ENVIRONMENTAL QUALITY ASSESSMENT ALONG CORRIDORS OF HIGH TRAFFIC ROADS IN KANO METROPOLIS, NIGERIA

BY

OKUNOLA, OLUWOLE JOSHUA
(BSc, MSc A.B.U)
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DECLARATION

I hereby declare that the work in this Dissertation entitled "Environmental Quality Assessment Along Corridors of High Traffic Roads in Kano Metropolis, Nigeria" was performed by me in the Department of Chemistry, under the supervision of Dr. A. Uzairu, Prof. C. E. Gimba and Prof. G. I. Ndukwe. The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this work has been previously presented for another Degree or Diploma at any Institution.

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Okunola, Oluwole Joshua Date

CERTIFICATION

This Dissertation entitled "Environmental Quality Assessment Along Corridors of High Traffic Roads in Kano Metropolis, Nigeria" by Okunola, Oluwole Joshua meets the regulations governing the award of the degree of Doctor of Philosophy of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

---------- ----------

Dr. A. Uzairu Date
Chairman Supervisory Committee
Chemistry Department, A. B. U., Zaria

---------- ----------

Prof. C. E. Gimba Date
Member Supervisory Committee
Chemistry Department, A. B. U., Zaria

---------- ----------

Prof. G. I. Ndukwe Date
Member Supervisory Committee
Chemistry Department, A. B. U., Zaria

---------- ----------

Prof. C. E. Gimba Date
Head of Department, Chemistry
A. B. U., Zaria

---------- ----------

Prof. A. A. Joshua Date
Dean Postgraduate School
A. B. U., Zaria

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ABSTRACT

This study was aimed at assessing the variation of concentrations of total and species of Cd, Cr, Ni, Pb, Cu and Zn in atmospheric dust particulate and roadside surface soil samples, and air pollutants (CO, H_2S, NO_2, SO_2, FL and NH_3) along busy roads in Kano Metropolis due to increase in automobile over the years. The study was carried out across cool and dry, hot and dry, warm and wet and warm and dry seasons. Other parameters which were investigated included, particle size distribution, pH, electrical conductivity (EC), organic matter (OM) and the cation exchange capacity (CEC) of the soil samples, and sound level and temperature. Atmospheric dust particulate and soil samples, traffic data and air pollutants (including hourly average) were collected from ten selected busy roads and a control site (from a garden) in the metropolis. The soil samples were sieved to produce samples of different particle sizes (1400µm, 355µm and 150µm). For total Cd, Cr, Ni, Pb, Cu and Zn concentrations, the samples were digested with aqua regia, and a six-stage sequential extraction protocol was used for their chemical fractionation. Statistical evaluation of the results obtained showed significant differences ($p < 0.05$) across the sites and seasons. Generally, total metal extraction revealed high concentration that depict high ecological risk, however, the sequential extraction showed that availability of these metals are low to the immediate environment. This implies that risk assessment using total metal concentration is not enough to conclude that an environment is polluted. The results of gaseous pollutants showed that concentrations of CO, H_2S, NO_2 and SO_2 measured with few exceptions at some sites were above the air quality index AQI stipulated by USEPA especially during the afternoon periods. This implies that traffic emission within Kano metropolis is not within the safe limits.

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LIST OF ABBREVIATIONS

FL	Flammable gases
EU	European Union
US	United States
ppm	part per million same as milli gram per cubic decimeter
SO_2	Sulphur (VI) Oxide
CO	Carbon monoxide
NH_3	Ammonia
H_2S	Hydrogen sulphide
NO_2	Nitrogen (VI) Oxide
PM	Particulate Matter
mg/dm^3	milli gram per cubic decimeter
cm^3	cubic centimeter
HC	Hydrocarbon
TSP	Total Suspended Particulates
COHb	carbon monoxide haemoglobin
%	Percentage
Hg	Mercury
MMT	methylcyclo-pentadienyl manganesetricarbonyl
TEL	Lead tetraethyl
As	Arsenic
Se	Selenium

Sb	Antimony
$mgkg^{-1}$	milli gram per kilogram
NaCl	sodium chloride
m	meters
Fe	Iron
V	Vanadium
Co	Cobalt
$CaCO_3$	calcium carbonate
ICRCL	Interdepartmental Committee for the Redevelopment of Contaminated Land.
FAO	Food Agriculture Organization
Mn	Manganese
µm	micro meters
Al^{3+}	Aluminium (III) ion
H^+	Hydrogen ion
meq	milli equivalent
mm	millimeter
KCl	potassium chloride
ANOVA	Analysis of Variance
F - ratio	Fisher's ratio

CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND TO THE STUDY

Over the years, vehicular traffic has increased multifold causing an associated increase in the total emissions from transportation sources (Vijayan, 2007). These vehicular emissions affect two human occupied environments most significantly: human occupied regions near and around the roads including residences, offices, schools, hospitals etc., and indoor vehicle compartments that act as individual microenvironments trapped inside the high concentration zone (Vijayan, 2007).

Jenkins *et al*. (1992) observed that urban populations spend almost 7% of their daily time commuting, most of which is to travel between their workplace and place of residence. Almost half of this commute time is spent stuck in traffic (CARB Report, 2003). This could be attributed to the quadrupled increase in the number of cars on the road as compared to 1960, in addition to the increase in the per capita driving over 2.5 times to 10,000 miles (U.S. Environmental Protection Agency, 2000). This increase in the number of vehicles on the roads and their total operation time has resulted in a tremendous increase in vehicular pollution.

According to United Nations, it was estimated that over 600 million people in urban areas worldwide were exposed to dangerous level of traffic-generated air pollutants (Cacciola *et al*., 2002). Some of the worst pollutants ranged from gaseous pollutants (carbon monoxide, nitrogen oxides and sulphur dioxide), heavy metals to particulate matter.

It has been known for a long time that many of the substances that are referred to as air pollutants produce human health effects at high levels of exposure. This has been well documented in case studies of a series of air pollution episodes in the mid-1900s which

showed dramatic effects on health, and in high dose toxicological studies in animals. Air pollution episodes in the Meuse Valley of Belgium in 1930, Donora in the United States of America in 1948 and London, England in 1952 were investigated in detail. In the 1952 London air pollution episode it was estimated that 4,000 extra deaths occurred as a result of the high concentrations of sulphur dioxide and particulate matter (Brimblecombe, 1987).

In recent years, numerous studies worldwide have linked particulate matter to a wide range of adverse health effects including deaths (Ostro *et al*. 1996; Kaiser 2000; Biswas and Wu, 2005; Chow and Solomon, 2006). There is evidence that exposure to particulate matter from traffic and other combustion sources have more severe impacts on human health than particulate (PM) from other sources, inferring that the health effects associated with PM would be related mostly to anthropogenic emission sources (K□nzli *et al*., 2000). Also, Fine particulate matter can be dispersed to longer distances from their place of origin and is a major cause of haze, which reduces visibility (Vijayan, 2007). Clearly, vehicle emissions are a major source of ambient air pollution that must be controlled if quality of road environment is going to be maintained.

Several environmental protection agencies (USEPA, EU and WHO) emission strategies have been implemented to reduce emissions over the years, the most recent one being implemented was in 2005 (WHO, 2011) and 2007 (USEPA, 2011). This was put in place for decision makers in the transportation industry to move towards a cleaner sustainable operation. Unfortunately, at present, there is neither a legislative framework nor a set standard in Nigeria to monitor emission from mobile sources. The regulatory framework put in place by the Federal Government through the then Federal Environmental Protection Agency (FEPA) in 1991 is limited to emission generated through stationary sources (Itua, 2011). Though the Ministry of Transport is working with the Ministry of

Environment to set guidelines on vehicular emissions, but this has not yet come to fruition. This could explain the reason that in Nigeria the enormous benefit of automobile transportation has prevented people from considering the great danger posed by its side effects like noise and air pollution.

With the growing fleet of vehicles, trucks and motocycles, the continuous impact of emission to commuters, business centers and residents close to the roads has become a concern to the general public. Therefore, monitoring of gaseous pollutants and particulate matter especially with heavy metals is imperative.

1.2 RESEARCH PROBLEM

One of the key indicators of the quality of life is a clean environment, which can be further disaggregated in terms of water, soil, noise and air qualities. During the last 200 years, humans began to significantly alter the composition of the atmosphere through pollution, especially in urban centres (Akanni, 2010). Hence, environmental pollution is a product of urbanization and technology, and other attendant factors of population density and industrialization (Olade, 1987).

Like any other cities of the world, Kano metropolis developed over the years in a steady progress in industrialization and increase in population and traffic density (Ministry of Information, Kano State, 2005). Industrially, it is one of the most developed cities in Northern Nigeria, tannery and textile are some of its dominating industries (Faboya, 1997). From 1991 the population of 2,166,554 grew to be now 3,127,894 people (TWG, 2010). The presence of raw materials, market, transportation networks, capital and labour makes Kano a major industrial centre in Nigeria. All these resulted in a rapid population growth especially through migrations (Malumfashi *et al*., 2011). With the growth in population,

economic activities have increased leading to more automobiles averaging 24,857 motocycles, 19,262 other vehicles and 1,209 trucks per day. Urban canopy pollution resulting from urbanization is one of the microclimatic problems faced in many urban centres (Akanni, 2010), which Kano metropolis cannot be an exception. The air along traffic corridors where majority of residents in the formal and informal sectors (p) subsist daily to conduct their daily activities could hardly be regarded as fresh. This is due to automobile emissions from various activities on the roads.

These activities emit pollutants into the air which subsequently are deposited into nearby soils. Sakagami *et al*. (1982) reported that there was close relationship between trace metal concentration in roadside soil and the dust falls. Trace metals in the soils can also generate airborne particles and dust, which may affect the air quality (Gray *et al*., 2003). In general the dispersal of air pollutant is favoured by warm, dry conditions with a steady side wind (Walker *et al*., 2001).

