – IV

PROFORMA FOR ANNUAL PROGRESS REPORT OF RESEARCH FELLOW

1. Name of the Fellow : B. Anjan Kumar Prusty
2. Nature of the Fellowship : SRF
3. CSIR Award No. : 9/845(4)/06/EMR - I
4. Name, designation and address of the Guide : Dr. PA Azeez,
Senior Principal Scientist and Head,
Environmental Impact Assessment,
Sálim Ali Center for Ornithology and
Natural History (SACON),
Anaikatty, Coimbatore – 641108
Tamil Nadu
5. Place of Work : Environmental Impact Assessment
Division,
Sálim Ali Center for Ornithology and
Natural History (SACON),
Anaikatty, Coimbatore – 641108
Tamil Nadu
6. Date of Joining : 01. 04. 2006
7. Period up to which fellowship is tenable : April 2006 to March 2007
8. Date of registration for higher degree (Ph. D) : 01. 01. 2004
9. (a) Topic of Research : Role of detritus in trace metal dynamics
of a wetland system: a case study of
Keoladeo National Park (KNP), Bharatpur
- (b) Broad subject area : Environmental Sciences
10. Objective in undertaking the work
 1. Evaluation of spatio-temporal variability in the nutrient distribution along the soil profile
 2. Assessment of spatio-temporal variability in the alkali and alkaline earth metals distribution along the soil profile
 3. Examination of the type of alkali metal enrichment
 4. Examination of the chemical fractionation of trace metals in soil along the soil profile in all the three habitats and their temporal variability
11. Period of Report : April 2007 to July 2007
12. Attendance :
 - (a) Total no. of working days during the period under project : 85 (*Details enclosed*)
 - (b) Out of these, total no. of days in which the fellow was present and worked : 78
 - (c) Number of days for which leave was sanctioned : 7
13. Detailed report of research work done : Separately Enclosed
14. Summary of research work done : Separately Enclosed
15. Plan of work for the next year : Not Applicable
16. Research Papers Published : Separately Enclosed
17. It is affirmed that I have devoted my time to research and that I did not take up any other, paid or unpaid assignments without taking written permission from CSIR. It is

also certified that due acknowledgement of CSIR Financial assistance has been made in the published papers.

Date:

Signature of Research Fellow

18. Overall assessment and comments of the Guide

- (a) It is certified that the information provided above and in separate pages enclosed with this report by the research fellow is correct to the best of my knowledge and belief.
- (b) My specific comments about the performance of the Research fellow are as under:-
Mr. B. Anjan Kumar Prusty, Senior Research Fellow, working under my supervision has performed / discharged his work up to satisfaction. The study on trace metals speciation has enormous scope. Moreover studies on trace metal speciation are scarce in India especially comparative studies based on different vegetation stands to evaluate the influence of detritic material on the geochemical partitioning of metals in soil. His approach to the assignment is as per the scientifically accepted standard protocols and appears to have a good scope for the further research. It will definitely serve as valuable information on the relation of detritic material and trace metal speciation for undertaking further research especially on the interaction of humic materials, viz. humic acid and fulvic acid, and trace metals.

His initiativeness in executing the work with scientific approach and logical sense is appreciable.

Mr. Prusty is committed to the assignment and I am sure the data which he proposes to collect in the following year will bring further valuable scientific information towards the study of trace metal speciation to examine the trace metal mobility and bioavailability in soil in an array of habitats.

Date:

Signature of Guide

ATTENDANCE CERTIFICATE

April 2007 to July 2007

Sl. No.	Month	No. of working days	No. of days attended	No. of days on leave
1.	April – 2007	20	20	Nil
2.	May	22	22	Nil
3.	June	21	18	3
4.	July-2007	22	18	4*
Total		85	78	7

*Relieved w.e.f. 26-07-2007

A copy of the intimation letter to the CSIR is enclosed herewith.

FORM GFR 19-A

{See Government of India's Decision (1) below Rule 150}

Form of Utilization Certificate

1. Certified that of Rs. 1,50,200 of grants-in-aid sanctioned during the year 2006-07 in favour of B. Anjan Kumar Prusty (Sálim Ali Centre for Ornithology and Natural History) under the CSIR/CSIR Complex Letter No. given in the below table and Rs --- on account of unspent balance of the previous year, a sum of Rs. 1,42,866 (including the fellowship paid for Mar'07) has been utilized for the purpose of undertaking a research project "**Role of detritus in trace metal dynamics of a wetland system: a case study of Keoladeo National Park (KNP), Bharatpur**" for which it was sanctioned and that the balance of Rs. 7,334 remaining unutilized at the end of the year will be adjusted towards the grants-in-aid payable during the next year 2007-08.

Sl. No.	Sanction letter No. and date	Amount (Rs.)	Cheque No.	Date & Amt.
1.	9/845/RE/2006-EMR-1 dated 09.06.2006	1,50,200	550471	21.08.06
		(Rs. 3,00,400 for two SRFs)		

2. certified that I have satisfied myself that the conditions on which the grants-in-aid was sanctioned has been duly fulfilled/are being fulfilled and that I have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned. The detail expenditure shown in the enclosed statement of account.

Kinds of checks exercised:

1. Each bill has been thoroughly checked and passed.
2. Consumables stock registers have been maintained and consumption accounted for.
3. Each bill has been passed after getting a certificate from the division head that the expenditure has been received for the purpose for which it was sanctioned.

Signature
Designation
Date

The utilization certificate and statement of account should be signed by Head of the Finance and Accounts and counter signed by the Registrar/Dean/Director/Comptroller

STATEMENT OF ACCOUNTS IN RESPECT OF **CSIR RESEARCH FELLOWS/ASSOCIATES** FOR THE GRANT RECEIVED & EXPENDITURE DURING THE YEAR 2006-07

Sl. No.	Name of the Fellow	Opening balance				Grant received during the year			
		Stipend	Cont.	HRA+MA	Total	Stipend	Cont.	HRA+MA	Total
(1)	(2)	(3)	(4)	(5)	(6) (3+4+5)	(7)	(8)	(9)	(10) (7+8+9)
1.	B. Anjan Kumar Prusty, SRF	----	----	----	----	1,08,000	20,000	16,200 6,000	1,50,200

Total Grant				Expenditure during the year				Unspent balance lying with the Univ/Inst.			
Stipend	Cont.	HRA+MA	Total	Stipend	Cont.	HRA+MA	Total	Stipend	Cont.	HRA+MA	Total
(11) (3+7)	(12) (4+8)	(13) (5+9)	(14) (6+10)	(15)	(16)	(17)	(18) (15+16+17)	(19) (11-15)	(20) (12-16)	(21) (13-17)	(22) (14-18)
1,08,000	20,000	16,200 6,000	1,50,200	1,08,000	13,951	16,200 4715	1,42,866 (including Mar'07 stipend)	----	6,049	----	7,334 1,285

1. It is also certified that there is no other Research Fellow or Research Associate in the institute during the period.
2. This information may please be forwarded to CSIR office in respect of all Research Fellows / RAs along with a list of cheques received during the year showing cheque No., date and amount.

MBR No. _____
Date: _____

TO BE SUBMITTED IN TRIPLICATE

To,
Head, HRDG
CSIR Complex

WHILE CLAIMING THE GRANT MAY KINDLY
BE ENSURED THAT STATEMENT OF ACCOUNT
AND UTILIZATION CERTIFICATE FOR THE
PREVIOUS GRANT HAVE BEEN SUBMITTED TO
CSIR

GRANT-IN-AID-BILL

CSIR Sanction No. _____
Name of the Fellows
(In case of single person)

Dated _____
RA
SRF **Statement enclosed**
JRF **in triplicate**

Number of Research Fellow
(In case of consolidated bill)

Please send a consolidated bill of all RAs/fellows as far as possible

PARTICULAR	AMOUNT OF GRANT			TOTAL	REMARKS
	STAFF	CONT.	HRA/MA		
1. Amount Sanctioned for the year	1,08,000.00	20,000.00	16,200.00 6,000.00	1,50,200.00	Provision for fellowship and HRA has been given from 01.04.07 to 31.03.08. HRA has been provided at 15% of the fellowship applicable to Coimbatore, 'B' class city. As regards the medical allowance, a provision of Rs. 6,000/- is given for the year 2006-07. It may be noted that SACON's medical rule is reimbursement of actual expenditure for the treatment.
2. Grant claimed for the period from 01.04.07 to 31.03.08	1,08,000.00	20,000.00	16,200.00 6,000.00	1,50,200.00	
DEDUCT 3. Unspent Balance brought forward	-----	-----	-----	-----	
4. Net Amount Claimed	1,08,000.00	20,000.00	22,200.00	1,50,200.00	

1. Certified that the amount claimed in the bill will be utilized for the purpose it is sanctioned and in accordance with the terms and conditions for CSIR Fellowship and Grants.
2. Certified that the attendance records have been maintained & checked.
3. Certified that the work of the Research Fellows/Associate for the past six months has been satisfactory.
4. Certified that the persons for whom HRA is claimed have not been provided any accommodation and HRA claimed is as per rules of this institute.

Signature
of the Supervisor

Counter-Signature & Designation
of Head of Institute
(Office Stamp)

(To be filled in by CSIR) Budget Head P-81-101

Gr _____ No. _____ -EMR-I
Dated: _____

Passed _____ for _____ Rs. _____
(Rupees _____)

_____)

Cheque to be issued in favour of

Under Secretary/Section Officer
CSIR Complex

Pay _____ Rs. _____ only _____ (Rupees
_____)

_____)

Sr. Finance Officer & Account Officer
CSIR Complex

Paid Vide
Cheque No. _____

Dated _____ Rs. _____

Sr. F & AO
(EMR)

ACKNOWLEDGMENT

I express my sincere gratitude to the **Council of Scientific and Industrial Research (CSIR)** for the financial assistance to carry out the research work as a Senior Research Fellowship grant.

It gives me great pleasure in expressing my deep sense of gratitude and indebtedness to my mentor **Dr. PA Azeez** who was instrumental and the driving force behind this whole exercise. His inspiring guidance, visionary advices, constant encouragement, constructive suggestion, invariable support and cooperation made me to structure the work in a constructive manner and complete it successfully.

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**13. DETAILED REPORT ABOUT THE RESEARCH WORK DONE (DURING
APRIL 2007 to JULY 2007)**

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. 2000). 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 report. 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. RESEARCH QUESTIONS

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 REPORT

The report is structured into 5 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** 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 the bed sediment. The **Chapter 4** 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 5** lists out the relevant literatures cited in the report.



2. STUDY AREA AND GENERAL STRATEGY OF SAMPLE COLLECTION

2.1. STUDY AREA

The Keoladeo National Park (Figure 2.1), 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 2.1), 56 km west of Agra. It is equidistant from New Delhi and Jaipur on either side (approximately 180 km, Plate 2.2.). 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, Gambhir 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), 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 2.3 and Plate 2.4) 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 out come 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).

Terrestrial area, that includes woodland and grassland, cover almost 20 km² Kadam (*Mitragyna parvifolia*) trees dominate large sized trees and the woodland (Plate 2.5 and Plate 2.6), 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 2.7 and Plate 2.8) 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, 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 (Figure 2.2). 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.

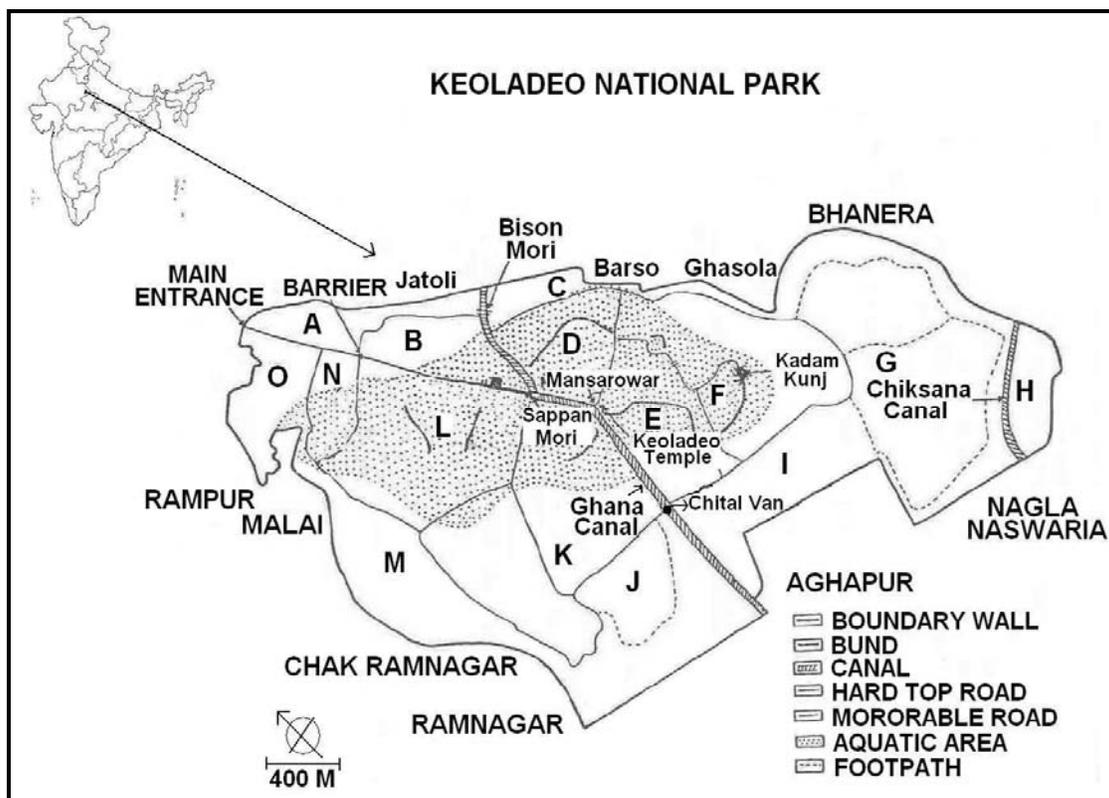


Figure 2.1. Study Area Map



Plate 2.1 Location map of Bharatpur city in India



Plate 2.2. Location map of Keoladeo National Park near Bharatpur city



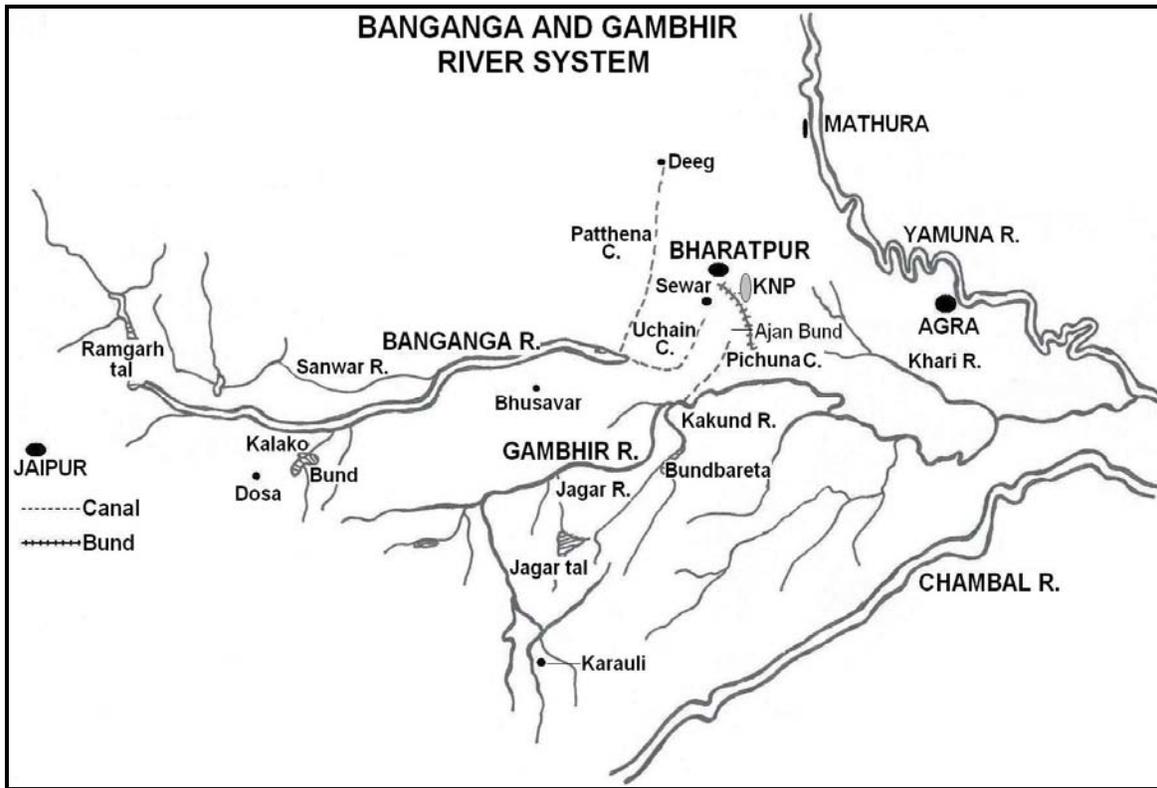


Figure 2.2. Map of Banganga-Gambhir river network



Plate 2.3. A view of the KNP wetland system (B Block)



Plate 2.4. A view of the KNP wetland system (E Block)



Plate 2.5. A view of the KNP woodland system (C Block)



Plate 2.6. A view of the KNP woodland system – Litters (C Block)



Plate 2.7. A view of the KNP grassland system (G Block)



Plate 2.8. A view of the KNP grassland system (G Block)



Plate 2.9. The Ajan Dam releases water to KNP through the sluice gates

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 2.2), 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 2.9.). 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.

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 2.3). 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 2.4).