Moreover, the fuel composition couple with large importation of used automobiles (regarded as super-emitter due to poor combustion) makes it likely that the automobiles in use in Kano metropolis will release high levels of pollutants. Automobile emissions are affected by fuel type, especially sulphur content. As sulphur content increases, the fuel efficiency decreases and emission of sulphur oxides, particulate matter, and volatile organic compound increase (World Bank, 2003). In the US, gasoline has a standard of 15ppm of sulphur, and in the EU, it has a standard of 50ppm. The concentration of sulphur in fuels in Nigeria most often range from 500 – 2000ppm, with a maximum allowable sulphur level of 5000ppm (UNEP, 2007). Therefore, it can be expected that vehicles will cause remarkably more pollution, especially sulphur oxides and particulate which has health implications. For instance Ossai *et al*. (1999), Okecha (2000) and Efe (2008) asserted that high rates of

respiratory diseases occasioned by increases in particulate matter (PM_{10}) concentrations were experienced by residents of most urban areas. Generally the researchers believed that gaseous pollutant in urban areas of Nigeria has the following health implications:

i. The oxides of sulphur and sulphur combined with water vapour in the atmosphere to cause acid rain in cities. When these acids are consumed, they cause acidosis in human body. Excess accumulation in human body can lead to death.
ii. Gaseous pollutants stimulate coughing in patients suffering from chronic bronchitis and those patients with heart and lung disease may fatally succumb to SO_2.

Also, interest in the levels of contaminants associated with road dusts has risen in the last decades, particularly in light of the impact of high blood–lead levels in children living in urban areas caused by contaminated hand-to-mouth activity (Akhter and Madany, 1993; Hwang *et al*., 2004; Maynard *et al*., 2003; Ademoroti and Oviawe, 2006). Recently, many environmental studies have revealed that atmospheric pollution, due to automobile exhaust emission, is a significant source of heavy metal contamination in urbanized areas (Thornton, 1991). In addition to combustion of leaded gasoline, a wide variety of human activities in the urban environment will generate particulate matter. These may include; foundries, power stations, water transported material, dry and wet atmospheric deposition, biological inputs, road surface wear, road paint degradation, and vehicle wear and particulate emissions (Sutherland and Tolosa, 2000).

The role of some heavy metals (Cd and Pb) is very critical in determining the quality of our atmosphere, because air, soil and water are directly interacting with each other. Growing heavy metal pollution especially in air has led to an increase in respiratory diseases, infant mortality and also act as poison that affect the functioning of the blood, liver, kidney and brain. The measurement of Pb, Cd, Cu, Zn and Ni accumulation in soil

and dust appears to be a useful tool for evaluating the potential heavy metal hazards of the environment (Mudassir *et al*., 2005).

A considerable number of studies on the concentration of harmful pollutants in the urban environment have been done in developed countries with long history of industrialization. However, scarce information exists in developing countries limiting the appropriate evaluation of the levels of risk of the people who live in the most important cities (Shinggu *et al.,* 2007). In Nigeria at present little data are available on the extent of air-soil pollution due to heavy metals and gaseous pollutants because no agencies have been charged with the routine monitoring and protection of the environment as done in developed countries. With variety of heavy metal and hazardous gaseous pollutants that demonstrate wide range of uptake capacity and interaction mechanisms as reported in literatures, clearly there is a gap in knowledge related to air-soil pollution especially in Nigeria and empirical data is needed as the basis for wider modeling and assessment.

1.3 JUSTIFICATION

Air pollution is the excessive concentration of foreign matter in air, which adversely affects the well being of the individual or cause damage to property (Kumar *et al*., 2004). The air that human breathe is basic life support system, and they depend upon it on every minute of their life, night and day, asleep and awake. A human being takes more than 50 million breaths in their life. If what is inhaled is not clean as it should be its effects on the lungs and health in general can have consequences resulting in serious health problems and exorbitant expenses (Kumar *et al*., 2004).

Pollution from motor vehicle has become an issue simply because of the steady increase both in the number of vehicles in use and the distance traveled by each vehicle

each year. The number of vehicle kilometer driven in the world rose significantly for past three decades. Figures have shown that it is expected for the yearly distance traveled by vehicles to increase by 653 billion kilometers by year 2010 (Marco, 2006). As a result of these increases, the use of motor vehicles now generates more air pollution than any other single human activity.

According to Alo (2008), roads in Nigeria are often constructed with no provision whatsoever to address problems such as the runoff quality, vehicle emissions and other probable consequences of the road user activities. Thus it is not unusual to find roads of mainly "flushed shoulder" passing through residential hubs, industrial estates and farmlands. Hence, since roads surfaces are impervious, they serve as temporary sinks for various types of pollutants which are washed off during rainfall as runoff to the proximate environment. Thus the need to identify, quantify and mitigate potential pollutants as a result of the transportation activities on these roads is most necessary.

Also, from various reports, contaminants associated with dust particulate have received a great interest, because elemental composition and concentrations in these dusts reflect the characteristics of the activities going on in a particular area. This system (particulate matter) have the potential to provide considerable loadings of several contaminants to receiving water and water bodies, particularly with changing environmental conditions (Lee *et al*., 2005).

Environmental and health implications of heavy metal contaminants in dust and soils are initially dependent on the mobility and availability of the metals. Mobility and availability of these contaminants are functions of their chemical speciation and partitioning within or on dust and soils matrices. However, most studies on heavy metals in roadside soils and dust in Kano have concentrated on total levels (Ayodele and Gaya, 1994;

Ayodele and Gaya, 1998; Ayodele and Oluyomi, 2011) with little emphasis on chemical forms. The identification of the main binding sites, phase associations of heavy metals in soils help in understanding the bioavailability of a metal and the signature of multiple sources (Kholoud *et al*., 2009). A comprehensive knowledge of interaction between the different species of the metal and environmental media such as dust is of importance in order to be able to predict their environmental impact.

In light of paucity of studies on the chemical fractionation of heavy metals in dust particulate matter in Nigeria, the present study was embarked upon to determine the heavy metal levels in different roads within the Kano Metropolis. The six stages modified analytical procedure a ccording to Finzgar *et al*. (2007) was used to determine the chemical fractionations of heavy metal in roads dust and roadside soils. The method provides comprehensive information on the interaction between different species of the metal and environmental media such as dust, in order to be able to predict their environmental impact. It is most likely that the chemical properties of street dust may, like those of soil and sediment, play an important role in heavy metal retention or removal from street dust. The impact of these properties may vary according to the nature of the roads. There was, therefore, a need to investigate the behaviour of heavy metal distribution from roads with different characteristics. Furthermore, this was the first detailed study of heavy metal in road dust and soil in Kano metropolis.

1.4 AIMS AND OBJECTIVES

The aim of this study is to assess the dynamics of air-soil pollution with special preference to particulate metals (Cd, Cr, Ni, Pb, Cu and Zn) and gaseous pollutants (CO,

H_2S, NO_2, SO_2, Flammable gas (FL) and NH_3) in Kano Metropolis, Nigeria. This shall be achieved through the following objectives:

i. Determination of aforementioned heavy metals in dust fall particulate matter during the four main seasons.
ii. Determination of heavy metals in different grain sizes (1400, 350 and 150µm) of roadside soils.
iii. Determination of content of gaseous pollutants (CO, H_2S, NO_2, SO_2, FL and NH_3) with respect to time across the seasons.
iv. To compare concentrations of heavy metals and gaseous pollutants with standard limits or other data from other countries.
v. Study the relationships between the two environmental compartments (air and soil) with respect to heavy metals.

1.5 HYPOTHESES

The study was guided by the following null hypotheses:

i. The heavy metal content of the air near busy roadsides in the city is not significantly different from that of air from control site.
ii. There is no significant difference in the heavy metal contents between soils from a busy roadside and that from control site.
iii. There is no significant difference in the gaseous pollutant contents between air from a busy roadside and that from control site.

1.6 SIGNIFICANCE OF THE STUDY

This is important as a baseline study to provide information for urban dwellers and policymakers on the environment as a guiding tool in urban planning.

1.7 SCOPE AND LIMITATION OF THE STUDY

Initially, the study was designed to study fifteen sites and five control sites, and to determine wind direction, wind velocity among other meteorological data. However, during the sampling, it was obvious that the research cannot be sustained due to finance and unavailability of some meteorological equipment to be use at the field. Hence the study was limited to few metrological data and sampling sites.

CHAPTER TWO
LITERATURE REVIEW

2.1 ENVIRONMENTAL POLLUTION

Environmental pollution is defined as any discharge of material or energy into land, water or air that may cause acute (short-term) or chronic (long-term) detriment to the Earth's ecological balance or that lowers the quality of life (Moja, 2007). Pollutants may cause primary damage, with direct identifiable impact on the environment, or secondary damage in the form of minor perturbations in the delicate balance of the biological food web that are detectable only over long time periods (Timbrell, 1997; Annergan and Scorgie, 2002). In the past, pollution used to be regarded as a local problem, close to where sources are located. However, the industrialization of society, the explosion of the human population, massive urbanization and the introduction and use of cars, have caused an exponential growth in the production of goods and services (USEPA, 1998). This growth has been coupled with an increase in waste by-products which change the physical, chemical or biological characteristics of the environment (air, land and water) that is now regarded as environmental pollution.

Common forms of pollution that affect human life are air, water and soil pollutions. Air pollution is a process that involves the release of gaseous chemicals and particulates into the atmosphere. Common examples regarded as pollutants includes carbon monoxide (CO), sulphur dioxide (SO_2), chlorofluorocarbons (CFCs), nitrogen oxides (NOx) and heavy metals in form of particulates. The composition of the air pollutants can be inorganic, organic or a complex mixture of both. According to Melaku *et al*. (2008) environmental sources for pollutants could include construction and demolition activities, mining and mineral processing, wind-blown dust, automobiles and transportation related activities on

the road. However in urban centers generally, human- generated air pollution sources can be divided into mobile and stationary sources (Bilos *et al*., 2001). While the former includes automobile such as buses, trains, airplanes and other powered modes of transportation sources, the latter have to do with factories, incinerators and other kinds of non-mobile sources (Itua, 2007). Today, mobile source emissions have tended to be the largest contributor to air pollution in many locations. For instance, in an Environmental International Agency study carried out by a construction company in Nigeria on behalf of Lagos Urban Transport Project in 1996, the profile of air pollution by type and source in Metropolitan Lagos revealed that road traffic is the major source of air pollution.

Water pollution affects oceans and inland water bodies. Examples include organic and inorganic chemicals, heavy metals, petrochemicals and microorganisms. The causes and forms of water pollution according to Strandberg (1971) include sewage and other oxygen demanding wastes, infectious agents, organic chemicals, other chemicals and mineral substances, sediments (turbidity), radioactive substances and thermal pollution. Additionally, several human activities that may result to water pollution include the following: agriculture, irrigation, urbanization, mining, fire, and industrialization (Goudie, 1990). These activities have been documented to have impacted negatively in some specified Nigerian surface waters especially in the Niger Delta region (Izonfuo and Bariweni, 2001). Also, these activities have affected the soils of industrial areas in Southern Nigeria (Olajire *et al*., 2003).

Soil pollution is one of the most relevant phenomena, which is mainly as a result of anthropogenic activity, also cumulating the pollutant from air and water through dry and wet deposition (Violante *et al*., 2008). Soil is a thin covering over the land consisting a mixture of minerals, organic materials, living organisms, air and water that together support

the growth of plant life (Schwela, 2000). Generally, soil serves as sink for all pollutants especially from the atmosphere which through leaching pollutants gets into other environment such as water. Pollution in urban soils may come from various human activities, such as industrial and energy production, construction, vehicle exhaust, waste disposal, as well as coal and fuel combustion. These activities emit heavy metals into the air and the metals subsequently are deposited onto urban soil as the metal containing dust fall (Chen *et al.,* 2005). Heavy metals may be transported through soils to reach groundwaters and cause groundwater contamination or may be taken up by plants (Manta *et al.,* 2002; Boularbah *et al.,* 2006). Vehicular traffic is a significant and increasing source of atmospheric and soil pollution in urban environments (Rossini and Fernández, 2007). Lead and cadmium are common pollutants in urban soils. Pollution induced by heavy metals in soil is a serious environmental problem because, in comparison with the atmosphere and water, the soil environment has a much lower ability to recover from toxic effects.

Noise is another serious environmental problem caused by transport. Road traffic and high speed trains cause a nuisance and harm to growing numbers of people living very close to road. Over 100 million people in the Organization for Economic Cooperation and Development (OECD) countries are exposed to road traffic noise in excess of 65dB (Atubi, 2009). In medical circles, it is known that noise produce some physiological effects which can create more burdens for people with heart diseases, high blood pressure and emotional problems, if they are continuously exposed to this type of pollution (Ndiokwere, 2004).

Generally, pollution is now regarded as a global problem since pollutants can cross borders with the help of wind and water. Environmental pollution is insidious and its harmful effects only become apparent after long periods of exposure (Alloway and Ayres, 1997). For this reason, environmental monitoring is recognized as being vitally important in

detecting where insidious pollution is occurring, the type of pollutants involved and their sources.

2.2 AIR QUALITY AND TRAFFIC EMISSION

According to Pereira *et al*. (2010), the term 'automobile emissions' can be defined as the set of all traffic-related pollutants emitted directly by automobiles which includes vehicles, trucks and motocycles that affect the quality of the air we breathe. Air quality is becoming of national concern in a large number of countries on the African continent, where anthropogenic emissions of combustion particles have considerably increased (Boko *et al*., 2003). Practically, automobile particle emissions are the result of a great many processes, e.g. combustion products from fuel and oil, wear products from brake linings, tyres, bearings, car body and road materials, and the re-suspension of road and soil dust (Laschober *et al*., 2004). Particulate matter originating from traffic can be present at elevated concentrations especially during high traffic density and poor dispersion conditions, e.g. in street canyons, thereby affecting air quality, which can lead to high human exposures to traffic-related pollutants (Vardoulakis *et al*., 2003). Emissions of many metallic elements from vehicular sources are mainly due to non-exhaust emissions, e.g., from the wearing of tyres, brakes and other parts of vehicles (Sternbeck *et al*., 2002; Adachi and Tainosho, 2004; Laschober *et al*., 2004; Lough *et al*., 2005).

Similarly, atmospheric pollution due to vehicular emission remains a threat to environmental health problems which is expected to increase reasonably as vehicle ownership increases in the world (WHO, 2000; and Abam and Unachukwu, 2009). In 2008, the World Health Organization (WHO) estimated that air pollution annually leads to the premature death of around two million people worldwide (WHO, 2008). Human exposure

to these air pollutants due to traffic is believed to have constituted severe health problems especially in urban areas where pollution levels are on the increase. Motor vehicle emission has been recognized as the main source of air pollution, particularly in highly urbanized areas (Sadullah *et al*., 2003). The main traffic-related pollutants are carbon monoxide (CO), nitrogen oxides (NO_x), hydrocarbons, heavy metals, particulate matter and sulphur oxide (SO_x) (Mohammed, 2011).

Studies around the world have indicated that CO is the most abundant pollutant per annum with practically 70% of all CO gas produced solely by motor transport vehicles (Kiely, 1997). According to Han and Naeher (2006), CO is a colourless, odourless, tasteless and non-irritating gas, after inhalation by the lungs, CO is absorbed by competing with oxygen for combining with haemoglobin and thus leads to hypoxia. In a research conducted a decade and half ago it was shown that transportation sources in the USA were responsible for 77% of CO levels, 80 – 90% of NO_x, 36% of volatile organic compounds and 22% of particulate matter (USEPA, 1998). Similarly, in UK the average concentration of NO_2 was found to increase by 35% from 1986 to 1991 due to increase in vehicular emission (CEC, 1992). On the global sense, Polymeneas and Pilinis (2008) and Abam and Unachukwu (2009) have all arrived at the same conclusion that transportation is the major culprit of air pollution accounting for over 80% of total air pollutants.

The concentration of pollutants in urban environments and especially in those areas where population and traffic density are relatively high, human exposure to hazardous substances is expected to be significantly increased. This is often the case near busy traffic points in the city center, where urban situation may contribute to the creation of poor air dispersion conditions giving rise to contamination hotspots (Sotiris *et al*., 2003). Like many other air pollutants, CO levels in urban centers are highly influenced by such factors as

traffic density, traffic congestion and meteorological conditions (Han and Naeher, 2006).

Also, urban city pollution has been caused by several factors including poor vehicle maintenance and insufficient use of vehicle emission control systems. Particularly, the study in Mexico city (Gomez-Perales *et al*., 2004) found lower CO levels in the three transport modes (15, 12 and 7ppm for minibus, bus and metro during the 180min rush hours respectively) compared with previous (Fernandez-Bremauntz and Ashmore, 1995) in the same area, though the decrease may be partly due to seasonal difference. Hickman (1976) indicated that the CO concentration was found to be higher at locations which have access to an elevated ring road, and a set of traffic lights compared to other locations with a free flow of traffic. The reason is that vehicles spend a longer time near junctions due to queuing and the acceleration and deceleration phase they go through are more polluting than steady speed cruising (Zellner and Mousiopoulos, 1986). This is clear indication that vehicle emissions are the major source of ambient air pollution in cities and must be controlled if acceptable air quality is to be assured.

2.2.1 Traffic Emission in Developing Countries

In most developing countries of the world vehicular growth has not been checked properly by environmental regulating authorities leading to increase levels of pollution (Han and Naeher, 2006). Traffic emissions contribute about 50-80% of NO_2 and CO concentration in developing countries (Fu, 2001; and Goyal, 2006). This situation is alarming and is predicated on the poor economic disposition of developing countries. Poor vehicle maintenance culture and importation of old vehicles which culminate to an automobile fleet dominated by a class of vehicles known as ‘’super emitters’’ with high emission of harmful

pollutants, has raised high this figure of emission concentration (Ibrahim, 2009).

Furthermore, in developing countries the super emitters contribute about 50% of harmful emissions to the entire average emission (Brunekreef *et al*., 1997). In Mexico City for example these supper emitters are reported to be responsible for 90% of hydrocarbon and CO emissions and 80% of NO_x emission accounting for 60% of the kilometres travelled in the country (OECD, 1999). The increase of this traffic-related pollution is not based on the aforementioned factors only, but also on low quality fuel, poor traffic regulation and lack of air quality implementation force. These are clear indices to high levels of traffic-related pollution in developing countries.

The United Nations Fund for Population Acts (UNFPA) (2007) reports show that the world urban population reached 50% in 2008 and is projected to increase to 60% by 2030. This increase will have a back effect in developing countries where 80% of the population will be living in urban centers by 2030. The rise in urban population will have a geometrical effect in the increased number of motorized vehicles in cities by 2050, aggravating the hazard even in countries with overall low motorization rates (World Bank, 2004). Statistics in China show that the concentrations of particulate and other traffic-related pollutants, in Chinese cities are six times higher than WHO recommended baseline (Faiz and Sturm 2000). The ratio of vehicle to person in China, India and Africa is 9, 7.6 and 22.8 vehicles per 1000 persons respectively in 1998 compared 35.7, 13.2 and 27.2 vehicles per 1000 persons respectively in 2008. By contrast in 1998 the USA has 780.46 vehicles per 1000 persons and increase to 841.67 vehicles per 1000 persons by 2008. From the data it will be assumed that developing countries release less emissions compared to developed nations. However, with proper regulations and guidelines in developed nations the emissions from vehicles are

reduced compared to developing nations

In Delhi, the data shows that of the total 3,000 metric tonnes of pollutants belched out everyday, close to two-third (66%) is from vehicles. Similarly, the contribution of vehicles to urban air pollution is 52% in Bombay and close to one-third in Calcutta. In Delhi, the contribution of vehicular pollution has increased only in past 2-3 decades, as the share, which was a paltry 23% in 1971 rose to 43% in 1981 and became 63% in 1991 (WWF, 1995). Also, In Bangkok, Thailand, vehicular pollution accounted for 80% of total pollution in 1987 (Israngkura, 2000). In Budapest, Hungary in 1991, NOx, CO and HC emissions from transport contributed 57%, 81% and 75% of total emissions of respective pollutants (Lehoczki, 2000).

In China, vehicular emissions accounted for 46%, 78% and 83% of the total NOx, CO and HC emissions, respectively, in the Beijing urban area. Of this, cars were the largest contributor, accounting for 35%, 56% and 44% of the total vehicular NOx, CO and HC emissions (Fu *et al*., 2000). Vehicular emissions comprised 68.8% and 76.5% of the ambient NOx and CO concentrations (Hao *et al*., 2001).