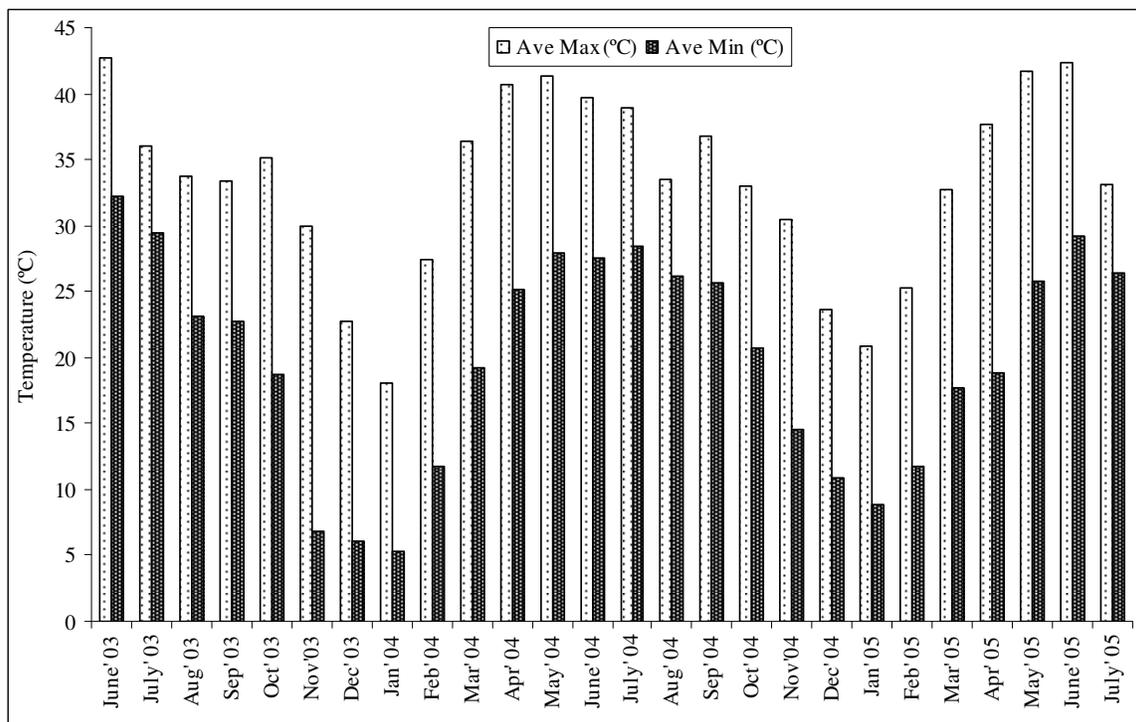


Figure 2.3. Seasonal variation of Temperature KNP during the period of the study



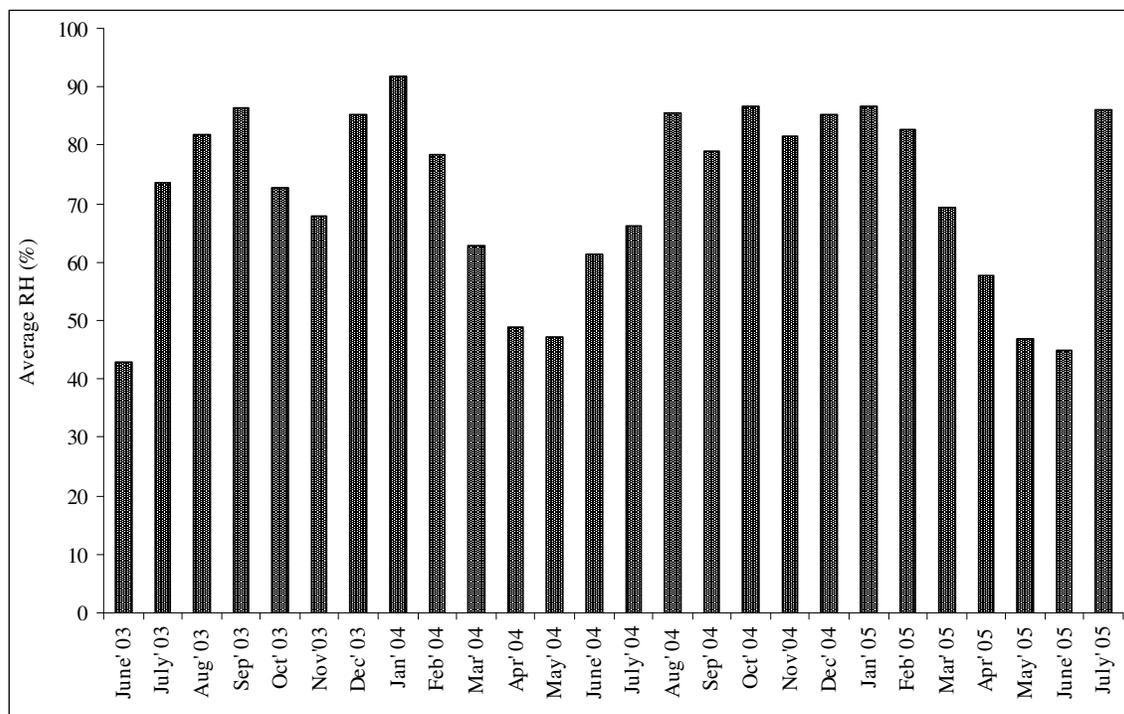


Figure 2.4. Seasonal variation of Relative Humidity in KNP during the period of the study

Table 2.1. 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 2.5). 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). 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.



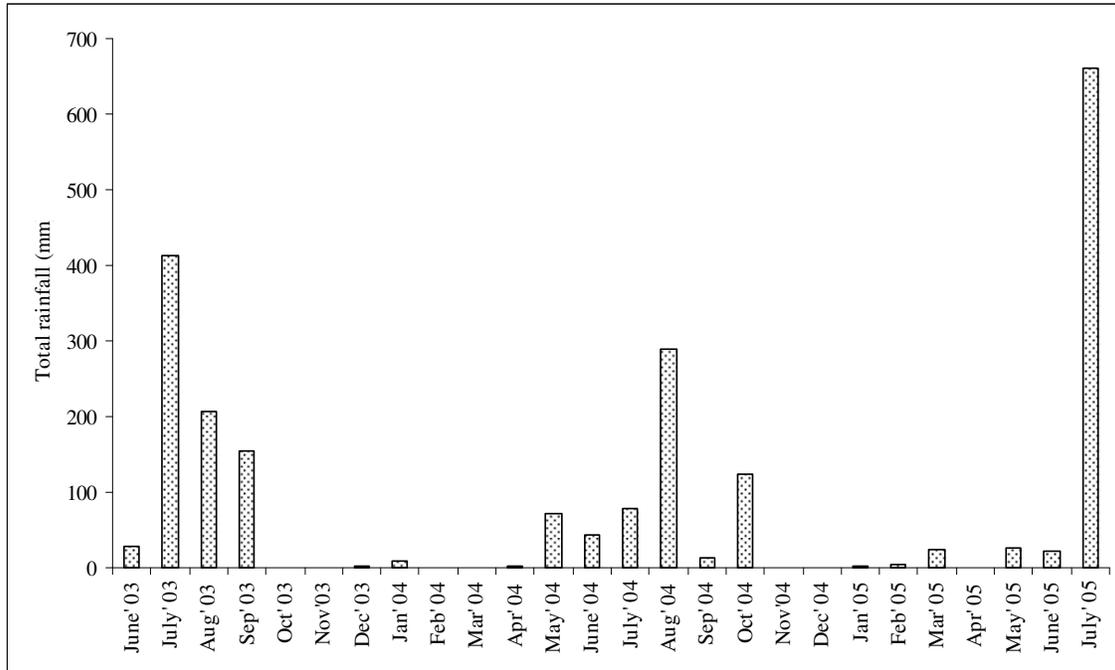


Figure 2.5. Seasonal variation of total rainfall in KNP during the period of the study

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 2.10). 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, slit 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 detailed methods of the soil processing for specific analysis are discussed under concerned chapters.

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 2.10) 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 major chemical characteristics of the samples used in the study were estimated/analysed by standard procedures and techniques as given in Table 2.2. The chapter 3 discuss about the temporal (bimonthly) variation in the distribution of alkali metals in KNP soil. In total 144 sediment samples (after pooling) was collected bimonthly from September 2003 to July 2005.

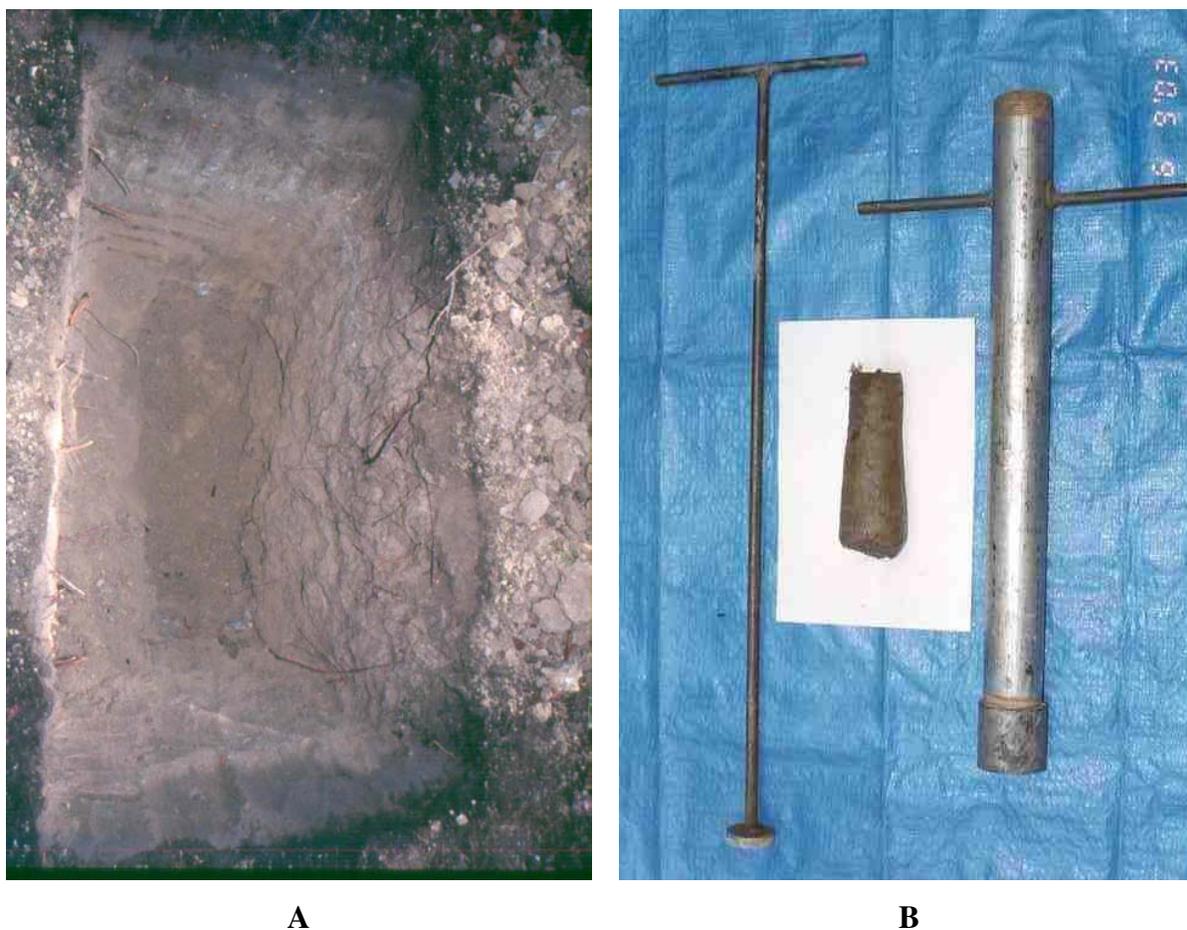


Plate 2.10. **A:** Trench dug for soil sampling (Spatial variation study) and **B:** Core sampler used for wetland bed sediment sampling (Temporal variation study)

Table 2.2. 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 alkali, alkaline earth and heavy 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. TEMPORAL VARIATION OF ALKALI AND ALKALINE EARTH METALS IN KNP WETLAND

3.1. 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 surfacial 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.