The worst thing about vehicular pollution is that it cannot be avoided as the vehicular emissions are emitted at the near-ground level where we breathe. Pollution from vehicles gets revealed through symptoms like cough, headache, nausea, irritation of eyes, various bronchial problems and visibility and are due to discharges like CO, unburned HC, Pb compounds, NOx, soot and aldehydes, among others, from the tail pipes of vehicles (Hao *et al*. 2006)

In Tehran, the capital of Iran, air pollution occasionally reaches dangerous levels particularly during the cold season because of the phenomenon known as temperature

inversion. Over the past three decades, air pollution in Tehran has been regarded as a multifaceted problem (Zahed *et al*., 2010). A study in Tehran, Iran by Masjedi *et al*. (2008) confirmed that the increasing number of hospital admissions of asthmatic patients and exacerbations of chronic obstructive pulmonary disease correlated with weekly NO_2 concentrations in ambient air. An investigation showed high CO levels in Tehran's air to be consistent with increasing numbers of daily hospital admissions due to angina pectoris. Developing cities in Asia and Africa are at high risk to exposure of this traffic-related pollution. Research conducted in Ethiopia, Mozambique, Kenya and Republic of Benin, show that there is a high level of DNA damage in urban residents and higher prevalence of asthma in urban school children exposed to traffic pollution compared to rural children (Autrup, 2006). The African continent may be highly heated if priority is not given in understanding the scale of this problem and its control.

2.2.2 Traffic Emissions in Nigerian Cities

In Nigeria much attention is given on general industrial pollution and pollution in oil industries, with little reference on damage of pollution caused by mobile transportation sources of air pollution (Faboya, 1997; Iyoha, 2002; Magbabeola, 2001). The situation of increased pollution from mobile transportation source is on the increase in per capital vehicle ownership, thus resulting to high congestion on Nigeria city road and increase in the concentration of pollutants in the air, consequently, increasing health risk to the human population. Similarly, compared with the large volume and varieties of studies carried out in the developed world, exposure studies carried in Nigeria are relatively scarce.

In Nigeria Mode of transportation is largely by road and air with little water

transport in the coastal areas. The fleet of road vehicles has steadily increased from the 1950 to date. A study by Obio and Adegbulugbe (1997) and Oyesiku (2005) indicate that from 1950 – 1994, vehicles increased from 12,544 to 2,087,973. This increase over 40 years has accounted for the rise in petrol consumption projected to reach 4.4 million barrel per day in 2015 (Peoples Daily, 2011). Similarly in Nigeria about 4200 million liters (1995 estimates) of gasoline is consumed annually in the country, giving a leaded gas emission of 2770 metric tonnes (Onianwa, 2001). On a scale of 1 – 59 for potential exposure to air pollution from gasoline for urban centres in developing countries, Nigeria is scored 57, which is one of the highest degrees of exposure (World Resources Institute, 2000).

This analysis corroborates that emissions from transport vehicles and industries primarily contribute to pollution problems of urban cities in Nigeria (Ibrahim, 2009). The transport induced environmental pollution in Nigeria, is further compounded by recent influx of motorcycles and tricycles, most of which have 2-stroke engines. Equally, the importation of used vehicles and lack of vehicular emission control also contributed to the high level of pollution in the atmosphere (Ibrahim, 2009). Pollutants like NO_2 and CO from automobile traffic are considered important in the assessment of air quality of urban environments. Nitrogen dioxide is the most abundant oxidized nitrogen compound in background air and its role in the formation of photochemical oxidants and smog has attracted the attention of several scientific researchers in recent years.

Early studies in Nigeria compared levels of air pollutants in urban and rural areas of western Nigeria (Oluwande, 1977). In his study five types of pollutants (dust, SO_2, CO, Pb and NO_X) were monitored. The results showed that the levels in urban areas were higher than WHO long term limits, while the levels in rural areas were very low. Also, the concentrations were highest at the roadside, where many people stay daily from morning

till evening to work and sell. It was then concluded that automobile emissions is the main source of these pollutants.

In another study by Nriagu *et al*. (1997) on the prevalence of elevated blood lead (PbB) levels in children in Kaduna, they observed high average PbB levels in 5 year old children and attributed to the tendency for this age group to play longer in contaminated outdoor environment. This was also supported with strong associations between PbB and whether the family owned a car or lived in a house on a tarred road. This implies that many children in towns and cities of the country are at risk of being poisoned by Pb. Similarly in 2006, Ademoroti and Oviawe assessed PbB of people living in traffic area in Benin City. The results showed high PbB levels for very high traffic areas and for residents with 20 – 30 years exposure. Low levels were recorded for low traffic areas and for residents with few years of exposure. It was concluded that traffic exhaust emission has been implicated as the source of lead in the atmosphere and human beings are the sink for this pollutant.

Studies conducted in Kaduna and Abuja cities show higher values of CO_2 concentration in heavily congested areas: 1840ppm for Sambo Kaduna, 1780ppm for Stadium round-about, Kaduna, and 1530ppm for A.Y.A, Abuja, 1160ppm for Asokoro Abuja, Akpan and Ndoke (1999). Similar work by Jimoh and Ndoke (2000) at Minna, a city in Nigeria shows the maximum value of 5,000ppm for CO_2 in congested areas, which was still lower than WHO stipulated maximum value of 20,000ppm. The maximum value for CO emission obtained was 15ppm still lower than the base line of 48ppm stipulated by WHO and 20ppm stipulated by Federal Environmental protection Agency of Nigeria (FEPA). The reason for this low emission concentration in Minna is due to low traffic and industrial activities in the city.

A comparative study of emission figures in Lagos and the Niger Delta (Oil

producing region) area has been reported by Jerome (2000). Two major cities in the Niger Delta were considered: Port Harcourt and Warri. The results obtained showed that the concentrations of TSP (Total Suspended Particulates), NOx, SO_2, and CO in Lagos and Niger Delta were above FEPA recommended limits. Concentration of CO emissions for Lagos was quite high, being in the range of 10 – 250ppm recorded higher than the ranges of 5.0 – 61.0ppm and 1.0 – 52ppm recorded for oil communities in the Niger Delta. The TSP concentrations were also high for both cities when compared to WHO's standard.

In Benin City, Ukpebor and Ahonkhai (2000) monitored the NO_2 levels. They recorded the highest concentration of NO_2 13.53μg/m^3 in dry season and lowest of 3.02 μg/m^3 in wet season and observed a positive relationship between NO_2 levels and traffic density. Similarly in the assessment of air quality in Benin City, Ukpebor and Ahonkhai (2000) also studied the levels of tropospheric ozone. The highest and lowest ozone levels were recorded at the Ring Road location and University of Benin campus, respectively. The monthly mean concentrations varied spatially. Differences in traffic volume or density and industrial activities was concluded to be responsible for this observation.

A study of the impacts of urban road transportation on the ambient air was conducted by Koku and Osuntogun (2007) in three cities of Nigeria: Lagos, Ibadan and Ado – Ekiti all in South-west region of Nigeria. Air quality indicators namely CO, SO_2, NO_2, and total suspended particulates (TSP) were determined. The highest levels obtained for the air pollution indicators in Lagos were CO- 233ppm at Idumota, SO_2 -2.9ppm also at Idumota, NO_2 -1.5ppm at Iyana–Ipaja and total particulates 852pm at Oshodi bustop. In Ibadan, the CO and SO levels of 271 and 1.44ppm, respectively, were recorded highest at Mokola round-about while NO_2 (1.0ppm) was highest at Bere round-about. In Ado-Ekiti the highest level obtained were CO - 317ppm at Oke Isha, NO_2 - 0.6ppm at Ijigbo Junction

and SO_2 - 0.8ppm at Old Garage Junction. The results obtained for CO, SO_2, NO_2, and particulate counts per minute were found to be higher than FEPA limits. Limits set also by FEPA are CO - 10ppm, SO_2 - 0.01ppm, NO_2 0.04 - 0.06ppm. The noise level in all the locations were found to be higher than FEPA limit of 90dB and the WHO limit of 70dB – 75dB WHO (2000). Conclusions of these investigations show a growing risk of traffic-related problems in Nigerian cities and demand for serious air quality measures.

Overall levels of vehicular related air pollution in Nigeria from all the studies conducted show an increasing trend and thus posses a potential hazard to the population. It is not out of place to state that the levels of these pollutants must have increased tremendously in the past ten years of democratic rule in Nigeria due to the influx of old and fairly used vehicles into the country following changes in government policy.

2.2.3 Health Implication of Vehicular Emission

Air pollution due to vehicular emission has become one of the serious environmental concerns in urban areas, especially in view of the adverse health effects that have been associated with ambient fine particles, gaseous pollutants and heavy metals (Dockery *et al*., 1989; Dockery and Pope, 1994; Bilkis *et al*., 2009). Due to enhanced human activities producing increased emissions, atmospheric pollution in urban areas has become a major issue in many developing countries all over the world.

Nowadays air over major cities throughout the world has become over burdened with gases produced by automobiles. The death rate due to automobile pollution is increasing rapidly in the metropolitan areas. With passage of time people realized that polluted air had serious effects on their health, climate and economics. Emissions from automobile that can produce health effects are the gases CO, NO_X, volatile organic

compounds, and SO_2, as well as solid particulate matter (Fisher *et al*., 2002). Additionally, other gases such as ozone and particles (sulphate and nitrates) can form in the atmosphere from reactions involving some of those primary emissions.

Sulphur dioxide is a recognized pollutant because of its role in forming cold time smog (Hermann, 1991). It is an acidic, irritant gas which in high concentrations can cause difficulties (Arch, 1954; Hermann, 1961; Purnendu, 1991). The pollutant causes constriction of the airways by stimulating nerves, nose, throat and airways of the lung (Frank, 1964; Wolff *et al*., 1975). People with asthma are more susceptible to the adverse effects of the gas as high concentrations may result in the fall of lung function in asthmatics and may lead to tight chest, coughing, wheezing and phlegm at high levels. It is a gas considered more harmful than other gases (Beilke and Elshout, 1983; Duesing and Duesing, 1980; Hutchinson and Havas, 1980). The effects are worse when exercising and the most vulnerable groups are healthy children, adults with lung disease and asthmatics and may aggravate such illnesses as bronchitis (Frank, 1964; Amdur, 1971; Wolff *et al*., 1975).

Carbon monoxide (CO) is an odourless gas formed as a result of incomplete combustion of carbon-containing fuels, including petrol and diesel. CO is readily absorbed in the lungs and is taken up in the blood where it is bound to haemoglobin (Hb) with the formation of carboxy-haemoglobin (COHb), thus impairing the oxygen carrying capacity of blood (Schwela *et al*., 1997). The dissociation of oxy-haemoglobin is also altered due to the presence of COHb in the blood thereby further impairing the oxygen supply to tissue (the affinity of haemoglobin for CO is about 240 times that of oxygen). CO exposure may also affect the foetus directly through deficit without elevation of COHb level in the foetal blood. During exposure to high CO levels, the mother's Hb less readily gives up its oxygen with a consequent lowering of the oxygen pressure in the placenta, and hence also the foetal

blood. The resulting effects are reduced birth weight (Mathai *et al*., 1990; Ash *et al*., 1989; Hebel *et al*., 1998), and retarded postnatal development (Campbell *et al*. 1988). Also, in Denver, USA, ambient CO exposure has been related to low birth weight in a control study (Alderman *et al*., 1987).

Nitrogen dioxide (NO_2) is an irritating gas and its toxicity is generally attributed to its oxidative capabilities. Long-standing exposure to NO_2 increases the risk of death in cardiopulmonary patients and causes lung cancer in nonsmokers (Yorifuji *et al*., 2010). Recently, the researchers at the McGill University in Canada identified a correlation between exposure to ambient NO_2 and postmenopausal breast cancer (Crouse *et al*., 2010). Delving *et al*. (1992) reported an impaired phagocytic activity in human alveolar macrophages after exposure to 2ppm for 4 hrs, with intermittent exercise. Damji and Richters (1989) have reported a reduction of T-lymphocyte subpopulations following acute exposure to NO_2, which may reflect a functional impairment of the immune response. Nitrogen oxide is oxidized to nitrogen dioxide in ambient air, which has a major role in atmospheric reactions that are associated with the formation of photochemical oxidants (such as ozone) and particles (such as nitrate) (Fisher *et al*., 2002).

It has been observed that about 10% of the mass of air pollutants is emitted as particles and liquids compared with 90% from gaseous compounds (Botkin and Keller, 1998). Particulate matter embraces a wide range of solid and liquid particles extending from more than 10m in diameter (Varney and McCormack, 1971). Over the last decades, there has been a growing concern about atmospheric particulates (including heavy metals) because evidence has shown that they are associated with respiratory and cardiovascular diseases (Dockery *et al*., 2005; Nyarko *et al*., 2004; Godinho *et al*., 2008), severe intestinal upsets, keratosis and skin cancer (Steinnes and Krog, 1997) in humans. According to Baike

and Rowland (1995), the effects of particulate matter on vertebrate animals also include impairment of the respiratory system, damage to eyes, teeth and bones, increased susceptibility to disease, pests or other stress-related to environmental hazards, and reduced ability to reproduce. Recently, other effects of suspended particles have been noted such as cough, catarrh, eye infection, asthma and chronic bronchitis (Efe, 2005; Efe, 2008).

However, the health effects caused by air pollutants may range from subtle biochemical and physiological changes to difficulty in breathing, wheezing, coughing and aggraviation of existing respiratory and cardiac conditions. These effects can result in increased medication used to increased doctor or emergency room visits, more hospital admissions and premature death. The human health effect of poor air quality is far reaching, but principally affects the body's respiratory system and the cardiovascular system. Individual reactions to air pollutants depend on the type of pollutant a person is exposed to, the degree of exposure, the individual's health status and genetics.

2.3 HEAVY METALS

Heavy metals constitute the largest class of elements in the periodic table. Heavy metals are conventionally defined as elements with metallic properties and have higher atomic numbers with densities greater than 5.0 gcm^{-3} (Adriano, 2001; Thomson, 2005). Heavy metals occur naturally at levels that are not considered to have any toxic effects to plants, animals and humans. The natural levels of heavy metals are normally increased through various anthropogenic processes (Alloway, 1995; Al-Chalabi and Hawker, 1996). Anthropogenic sources of metals include agriculture (fertilizers, animal manures and pesticides), metallurgy (mining, smelting and metal finishing), sewage sludge, scrap disposal and energy production (power plants, leaded and unleaded petrol) (Adriano, 2001).

Heavy metals such as manganese, zinc, copper, chromium and iron are essential elements when present in small amounts (Rollin *et al*., 2005). However, if present in excessive concentrations they become toxic (Hill, 1997; Rollin *et al*., 2005). Heavy metals such as Pb and Hg are toxic at all levels (Davidson *et al*., 1998; Infotox, 2000). Depending on their form, heavy metals and their compounds may enter the body as part of food, water or air or by absorption through the skin (Sparks, 2005; Adriano, 2001). Once in the body, heavy metals can be distributed in the body by the blood. They can compete with essential minerals such as zinc, copper, magnesium, and calcium and interfere with the function of the organs.

The behaviour and toxicity of heavy metals or their compounds in the environment depend largely on their concentrations and their chemical forms (Kot and Namiesnik, 2000; Tokalioglu *et al*., 2003). For example, Cr (III) in food is an essential element and is stable and innocuous in soil, whereas Cr (VI) is mobile and harmful. Also, the organic form of mercury is more toxic than its inorganic derivative. For arsenic, the inorganic form is more toxic than its organic form.

2.3.1 Uses of heavy metals

Heavy metals are important components of our homes, vehicles, appliances, tools and computers. They are also essential to our infrastructure including highways, bridges, railroads, airports, electrical utilities and food production and distribution (Sparks, 2005).

Civilization was founded upon the metals of antiquity, gold, copper, silver, lead, tin, iron and mercury (Sparks, 2005). Natural and consumer products contain small concentrations of different heavy metals. For example, cadmium is mainly used in batteries, plastics and it is also found in cigarette smoke, in shellfish and vegetables (ATSDR, 1999).

Mercury is found in batteries, dental amalgam, vacuum pumps and valves. Airborne mercury comes from the combustion of diesel, jet fuel and heating oil. Arsenic is high in seafood and may also be found as a contaminant in animal feeds. It is also present in wood preservatives, herbicides, corrosion inhibitors, in lead and copper alloys. Cadmium is used industrially as an anti-friction agent, as a rust-proofer, in plastics manufacture, in alloys and in alkaline storage batteries. Chromium is found in fresh foods, copy machine toner and nickel in coins, kitchen utensils and milk (ATSDR, 1999). Copper is essential to all living organisms and has a wide range of effects depending on concentration and chemical formulation (ATSDR, 1999). It is used in the electrical industry in alloys such as brass, in chemical catalysts and in wood preservatives.

Lead has been used in batteries, electronics, in petrol, toys, paint, etc. Lead has been used as fuel additive in many countries for several years, although this practice has since stopped in most of the countries of the world, because of the health implications of lead.

Manganese compounds are used in manufacturing of products such as batteries, steel and unleaded petrol. Manganese dioxide is commonly used in the production of dry-cell batteries, matches, fireworks, porcelain and glass-bonding materials. It is also used as the starting material for the production of other manganese compounds (USEPA, 1984). Manganese chloride is a precursor of other manganese compounds. It is used as a catalyst in the chlorination of organic compounds, in animal feed to supply essential trace minerals and in dry-cell batteries (USEPA, 1984). Manganese sulphate is used as a fertilizer, livestock nutritional supplement and in ceramics (USEPA, 1984). Potassium permanganate is used as an oxidizing agent and disinfectant in water purification and in waste-treatment plants. It is used in metal cleaning, bleaching and as a preservative for fresh flowers and fruits. Currently, methylcyclo-pentadienyl manganesetricarbonyl (MMT) is the most

popular lead replacement compound due to its lower production costs (Chevron. 2002; Graboski, 2003). The manganese based additive is added in smaller amounts than TEL, with a maximum concentration of 18 mgL^{-1} both in Canadian and South African petroleum fuels (Chevron. 2002; DEAT and DME, 2003; Goosen, 2003).

2.3.2 Behaviour of Heavy Metal in the Environment

The main source for metal input to plants and soils is atmospheric deposition. Volatile metalloids such as As, Hg, Se, and Sb can be transported over long distances in gaseous forms or enriched in particles, while trace metals such as Cu, Pb, and Zn are transported in particulate phases (Adriano, 2001; Adriano *et al*. 2005). In terrestrial ecosystems, soils are the major recipient of metal contaminants, while in aquatic systems sediments are the major sink for metals (Sparks, 2005). Freshwater systems are contaminated due to runoff and drainage via sediments or disposal, while groundwater is impacted through leaching or transport via mobile colloids (Adriano, 2001). A number of biogeochemical processes take place at the heterogeneous interface between the rock, soil, water, air and living organisms (Spark, 2005). These processes or interactions in turn control the solubility, mobility, bioavailability and toxicity of metals (Sparks, 2005).

Metal ions may enter the soil solution and be subject to numerous pathways, all of which can potentially overlap. Metals are found in soil solution as free ions or complexed to inorganic or organic ligands. Both the free ions and the metal–ligand complexes can be (1) taken up by plants, (2) retained on mineral surfaces, natural organic matter, and microbes, (3) transported through the soil profile into groundwater via leaching or by colloid- facilitated transport, (4) precipitated as solid phases, and (5) diffused in porous media such as soils.

Heavy metal contamination of soils is a far more serious problem than air or water pollution because heavy metals are usually tightly bound by the organic components in the surface layers of the soil. Consequently, the soil is an important geochemical sink which accumulates heavy metals quickly and usually depletes them very slowly by leaching into groundwater aquifers or bioaccumulating into plants (Infotox, 2000).

Heavy metals can also be very quickly translocated through the environment by erosion of the soil particles to which they are adsorbed or bound and re-deposited elsewhere. The transport, cycling, fate, bioavailability and toxicity of heavy metals are markedly influenced by their physico-chemical forms in water, sediments and soils. Whenever a heavy metal or its compound is introduced into an aquatic environment, it is subjected to a wide variety of physical, chemical and biological processes. These include hydrolysis, chelation, complexation, redox, biomethylation, precipitation and adsorption reactions. Often, heavy metals experience a change in the chemical form as a result of these processes and so their distribution, bioavailability and other interactions in the environment are also affected. They can leach into living systems from natural ore deposits and other sources such as disposal of heavy metal containing waste. In fact, waste disposal accounts for higher percentage of most heavy metals including manganese in the environment.