3.2. 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. Moreover, details of the analysis are discussed in section 2.2.2.

3.3. RESULTS

Figure 3.1, Figure 3.2 and Figure 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 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 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 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 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 3.3, $P < 0.05$).



Table 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 20004, March 2005 and May 2005, it did not show distinguishable trend of either decrease or increase with depth (Figure 3.2). Li varied significantly among the months ($P < 0.05$, Table 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 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 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 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 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 $Mg > Ca > K > Na > Li$.

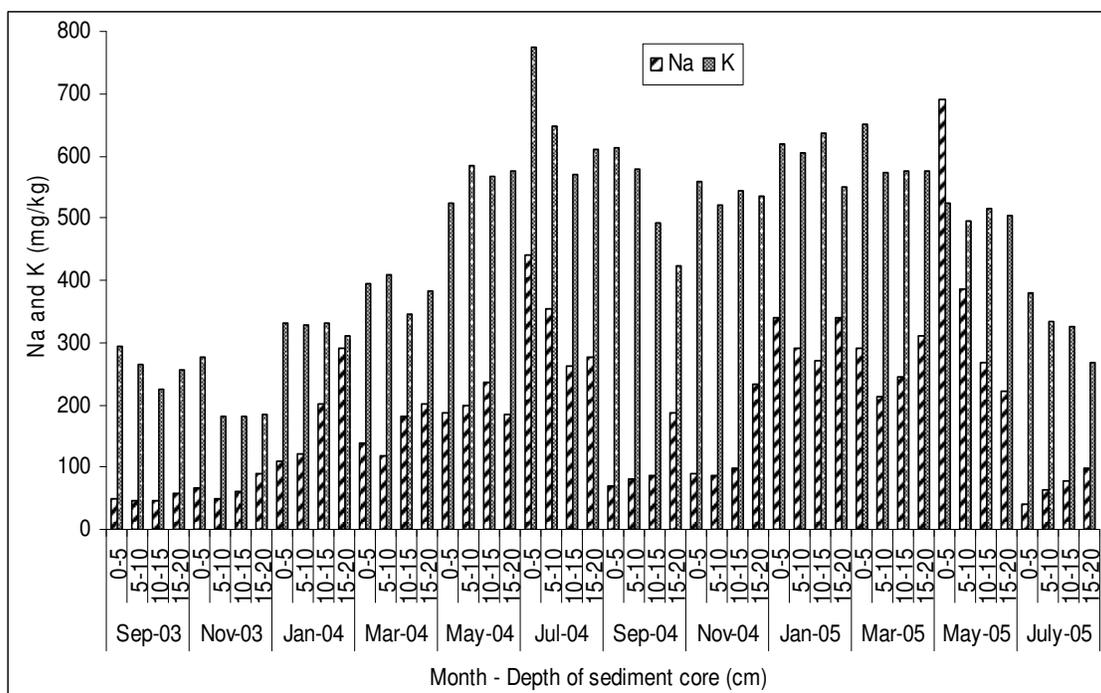


Figure 3.1 .Temporal variation in Sodium and Potassium



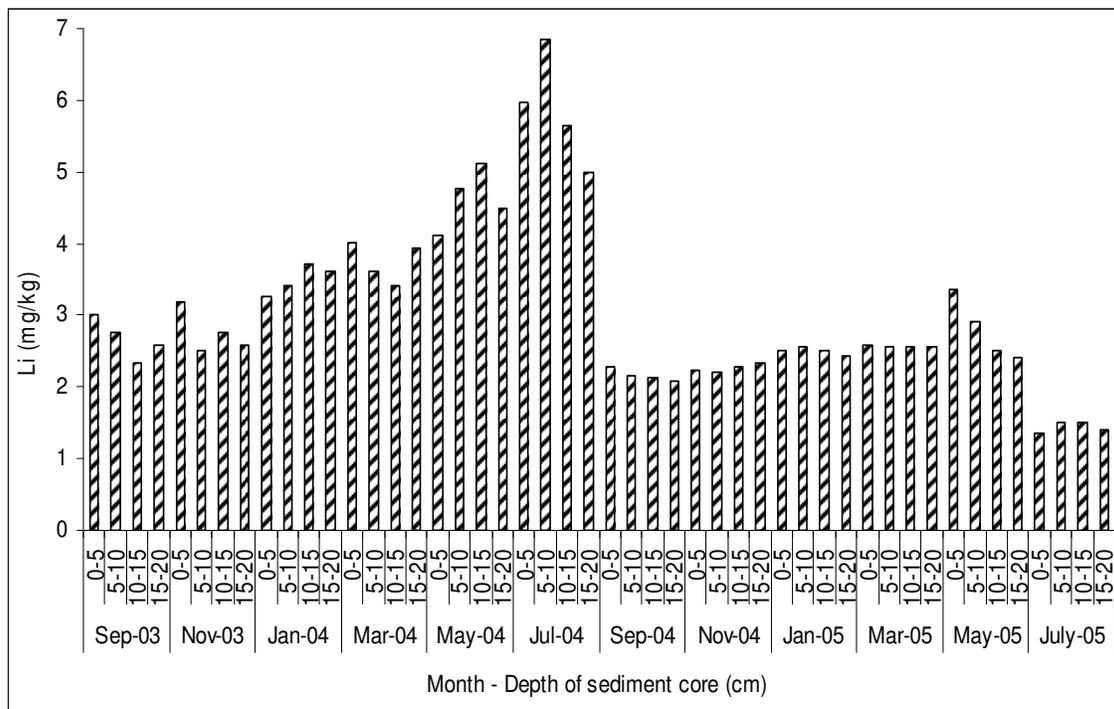


Figure 3.2. Temporal variation in Lithium

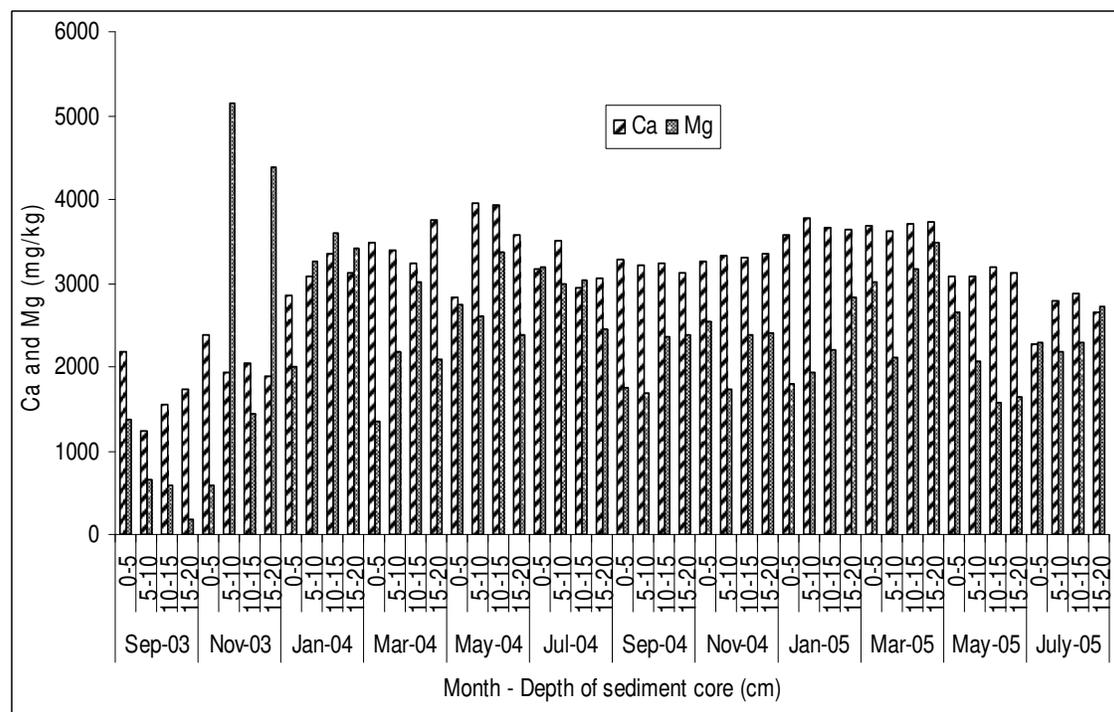


Figure 3.3. Temporal variation in Calcium and Magnesium

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 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 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 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 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 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 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 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 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 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 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 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 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 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 font types in a same row differ significantly (P < 0.05)												

Table 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 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				