2.3.3 Heavy Metal and Automobiles

The pollutants emitted from automobiles are very diverse. They have various adverse effects on human health as well as the environment. It is well known that tetraethyl lead, added as an antiknock agent, cause serious air pollution in urban areas (Davis, 1990), and problems of exposure to workers in related industries and residents (Suzuki, 1990; Kamal *et al*., 1991). Fossil fuels contain many kinds of heavy metals which are emitted

during the combustion of those fuels (Leygonie, 1993; Pirrone *et al*., 1999). Furthermore, the wear of auto tires, degradation of parts and greases, peeling paint and metals in catalysts are all suspected as sources of heavy metal pollution (Sadiq *et al*., 1989; Wei and Morrison, 1994; Åberg *et al*., 1999; Monaci *et al*., 2000; Pecheyran *et al*., 2000).

It is believed that automobiles are not only responsible for previously known forms of heavy metal pollution (Cu, Zn and Pb), but also many other elements, emitted from similar sources. Vehicular traffic is a significant and increasing source of atmospheric and soil pollution in urban environments (Rossini Oliva and Fernández Espinosa, 2007). Lead and cadmium are common pollutants in urban soils. The main sources of Pb and Cd are the leaded fuel used in the past (Fernández Espinosa and Ternero Rodríguez, 2004) and the tyre wear, respectively (Chronopoulos *et al.,* 1997; Moller *et al.,* 2005). Although some heavy metals are essential for vital processes in many living organisms, including humans (Guney *et al*., 2010), these metals are generally toxic when their concentrations exceeded certain thresholds.

The most common heavy metals introduced to the environment by automobiles are Pb, Cd, Zn, Ni, Cr and Cu (Li *et al*., 2007). The key source of these metals is: Pb from leaded gasoline, Cu, Zn and Cd from car components tyres abrasion and lubricants (Wilcke *et al*., 1998). The source of Ni and Cr in dust is believed to be corrosion of cars (Akhter and Madany, 1993) and chrome plating of some motor vehicle parts (Al-Shayep and Seaward, 2001).

Other metals such as aluminium, barium, magnesium, manganese, silicon, silver, tin and titanium have been reported to be associated in trace amounts with automobile-related pollution of topsoil (Lagerweff and Specht, 1970; Hopke *et al*., 1980; Monaci *et al*., 2000). These are derived from varied sources such as exhaust emissions, tyre abrasion, lubricating

oil spills, and engine wear. They are also derivable from the other aforementioned pollution sources.

The monitoring of heavy metals in roadside environment has provided useful data on the exposure risk from pollution in urban areas. Speciation studies have been used to describe the distribution of metals in the various geochemical phases of the soil and hence evaluate the relative bioavailability and mobility of the metal burden of the soil (Ge *et al*., 2000; Maiz *et al*., 2000; Onianwa, 2001).

2.4 HEAVY METALS IN ROADSIDE ENVIRONMENT

Roads play a major role in stimulating social and economic progress. However, road construction has also resulted in heavy environment pollution of foods and homes along the roadside (Liu *et al*., 2006), since road traffic is an important negative factor regarding air quality, noise and land consumption (Zechmeister *et al*., 2005). The contribution of cars and road transports to the global emission of atmospheric pollutants is regularly increasing (Viard *et al*., 2004). The road transports also induce the contamination of nearer soils by a pollutant transfer via the atmospheric fallouts (Viard *et al*., 2004; Nabuloa *et al*., 2006) or road runoff (Mitsch and Gosselink, 1993; Nabuloa *et al*., 2006).

Vandenabeele and Wood (1972), in their study on highway soil samples in Utah, found 180 – 215mgkg^{-1} Pb in surface soil and 65 - 125mgkg^{-1} Pb at 10cm depth, 10m away on the east and west side of the Utah Highway. They found the amounts of Pb at 10cm depth as usually high and concluded that although contamination was limited to a narrow zone along highways, it was not limited to surface soil. They further stated that Pb in soil could be leached and mobilized by solutions containing NaCl from road salting. In a similar study, Ward *et al*. (1975) investigated the Pb content of soil and vegetation along a part of

state highway passing through an unhabited area of New Zealand. They observed an inverse relationship between Pb content of vegetation and distance from the road. Their analysis also showed that washed vegetation samples contained 70 – 80% of Pb vegetation samples, indicating that the majority of Pb is relatively immobile. The same fall-off of Pb levels was also found in soil samples with increasing distance from the road. The highest levels of soil Pb reaching 160mgkg^{-1} were obtained from the top 5cm of the soil (the background level of Pb was 40mgkg^{-1}). They concluded that the elevated levels of Pb in the top 6cm of soil were primarily sourced from leaded gasoline. In conclusion, their results suggested that up to 60% of vehicular Pb emitted was retained by surface soils and vegetation close to the highway.

Wheeler and Rolfe (1979) also found that Pb from automotive sources in roadside soil and vegetations of Cincinnati follows a double exponential function related to the average daily traffic volume and the different particle sizes. The study showed that larger particles were deposited within 5m of the roadside and were inert in the soil whereas small particle were deposited more slowly and are deposited within 100m from the roadside. The highest amount of Pb found was 1,225mgkg^{-1} in soil and 196mgkg^{-1} in vegetation at 0.3m away from highways of central Illinois with 8100 vehicles per day traffic density. In this area, background levels, which were 16mgkg^{-1} for soil and 10mgkg^{-1} for vegetation, were reached at 50m from the highways. In a similar view, Tiller *et al*. (1987) remarked that the dispersal of Pb derived from vehicular emission on soils had been observed up to distance of 50km from metropolitan Adelaide in Australia.

In Madrid, Spain, Hernandez *et al*. (1987) found significant positive correlation between Pb levels in rose-bay leaves and traffic density at sites. However in Thessaloniki, Greece, Sawidis *et al*. (1995) reported that Pb levels were not proportional to traffic

density, and higher levels of Pb were associated with sites near road junctions. Similarly, it was discovered in a study of trace metals in roadside soils of Uppsala city, Sweden (Paola, 2005), that metal accumulation, especially Pb, Cd and Ni did not conform to trends of traffic density rather it tended to follow the age of the road.

An examination of the Pb, Cu, Zn, Fe, Mn and Cd contents in roadside soils and grass from 36 sites on the Island of Hong Kong indicated that both soil and grass contained elevated levels of the metals studied (Ho and Tai, 1988). Linear regression analysis between the logarithmic concentration of the metals in the samples and logarithmic traffic volume of the sites revealed that apart from Cd in soil, the concentration of metals and traffic volume were strongly related (variance ratios' p values < 0.001), thus indicating that vehicular emission forms a major source of metals in the roadside soil and grass, and that the high levels of contamination occurred mainly in highly urbanized Northern part of the Island where most of the traffic was concentrated.

Association between Zn and Cu concentrations in soil and grass, and distance from road traffic were studied by Fatoki (1996). An association between Zn concentration and distance from road traffic and between soil Zn and grass Zn were found, suggesting the same source for the metal in both soil and grass samples. There were also no correlation between Cu concentration and distance from road traffic, soil Zn and soil Cu or between grass Zn and grass Cu which suggested different sources for the elements in Alice, South Africa. Marked differences in the concentration of Zn and Cu between May and November samples were also observed, which was attributed to a wash out process of the metal deposition by rain during the summer months.

Remarkable metal contamination, especially lead pollution, has been caused by automobile emissions in the roadside ecosystems (Garcia and Milan, 1998; Von Storch *et*

al., 2003; Sezgin *et al*., 2003; Nabuloa *et al*., 2006). The large particles of lead from vehicle emissions deposit close to the road (>90% within 1.5 m when the size <5µm) (Hamamci *et al*., 1997). Nabuloa *et al*. (2006) reported that the leaves of roadside crops can accumulate trace metals at high concentrations, causing a serious health risk to consumers. Therefore, accurate measurements of the heavy metal contents in polluted soils are required to assess the potential ecological risk of these areas. Most researchers have reported the influence of the traffic load on heavy metal contents in top soils and their variability with distance (Rodriguez and Rodriguez 1982; Garcia and Milan, 1998; Zhang *et al*., 1999; Turer and Maynard 2003).

Also, Viard *et al*. (2004) reported that the deposition of metals, the levels of metals in surface soils decreased with increasing distances from the highway. Moreover, he also found that the impact of the highway was clear up to 320 m, at least (lead), but the most important contamination was observed near the road. Nabuloa *et al*. (2006) also showed total trace metal concentrations in roadside soils decreased exponentially with increasing distance from roadways. Although the concentrations of metals in the roadside soil were influenced by meteorological conditions (Othman *et al*., 1997; Sezgin *et al*., 2003), traffic density (Garcia and Milan 1998; Nabuloa *et al*., 2006), the kind of vehicle in traffic (Sezgin *et al*., 2003; Nabuloa *et al*., 2006), and soil parameters (Viard *et al*., 2004), little information was still known about the heavy metal accumulation in roadside soils along the roads with different transportation periods.

Recently, study of roadside soils in Hail city, Saudi Arabia (Odat and Alshammari, 2011) have shown that metals (Pb, Cd, Cu, Co, Ni, Cr, V, Hg and Zn) are concentrated on the surface soil and decrease in the lower part of the soil. This study, suggested physicochemical factors such as pH, total organic matter, $CaCO_3$, cation exchange capacity,

and electrical conductivity to affect the mobility of metals in the soils. It was concluded that the relatively high concentrations of Cd, Pb, Zn, Cr and Cu in the soils were related to anthropogenic sources mainly from vehicle emissions.

2.5 HEAVY METALS IN ROADSIDE SOILS IN NIGERIA

Heavy metals are known to be insidious toxic pollutants and their presence in the environment is increasing daily (Ideriah *et al*., 2005). There is increasing awareness of the impact of Pb exposure, on past civilizations as a result of rapid growth in population, expansion of industrial activities, exploration and exploitation of natural resources (Chindah and Sibendu, 2003). The national consumption of petrol in the country is estimated at 20 million litres per day with about 150 people per car. It is therefore predicted that at least 15,000 Kg of lead is emitted into the environment through burning (Agbo, 1997). The effect of this indicates increase in amount of Pb in the environment, since Pb is known to be use as antiknock additive in petrol (Okonkwo and Maribe, 2004). It has been pointed out that Africa's contribution to global Pb pollution has increased from just 5% in 1980's to about 20% in 1996 (Anon, 1996). More than two thirds of the nations in Africa have maximum Pb levels above the world median value. In Nigeria, heavy metal pollution of roadside soil and resulting health effects present some of the biggest challenges currently affecting the urbanized areas of Nigeria. Vehicular emission was reported to play a predominant role in the development and modification of the soils from these areas (Francis, 2005).

Soil Pb levels varies depending on the location and nearness of Pb based activities and vehicular density. A study in Ibadan (Sridhar, 2001) showed that in residential areas, the levels ranged from 364.0 – 185.2mgkg^{-1} in high-density area, 269.01 – 133.9mgkg^{-1} in

medium density area, and 307.01 – 161.3mgkg^{-1} in low-density area. In mechanic's villages, the values of Pb concentration in soil ranged between 292.3 and 491.2mgkg^{-1}. Near petrol stations, Pb values ranged between 190.0 – 1029mgkg^{-1} on the top 10cm level of soil and 237.5 – 3862mgkg^{-1} in 11 – 20cm layers. Near a Pb acid battery industry, the soils showed values of 7339mgkg^{-1} in the top 10cm layer and 6263mgkg^{-1} in the 11 – 20cm layers.

In Warri, Nigeria, Uwagboe and Hymore (2001) reported that higher concentrations of Pb, Cd, Cu and Zn for soil samples correlated with traffic conditions and decreased exponentially with the distance from the road edge, dropping to background levels and about 20m, whereas lower concentration were found in stagnant pools and sediments. The concentration levels found in soil samples (mgkg^{-1}) were Pb, 11.1 – 235.4; Cd, 0.12 – 0.87; Ni, 26.8 – 64.86; Cu, 2.91 – 22.76 and Zn, 16.38 – 76.31. They, however concluded, that the concentration of the heavy metals did not appear to pose very serious environmental problems, but significant increase in levels may occur within the next decades as the level of industrialization soars and number of vehicles increase.

In another study carried out along Kaduna – Zaria highway (Oyewale and Funtua, 2002), it was reported that the level of Pb, Zn and Cu from soil samples were found to be higher than the control samples collected 12m away from the highway. The mean concentrations ranged Pb (left), Pb(right), Cu(left), Cu(right), Zn(left) and Zn(right) in the samples were 23 – 121, 21 – 99, 40 – 156, 39 – 262, 30 – 118 and 30 – 162mgkg^{-1}, respectively. They then concluded that Pb and Zn levels might be attributed to pollution emanating from automobile emission and contamination while Cu levels could be due to pollution from fungicides and insecticides use on farms along the road.

In yet another study conducted at Abuja (Kakulu, 2003), heavy metals were observed in the soil and tree bark samples from commercial/high traffic areas of the city and compared to background values. The result showed that concentrations of Pb and Zn in soil and tree bark samples were very high due to traffic density (> 2400 vehicles/hr).

A survey of heavy metals in vegetation, soil and lower animal along some selected roads in metropolitan city of Lagos revealed that levels of metals in soil samples were higher than the background levels with the exception of Zn but lower than European Union (EU) limits. However, the results generally revealed the presence of metals in plant and animal samples and metal dynamics up the food chain is highly possible (Awofolu, 2005).

Similarly, Okunola *et al*. (2007), in their study investigated the impact of automobile emission of heavy metals on roadside vegetations and surface soils along some major and minor roads in Kaduna Metropolis and found elevated level of Cd in soils and plants in excess of EU, ICRCL and FAO guidelines among other heavy metals studied (Pb, Cu, Zn, Mn). The study also revealed poor correlation between traffic density and the metals in samples suggesting that automobile might not be the only source of these metals. Other anthropogenic sources such as waste from petroleum products, for instance lubricating oils that were dumped along these roads and industrial emissions via atmospheric emission, were suggested.

In a recent study by Yahaya *et al*. (2010), seasonal variation in physiochemical properties and concentration of the heavy metals were assessed in roadside soil in Yauri, Nigeria. Soil samples collected during the 2007/2008 rainy and dry seasons were treated and digested using microwave acid digestion methods. The heavy metal concentrations were determined with atomic absorption spectrophotometer. The mean levels range of As, Cd, Cr, Cu, Fe, Ni, Pb and Zn were 1.15 - 3.14, 0.14 - 7.0, 1.64 - 22.36, 4.86 - 29.30, 2001 -

8091, 351.6 - 843.3, 35.9 - 306.7, and 79.6 - 202.4 µg/g for dry season and ND – 13.04 µg/g, ND - 7.02, ND - 13.79, 0.99 - 23.72, 748 - 6000, 201.13 - 507.10, 24.00 - 316.14 and 33.84 - 131.06 µg/g for wet season, respectively. When metals concentrations in the soil of dry and wet seasons were correlated ($p < 0.05$) it was revealed that there were strong correlations between all the metals with the exception of Ni. Generally, higher mean heavy metal concentrations were recorded in the soil during the dry season than in wet season. The analytical results indicated that in both wet and dry seasons most of the heavy metals were above the natural heavy metals concentrations of surface soil which course for concern as these metals can accumulate to pollute the environment.

2.6 HEAVY METALS IN ROAD ATMOSPHERIC PARTICULATE MATTER

Particulate matter refers to solid and liquid particles that are dispersed into ambient air. These particles can be classified in several ways. Firstly, they can be classified into primary and secondary particle based on the mechanism on their formation. Primary particles are emitted directly as particles, whereas secondary particles are formed from gases in the atmosphere via gas- to – particles conversion (Vallius, 2005). Secondly, particles can be classified by their physical size. Size is the single most important determinant of the properties, transformation, transport, and removal of particles from the atmosphere (Seinfield and Pandis, 1998). Both types of particles are subject to growth and transformations through acquiring of pollutants leading to formation of secondary material on the surface of existing particles (Vallius, 2005).

Also, the concentration and other characteristics of suspended particulate matter are determined by the presence and activity of sources. Once formed, particles change their size and composition by condensation or evaporation, by coagulation with other particles or

by chemical reactions (Seinfield and Pandis, 1998). In all, meteorological factors such as wind speed and direction, temperature, amount of precipitation, and height of the atmospheric boundary layer, are most important in governing the concentration variations of particulate matter and its fallout (Pohjola *et al*., 2000). The balance of the factors leads to pollutant accumulation and pollutant dispersion controls of temporal and spatial variations in concentrations of pollutants (Fang *et al*., 2000).

However, the major source of these pollutants is anthropogenic activities that include: transportation, stationary combustion and industrial emissions which inorganic pollutant is one of the compositions. Among the many inorganic pollutants originating from anthropogenic activities heavy metals such as Cu, Zn, Pb, Fe, Cd, Ni and Cd (Kemp, 2002; Morawska and Zhang, 2002; Melaku *et al*., 2008) have often been associated with vehicular emission. Also, emission of heavy metals from non-exhaust emissions have been identified e.g like the wearing of tyres, brakes and other parts of vehicles (Sternbeck *et al*., 2002; Laschober *et al*., 2004; Lough *et al*., 2005).

Dust being one of the atmospheric particulate matter fallout, is the most pervasive and important factor affecting human health and well-being (Youngming *et al*., 2006). Components and quantity of dusts are environmental pollution indicators, especially in big cities. Interest in the levels of contaminants associated with urban dusts has risen in the last decades, particularly in the concentration and distribution of lead (Jones and Mcdonald, 1983; VonSchirnding and Fuggle, 1996; Chatterjee and Banerjee, 1999) and other elemental concentrations, such as copper, zinc and cadmium, and their source identification (Ferguson and Kim, 1991; Nagerotte and Day, 1998). Many studies throughout the world have identified the sources of these contaminants in urban dusts as those associated with vehicular traffic, industrial and commercial areas (Day *et al*., 1975; Thornton, 1990; Al-

Chalabi and Hawker, 1997) as well as weathering or building facades, and have in fact recognized roadside dusts as a significant pollution source itself (Akhter and Madany, 1993).

2.7 HEALTH IMPLICATION OF ROAD ATMOSPHERIC PARTICULATE MATTER

Several decades ago industrialization and urbanization have resulted in dramatic increases in vehicle-associated emissions. According to Briggs *et al*. (1997), more than 50% of the total particulate matter (PM) emissions in urban areas are related to road traffic. A number of studies have reported significant associations between traffic density or proximity to raods and various respiratory symptoms in children (Brunekreef *et al*., 1997; Edwards *et al*., 1994; Venn *et al*., 2001). A recent study from London reported that asthmatic individuals showed increased symptoms (lung dysfunction and inflammation) while walking around heavily trafficked Oxford Street compared with performing similar activities in Hyde Park (McCreanor *et al*., 2007). In addition, increased cardiovascular effects have also been reported with environmental exposure to vehicle-traffic-derived pollutants (Peters *et al*., 2004; Dockery *et al*., 2005).

Riddle *et al*. (2008) have reported larger particulate matter emissions from diesel trucks compared with gasoline vehicles, with higher levels of direct vehicle emissions related to proximity to the roadside. Because the physicochemical characteristics of roadside airborne particles are also influenced by factors such as location, climatic conditions, traffic volume, type of fuel and engine, and operating conditions the toxic potential of these mixtures can be quite diverse (Singh *et al*., 2004; Gilmour *et al*., 2007).

Direct exposure to combustion emissions has resulted in a wide variety of cardiopulmonary effects in animals and humans (Sydbom *et al*., 2001; Lewtas, 2007; Hesterberg *et al*., 2009). In a more recent study by Cho *et al*. (2009) on effect of size-fractionated particulate matter on acute cardiopulmonary toxicity in mice, it was concluded that on a comparative mass basis the coarse (2.5-10μm) and ultrafine (< 0.1μm) particulate matter from an interstate highways in Raleigh, North Carolina, affected the lung and heart, respectively. The results then suggested that particulate of different size-specific chemistry might be associated with different toxicology mechanism in cardiac and pulmonary tissues.