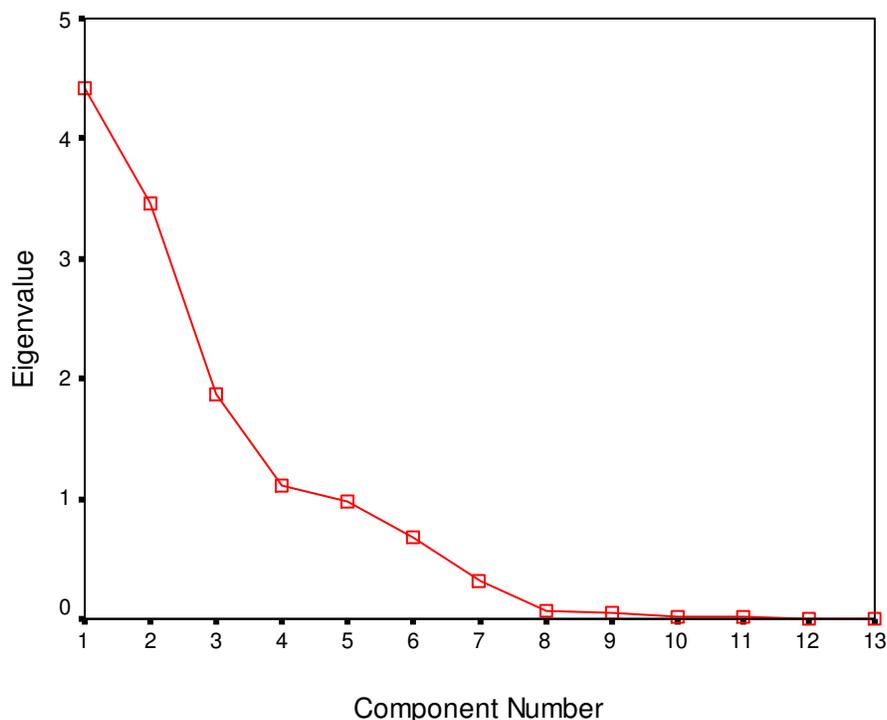


Figure 3.4. Scree plot of principal component analysis

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 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 3.4. Table 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.

3.4. 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 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 3.6).

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. 2006b) 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 3.6). 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 3.6). 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 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 3.6). 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 3.6. 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. (2006b)	Urban wetlands, Coimbatore, India
K	180-775	110 - 1042	Prusty et al. (2006b)	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. (2006b)	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

3.5. 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.



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

4.1. 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.



4.2. MATERIALS AND METHODS

4.2.1 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. 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). Aqua regia 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 4.1.

Table 4.1. 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 Tokalioğlu et al. (2003) for F-5	

4.3. RESULTS AND DISCUSSION

4.3.1 Cu

The variation of Cu concentration in the soil profile among different years and habitats is given in Figure 4.1. 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. (2000) 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 4.2). 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.

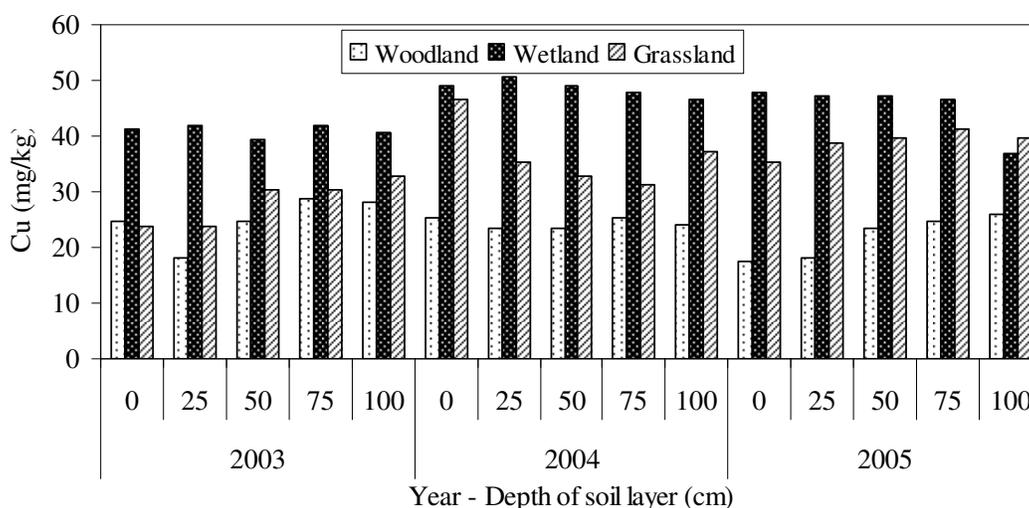


Figure 4.1. Habitat – Depth wise Variation of Cu in soil

Table 4.2. 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 4.2 to Figure 4.4. 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 4.2). 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 4.3). 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 4.4). 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.

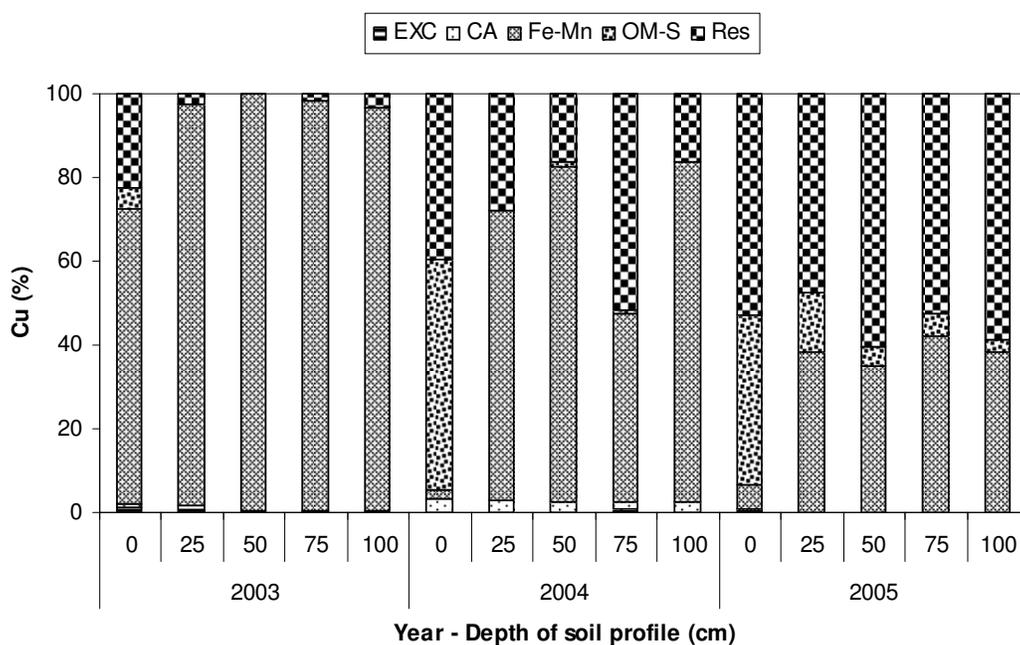


Figure 4.2. Cu fractionation in woodland

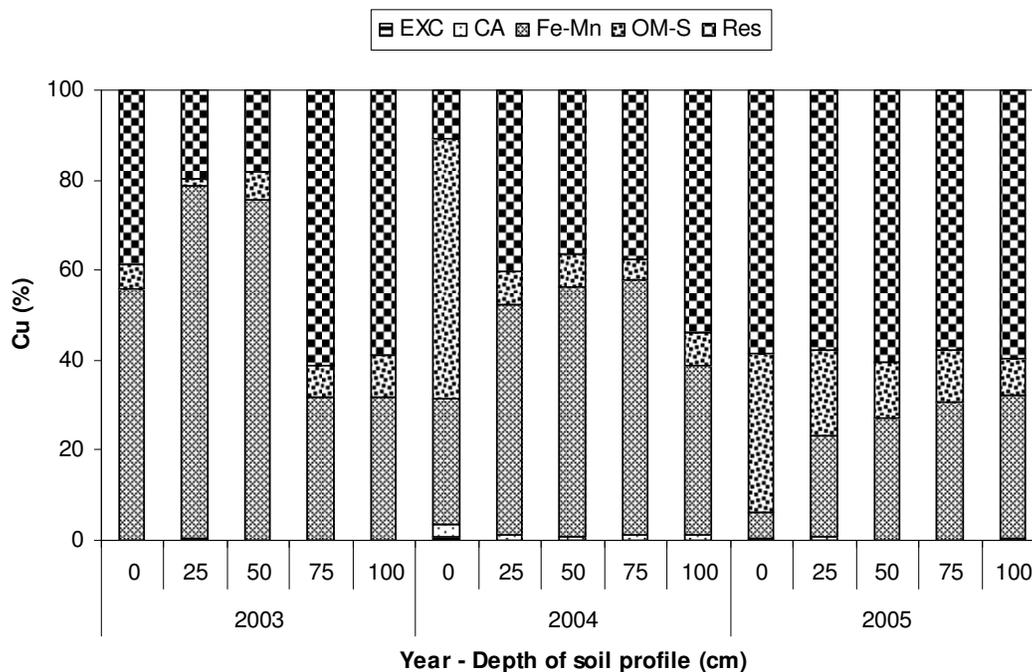


Figure 4.3. Cu fractionation in wetland

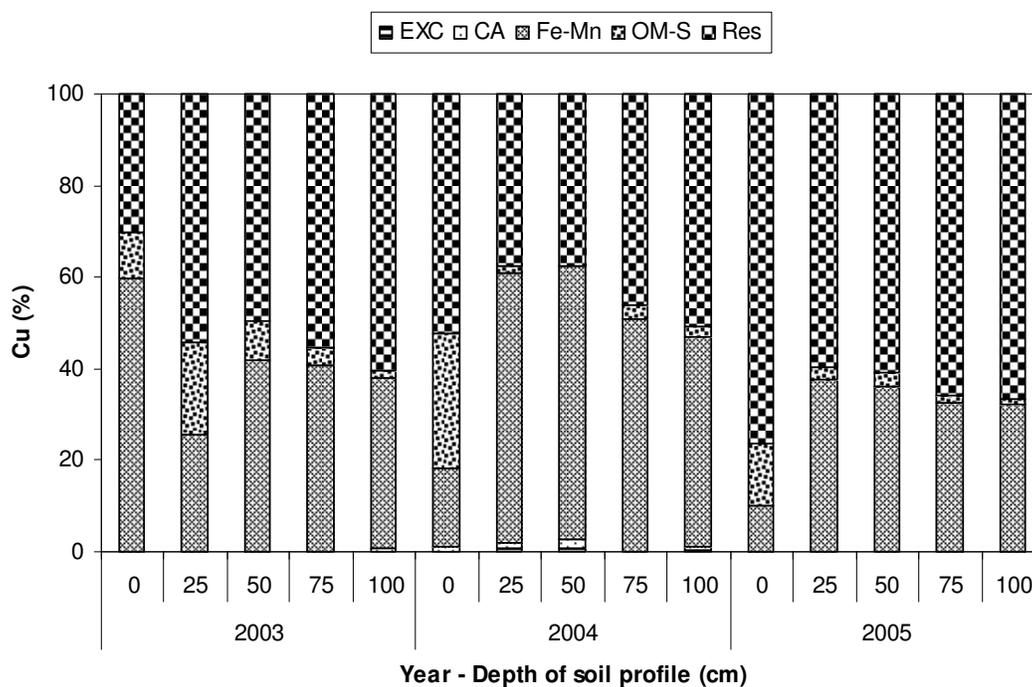


Figure 4.4. Cu fractionation in grassland

The extent of association among different fractions, and with TOM (%) and CO₃-C (%) is shown in Table 4.3. 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) CO₃-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 CO₃-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 4.4 to Table 4.6. 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 4.5). 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 4.3. 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, CO ₃ -C = Carbonate carbon								

Table 4.4. 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 4.5. 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 4.6. 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.



4.3.2 Pb

The distribution and variation of Pb concentration in the soil profile among different years and habitats is given in Figure 4.5. 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 (2000), 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 4.5). 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 4.7). 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. 2000).



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 for Cu and Zn (Friendland et al. 1984).

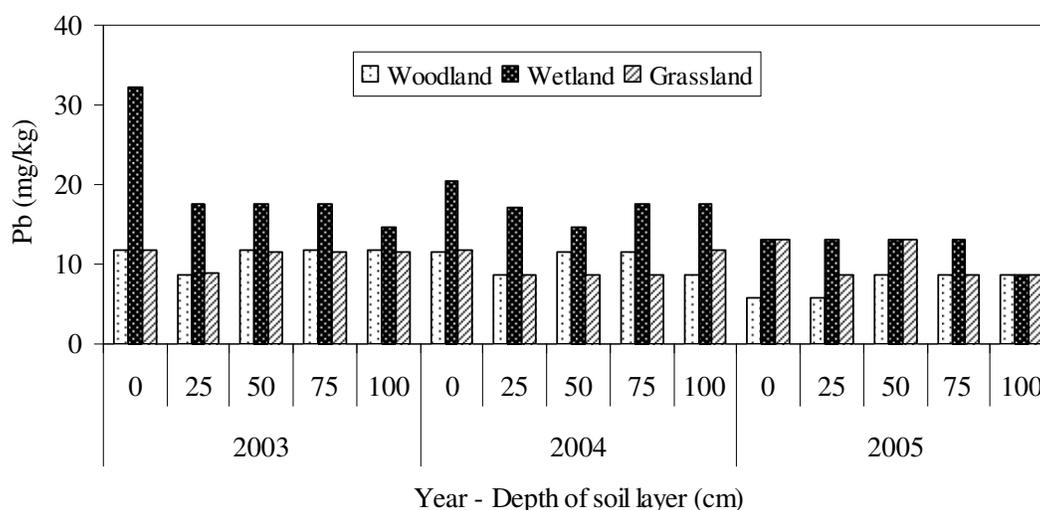


Figure 4.5. Habitat – Depth wise Variation of Pb in soil

Table 4.7. 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 4.6 to Figure 4.8). 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 4.6, Figure 4.7 and Figure 4.8). 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 4.6). 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 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.

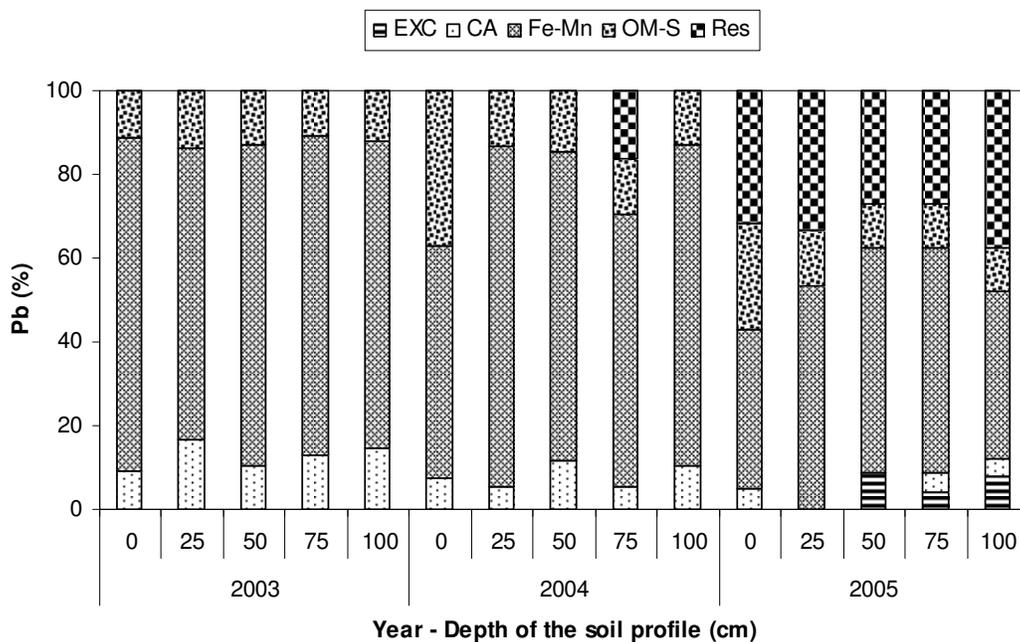


Figure 4.6. Pb fractionation in woodland

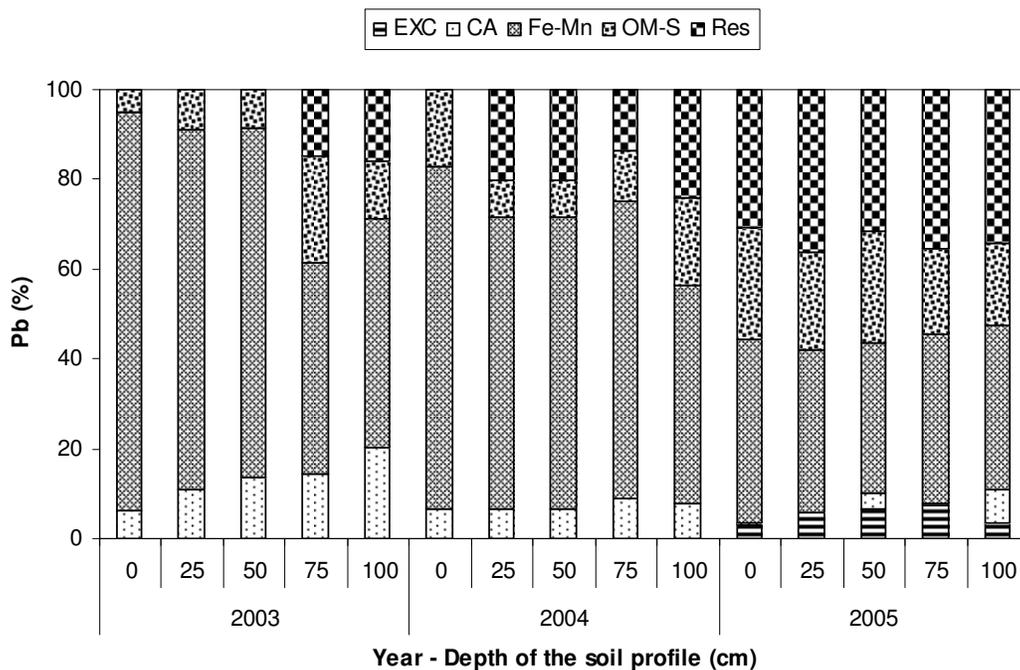


Figure 4.7. Pb fractionation in wetland



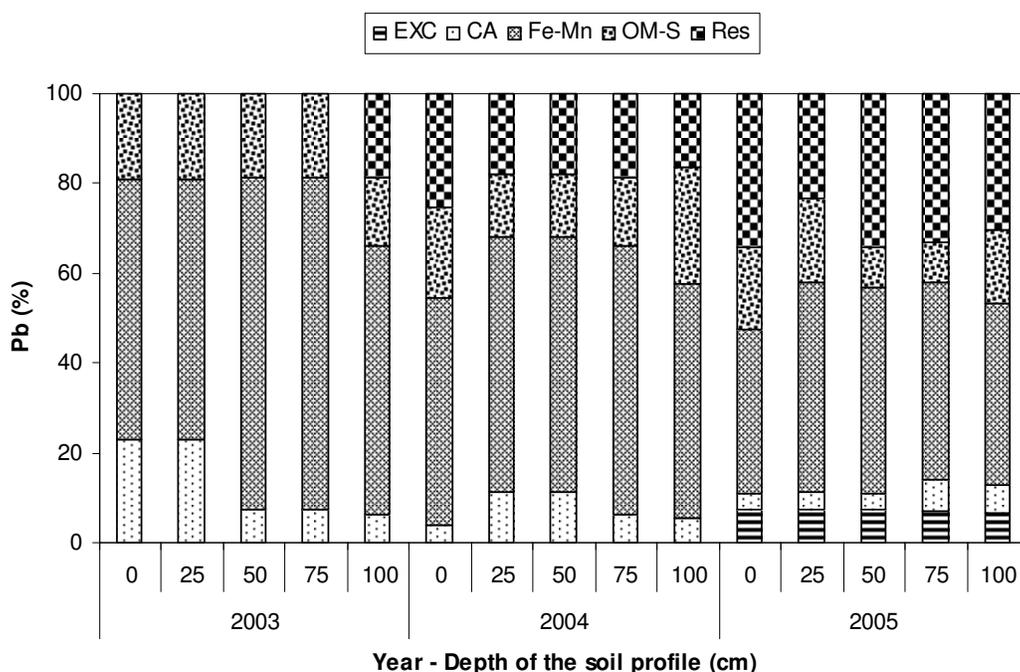


Figure 4.8. Pb fractionation in grassland

Table 4.8. 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, $\pm .514$ 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 extent of association among different fractions, and with TOM (%) and CO₃-C (%) is shown in Table 4.8. 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 4.8). 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.

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 4.9 to

Table 4.11. 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 CO₃-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.

Table 4.9. 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 4.10. 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 4.11. 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.



4.3.3 Zn

The variation in the level of Zn in the soil profile among different years is presented in Figure 4.9. 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 4.9).

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 4.9). 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 4.9). However, in grassland, Zn showed an increasing trend along the depth in the soil profile during all the years (Figure 4.9). 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 4.12).

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.

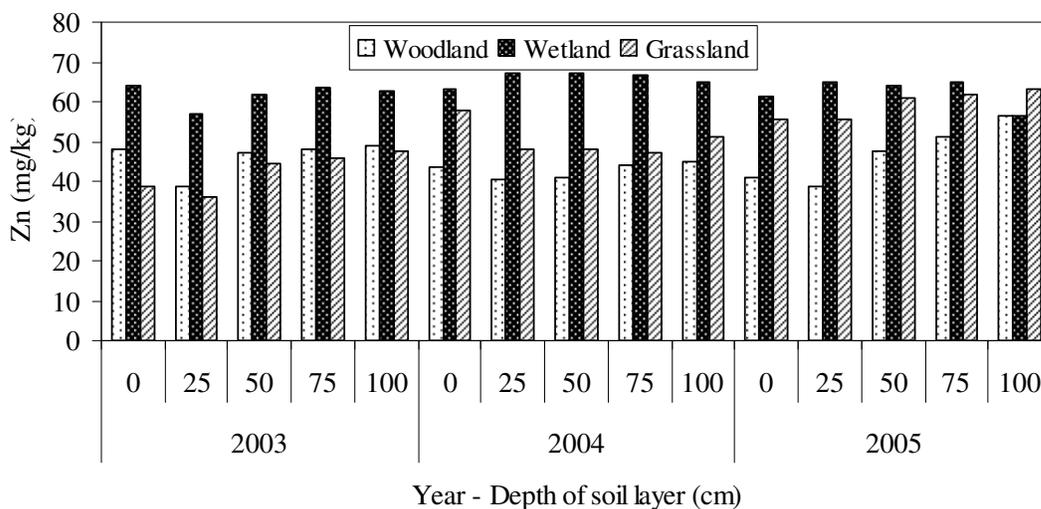


Figure 4.9. Habitat – Depth wise Variation of Zn in soil

Table 4.12. 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 4.10 to Figure 4.12. 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 4.11). 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 4.10). 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 4.12). 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 4.11). 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).

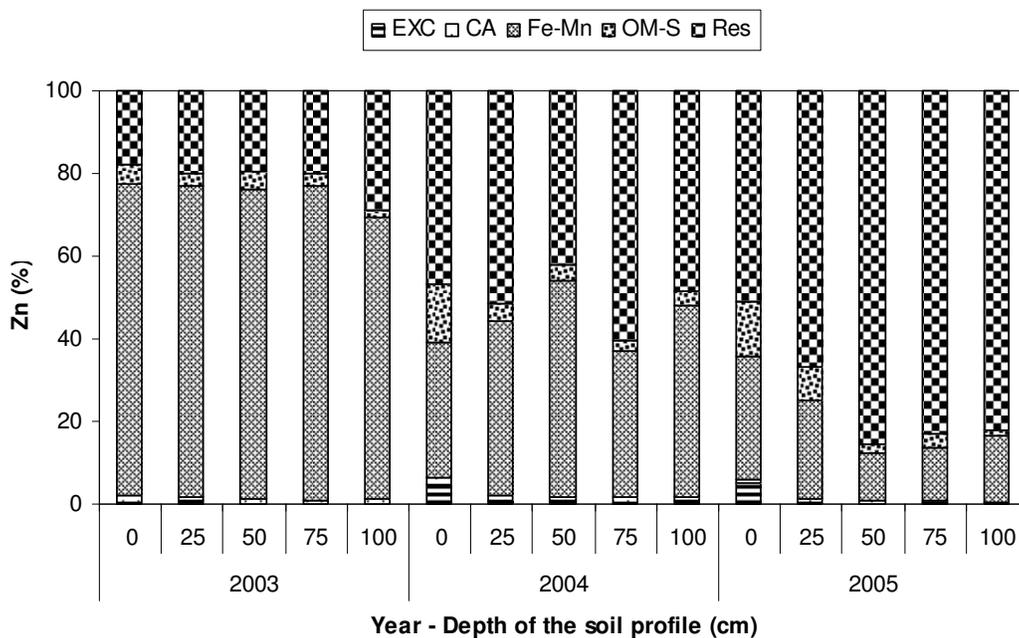


Figure 4.10. Fractionation of Zn in woodland

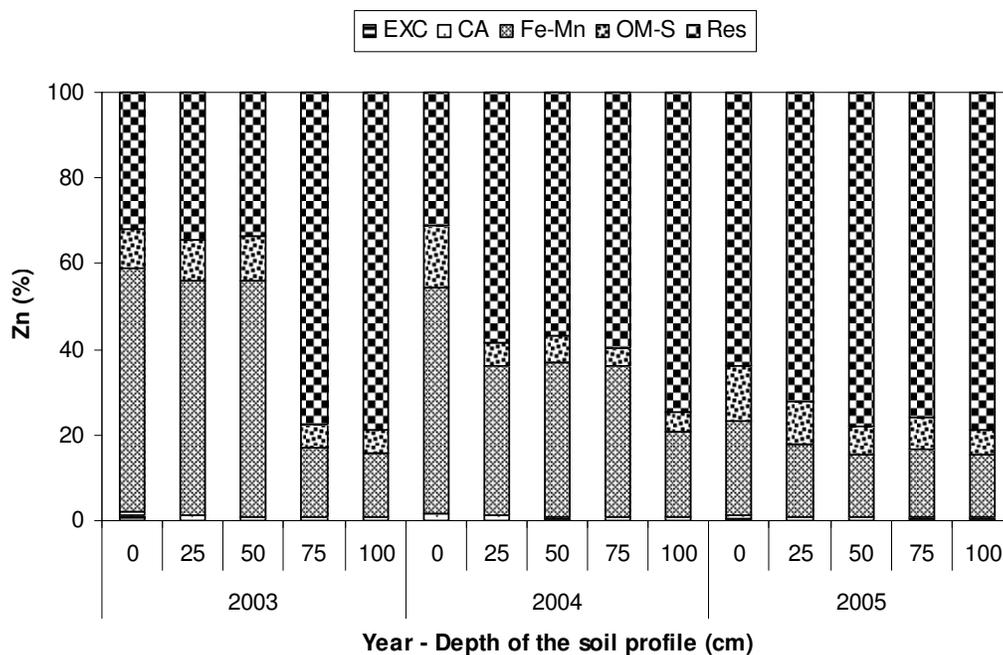


Figure 4.11. Fractionation of Zn in wetland



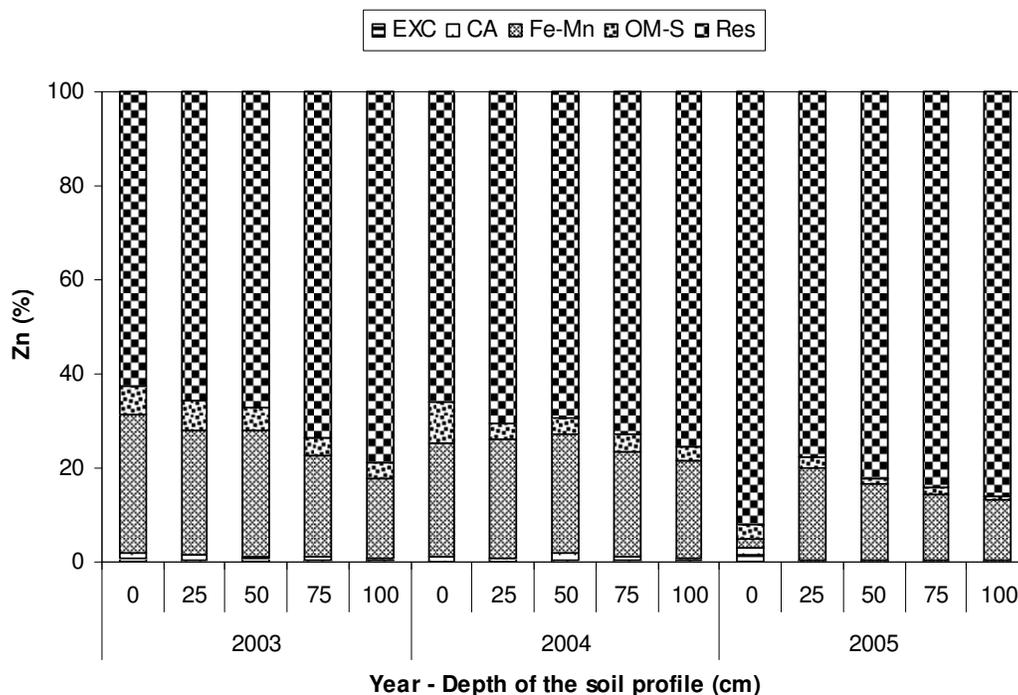


Figure 4.12. Fractionation of Zn in grassland

The extent of association among different fractions, and with TOM (%) and CO₃-C (%) is shown in Table 4.13. For Zn, among the non-residual fractions only Fe-Mn was negatively correlated with the RES fraction in all the habitats. The TOM (%) was negatively correlated with the RES fraction only in wetland soil. 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 ($r = 0.542$, $P < 0.05$), 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 4.14 to Table 4.16. 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 4.14). In the case of wetland soil, only RES and Fe-Mn (Table 4.15) were distinct from the rest. In this case RES and Fe-Mn phase were found to be distinct from others (Table 4.16). 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 4.13. 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, CO ₃ -C = Carbonate carbon								

Table 4.14. 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 4.15. 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 4.16. 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.

4.4. 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 pre-concentration 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.



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14. SUMMARY OF RESEARCH WORK DONE

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. Variations were also found on a temporal scale. Irrespective of the habitat type and year, most of the nutrients, such as Total organic carbon (TOC), Total Nitrogen (TN), Total Available Phosphorus (TAP) and Total Available Sulphur (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 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 found to be 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 cause in the 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.

The temporal distribution of SOM 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, one of the driving forces for the detritus decomposition. 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. P, the most limiting nutrient, seems to come to this wetland system from agricultural sources, whereas S comes from runoff from the catchment. Plant uptake of nutrients seems to be a significant factor in the case of P, as it was found within 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 TAN was high. Both the autochthonous and allochthonous materials significantly influence the nutrient distribution in the wetland.

Contrary to the expectations, K, Ca and Li showed gradual declining trend downward in the soil profile in all the habitats whereas Na had a downward increasing trend. 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. 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, their wetland counterparts 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.

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 and confined geographical realm. In order to get a better insight into the nutrient 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 more importance than the concentrations for studying internal nutrient transfers within ecosystems as well as for comparisons between different sites as in the Keoladeo National Park. Hence, it is important that future studies on the vertical nutrient distribution and mobilization examines ground water nutrient levels and dynamics.



16. Research papers (Published, Accepted/In Press, and Communicated)

Research Publications:

- Research Articles in Journals: 16
- Chapters in Books: 05
- Technical Reports (including Ph D. thesis): 02

In Scientific Journals (Total No: 16):

- 2005) **B Anjan Kumar Prusty** and PA Azeez. Humus: The Natural Organic Matter in the Soil System. *Journal of Agricultural Research and Development*. 1: 1-12.
- 2006) PA Azeez, **B. Anjan Kumar Prusty** and EP Jagadeesh. 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.
- 2006) Rachna Chandra and **B. Anjan Kumar Prusty**. Sighting of nests of dusky horned owl (*Bubo coromandus*) in Keoladeo National Park, Bharatpur, Rajasthan. *Newsletter for Birdwatchers*. 46 (5): 79 (September-October 2006).
- 2007) **B. Anjan Kumar Prusty**, EP Jagadeesh, PA Azeez and DK Banerjee. Distribution and chemical speciation of select transition metals in the waters of river Yamuna, New Delhi. *Environmental Science: An Indian Journal*. 2 (2): 139-144 (September 2007).
- 2007) **B Anjan Kumar Prusty**, PA Azeez and EP Jagadeesh. Alkali and transition metals in macrophytes of a wetland system. *Bulletin of Environmental Contamination and Toxicology*. 78 (5): 405-410 (May 2007).
- 2007) **B Anjan Kumar Prusty** and PA Azeez. Role of detritus on trace metals in wetland-terrestrial systems: A review. *Environmental Science: An Indian Journal*. 2 (2): 109-129 (June 2007).
- 2007) R Chandra, **B. Anjan Kumar Prusty**, D Maithily, SR Sarimol and PA Azeez. 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).
- 2007) **B. Anjan Kumar Prusty**. The eclipsed link between aboveground and belowground biota. *Malabar Trogon*. 5 (1): 15.
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- 2007) **B Anjan Kumar Prusty** and PA Azeez. Vertical distribution of alkali and alkaline earth metals in the soil profile of a wetland-terrestrial ecosystem complex in India. *Australian Journal of Soil Research*. 45 (7): 533-542 (November 2007).
- 2008) PA Azeez and **B. Anjan Kumar Prusty**. Transition metals in decomposing macrophytes in a wetland system. *Asian Journal of Water, Environment and Pollution*. 5 (1): 27-35 (January-March 2008 issue).
- 2008) **B. Anjan Kumar Prusty**, Rachna Chandra and P A Azeez. Vertical and temporal variation of Zn in the soils of a multiple habitat system. *Journal of Food, Agriculture and Environment*. 6 (2): 381-387 (April 2008).



In Press) B. Anjan Kumar Prusty, Rachna Chandra and PA Azeez. Biodiesel: freedom from dependence on fossil fuels and a step towards sustainable development. *Journal of Environment and Energy*.

In Press) B. Anjan Kumar Prusty, Rachna Chandra, M. Shah Hussain and PA Azeez. Annual recruitment pattern of fishes into Keoladeo National Park wetland system, India. *Environmental Research Journal*.

In Press) Rachna Chandra, B Anjan Kumar Prusty and PA Azeez. Biomass and productivity assessment of plant community in a monsoonal wetland ecosystem. *Environmental Research Journal*.

In Press) R Chandra and B. Anjan Kumar Prusty. “A new record of a fish species, *Rasbora daniconius*, in the wetlands of Keoladeo National Park, Bharatpur, India, and conservation concerns”. *Environmental research Journal*.

In Books (Edited Chapter, Total No: 5):

- **2007) PA Azeez, NR Nadarajan and BAK Prusty**. Macrophyte decomposition and its impact on the water quality. Edited Book on “**Environmental Degradation and Protection**” Volume – II, MD Publications, New Delhi, pp. 115-156.
- **In Press) B. Anjan Kumar Prusty** and P. A. Azeez. Wetlands: Efficient systems for waste water treatment. Edited book on “**Environmental Studies**”, Atlantic Publishers and Distributors, New Delhi, India.
- **In Press) B. Anjan Kumar Prusty** and P. A. Azeez. Sustainable Development: A key environmental debate. Edited book on “**Environmental Studies**”, Atlantic Publishers and Distributors, New Delhi, India.
- **In Press) B. Anjan Kumar Prusty**, Rachna Chandra, M Shah Hussain and PA Azeez. Catchment Changes Influence the Arrival Pattern of Fishes into a Semitropical Monsoonal Wetland System. “**Wetlands: Ecology, Conservation and Restoration**”. Nova Publishers, New York, USA.
- **In Press) Rachna Chandra, B Anjan Kumar Prusty** and PA Azeez. Biomass, productivity and species diversity of plant community in a rainfed monsoonal wetland ecosystem with specific emphasis on its temporal variability. “**Wetlands: Ecology, Conservation and Restoration**”. Nova Publishers, New York, USA.

In Scientific Journals (Under revision; Total No: 4):

- **B. Anjan Kumar Prusty**, V. Jayalakshmi and PA Azeez. “Distribution of select transition metals in monsoon fed urban wetland sediments”. *Journal of Environmental Science and Health*”.
- PA Azeez, **B Anjan Kumar Prusty** and EP Jagadeesh. “Select alkali and alkaline earth metals in decomposing macrophytes in a wetland system”. *Acta Ecologica Sinica*”.
- **B. Anjan Kumar Prusty**, Rachna Chandra and P A Azeez. Day-night variation in the movement of fry in a feeder canal of a monsoonal wetland, Keoladeo National Park (KNP), Bharatpur, India. *Biological Letters*”.
- Rachna Chandra, **B Anjan Kumar Prusty**, and PA Azeez. A revised checklist of the flora of Keoladeo National Park, a world heritage site in India. *Tropical Conservation Science*.



Research Papers Submitted (Total No: 6):

- **B. Anjan Kumar Prusty**, Rachna Chandra and PA Azeez. Cu, Pb and Zn fractionation in a savannah type grassland soil. *Bioscan*.
- **B. Anjan Kumar Prusty**, V Jayalakshmi and PA Azeez. Alkali and alkaline earth metals in monsoon fed urban wetland sediments. *Biogeochemistry*.
- **B. Anjan Kumar Prusty** and PA Azeez. C-N-P-S distribution in the soil system at Keoladeo National Park, Bharatpur, India. *Acta Ecologica Sinica*.
- **B. Anjan Kumar Prusty**, Rachna Chandra and PA Azeez. Macronutrients along the sediment core in a semitropical monsoonal wetland in India. *Wetlands Ecology and Management*.
- **B. Anjan Kumar Prusty**, Rachna Chandra and PA Azeez. Temporal variation and distribution of select alkali and alkaline earth metals in the sediment of a monsoonal wetland in India. *Fresenius Environmental Bulletin*.
- **B. Anjan Kumar Prusty** and Pramod Chandra Mishra. Some Observations on Intake and Utilization of *Calotropis procera* Leaves by the Aak Grasshopper, *Poecilocerous pictus* (Orthoptera: Acrididae). *Malabar Trogon*.