2.8 FACTORS INFLUENCING METAL MOBILITY IN SOIL

pH: pH is generally acknowledged to be principal factor governing concentration of soluble and plant available metals (Brallier *et al*., 1996). Metal solubility tends to increase at lower pH and decrease at higher pH values (Tills and Alloway, 1983; Garcia-Miragaya, 1984; Ram and Verloo, 1985; Sanchez-Camazano *et al*., 1994; Chuan, *et al*., 1996; and Thorton, 1990). Studies of roadside soil showed that pH of the soil samples ranged from 6.6 (slightly acidic) (Chimuka *et al*., 2005) to 8.0 (Mohammed *et al*., 2006). Such pH value ranges are common to areas that receive low rainfall (Brandy and Weil, 1996), where leaching tends not to be very intense and the base forming cations are left to dominate the exchange complex in the place of Al^{3+} and H^{+} ions. The importances of pH in the solubility have also been demonstrated in numerous laboratory studies. For example, Tyler (1978) predicted from leaching experiment that, at a pH level of 4.2, 70 – 200years would elapse before 10% Pb in an organic horizon had leached out of the soil compared with 17 – 20years at pH 2.8. Xiong and Lu (1993) observed that the solubility of Zn in soil decreased 100-fold for each unit increase in pH. An important aspect of the effect of pH on metal

mobility is the buffering capacity of soils for acidity. For example, Helios-Rybicka *et al*. (1994) reported that a high carbonate content of smelter-impacted soils enhanced the soils' buffering capacity and that, as a consequence of the constant and elevated pH, the high concentrations of metals in the soils would not be rapidly leached. Young *et al*. (1993) found that the ability of clay soils to retain metals as pH decreases was directly dependent on the initial soil pH and on the soils' buffering capacities.

In summary, according to Rieuwerts *et al*. (1998) adsorption of metals may become significant at approximately pH 3 – 5 for Pb and Cu and around pH 5 – 6.5 for Zn and Cd. However adsorption of Cd has been observed at pH values of 3.7 and 4. Precipitation of insoluble solid appears to become important at approximately pH 6 – 7 for Pb, Zn, Cd and Cu.

Cation exchange capacity: The cation exchange capacity (CEC) of a soil is simply measure of the quantity of sites on soil surfaces that can retain positively charged ions (cations) by electrostatic forces (McEldowney *et al*., 1993). Cations retained electrostatically are easily exchangeable with other cations in the soil solution and are thus readily available for plant uptake (Summer and Miller, 1996). Cation exchanges of metals is dependent on the density of negative charges on the surface of soil colloids and the relative charges of metal species in solution and on soil surface (Evans, 1989). The surface negative charges may be pH dependent or permanent, where isomorphous substitution of Si^{4+} by Al^{3+} for example, has occurred in clay minerals (Evans, 1989).

Studies of roadside soils by Mohammed *et al*. (2006) showed that CEC of the soil samples ranged from 10.2meq/100g – 25.6meq/100g. They concluded that results showed opposite patterns to the expected, which probably could be due to large sand fractions

within the soil. Similarly, according to McEldowney *et al.* (2003), the mobility and bioavailability of metals present in soils depend on physicochemical properties of both the metal and the soil. Soils that have high organic and clay mineral contents are able to accumulate large quantities of metals due to abundance in the soil matrix of cation exchange surfaces and organic ligands capable of complexing with metal ions.

Soil Texture: The influence of soil texture on metal solubility in soils is best expressed in terms of the division of soils into clay, silt and sand fractions. These terms are in turn defined by particle size fractions of the soil with respective classifications of < 2µm, 2 - 50µm and > 50µm (Qian *et al*., 1996). The strong affinity of Pb and other metals to clay fraction is demonstrated by the ranking, in terms of adsorption, of clay > silt > sand (Andersson, 1979). Eriksson (1989) found that for a given total Cd concentration, Cd was more soluble and plant available in sandy soil than in clay soil. In another study, the extractability of Pb, Zn, Cd and Cu by ammonium acetate was always lower in loamy soils than in sandy soils (Scokart *et al*., 1983).

Qian *et al***.** (1996) studied soil texture in relation to extractable (0.1M HCl and DPTA) concentration of Pb and Cu. Metals were generally enriched in the clay fraction. Whilst relatively large amounts of available Cu and Pb were recorded in fine sand fraction, available Pb concentration was also high in the clay fraction. The authors suggested that the metals were probably adsorbed on clay minerals or occluded in clay lattice. The susceptibility of Pb to extraction from the clay fraction was attributed to high proportion of the metal in adsorbed form that is easily extracted compared to that present in the crystal lattice. A high degree of extractability was also observed in sand fractions of the soil and this was attributed to the low binding strength of these fractions.

Organic matter content: Organic matter accumulates at the soil surfaces, mainly as a result of decomposing plant material. While the organic matter content of soils is often small compared to that of clay, the organic fraction has a significant influence on metal substances, or humus, and non-humic substances. The humus comprised of humic and fulvic acids and humus, is the fraction of soil organic matter, which has been extensively decomposed and is resistant to further alteration (Foth, 1978). The remaining organic matter is mainly undecomposed plant material (Zimdahl and Skogerboe, 1977).

The mechanisms involved in the retention of metals by organic matter appear to include both complexation and adsorption, i.e. inner sphere reactions may take place as well as ion exchange (Evans, 1989). This is reflected in the literature where some authors describe interactions between metals and organic matter in terms of ion exchange (Singh and Sekhon, 1977; and Elliot *et al*., 1986) and others in terms of complexation (Zimdahl and Skogerboe, 1977; Jones and Jarvis, 1981; and Elliot *et al*., 1986). The active components in metal binding by organic matter are the negatively charged functional groups such as phenol, carboxyl(-ate) and amino group (Van Dijk, 1971; Foth, 1978; Elliott *et al*., 1986; and Ericksson, 1989). These groups increase in number during humification of organic matter (Foth, 1978). The functional groups also ionize increasingly as pH rises and organo-metal complexes thus become increasingly stable at higher pH levels (Zimdahl and Skogerboe, 1977; and Jones and Jarvis, 1981).

Several studies have investigated that influence of soil organic matter content on plant uptake of metals. Organic matter content shows no correlation with Pb uptake (John, 1972), positive associations with Zn uptake (MacLean, 1976; and Martin *et al*., 1982) and negative associations with Cd uptake (MacLean, 1977; and Street *et al*., 1977).

Chemical Speciation: The term chemical speciation denotes to the formation of specific chemical forms of an element in the system, although in the context of environmental analytical chemistry the term differs in its minutiae among authors. The word speciation while referring to the chemical form of an element also refers to the oxidation state in which that element exists in the environment. Recently the International Union of Pure and Applied Chemistry (IUPAC) sums up that "speciation" denotes to the distribution of an element amongst defined chemical species in a system (Templeton *et al*., 2000; Cornelis *et al*., 2003).

Generally, speciation (in fact fractionation) studies involve estimating individual physico-chemical or geochemical forms of an element that collectively make up the total concentration of that element in a sample. While the term is being debated for a definite meaning, various authors have been using it to explain one or more of the following: the chemical reactions that transform a set of metal compounds in a sample into another set of components, the assembly of compounds containing a particular element that are present in a sample and the process of identifying and quantifying the metal species present in a sample. The elemental speciation is studied and described by various pioneering researchers (Tessier *et al*., 1979; Ogunfowokan *et al*., 2009). Environmental and health effects of heavy metals in the soils depend on their mobility and bioavailability which are functions of their partitioning with soils (Lee *et al*., 2005). Hence, not only the determinant of metal concentrations but also the identification of binding sites and phase associations is essential for assessing environmental quality and human health in urban areas. Thus, to provide reliable information on the forms of association of heavy metals regarding their availability levels and hence potential mobility to food and water sources, a sequential

extraction procedure has been largely relied upon to partition heavy metals, such that their chemical reactivity can be elucidated (Olajire *et al*., 2003; Ogunfowokan *et al*., 2009).

2.9 HEAVY METAL TOXICITY

The biotoxic effects of heavy metals refer to the harmful effects of heavy metals to the body when consumed above the bio-recommended limits. Although individual metals exhibit specific signs of their toxicity, the following have been reported as general signs associated with cadmium, lead, arsenic, mercury, zinc, copper and aluminium poisoning: gastrointestinal (GI) disorders, diarrhoea, stomatitis, tremor, haemoglobinuria causing a rust–red colour to stool, ataxia, paralysis, vomiting and convulsion, depression, and pneumonia when volatile vapours and fumes are inhaled (McCluggage, 1991). The nature of effects could be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic.

Cadmium is toxic even at extremely low levels. In humans, long term exposure results in renal dysfunction, characterized by tubular proteinuria. High exposure can lead to obstructive lung disease, cadmium pneumonitis, resulting from inhaled dusts and fumes. It is characterized by chest pain, cough with foamy and bloody sputum, and death of the lining of the lung tissues because of excessive accumulation of watery fluids. Cadmium is also associated with bone defects, osteomalacia, osteoporosis and spontaneous fractures, increased blood pressure and myocardic dysfunctions. Depending on the severity of exposure, the symptoms of effects include nausea, vomiting, abdominal cramps, dyspnea and muscular weakness. Severe exposure may result in pulmonary odema and death. Pulmonary effects (emphysema, bronchiolitis and alveolitis) and renal effects may occur

following subchronic inhalation exposure to cadmium and its compounds (McCluggage, 1991; European Union, 2002).

Lead is the most significant toxin of the heavy metals, and the inorganic forms are absorbed through ingestion by food and water, and inhalation (Ferner, 2001). A notably serious effect of lead toxicity is its teratogenic effect. Lead poisoning also causes inhibition of the synthesis of haemoglobin; dysfunctions in the kidneys, joints and reproductive systems, cardiovascular system and acute and chronic damage to the central nervous system (CNS) and peripheral nervous system (PNS) (Ogwuebgu and Muhanga, 2005). Other effects include damage to the gastrointestinal tract (GIT) and urinary tract resulting in bloody urine, neurological disorder and can cause severe and permanent brain damage. While inorganic forms of lead typically affect the CNS, PNS, GIT and other biosystems, organic forms predominantly affect the CNS (McCluggage, 1991; Ferner, 2001; and Lenntech, 2006). Lead affects children by leading to the poor development of the grey matter of the brain, thereby resulting in poor intelligence quotient (IQ) (Udedi, 2003). Its absorption in the body is enhanced by Ca and Zn deficiencies. Acute and chronic effects of lead result in psychosis.

Zinc has been reported to cause the same signs of illness as does lead, and can easily be mistakenly diagnosed as lead poisoning (McCluggage, 1991). Zinc is considered to be relatively non-toxic, especially if taken orally. However, excess amount can cause system dysfunctions that result in impairment of growth and reproduction (Nolan, 2003). The clinical signs of zinc toxicosis have been reported as vomiting, diarrhea, bloody urine, icterus (yellow mucus membrane), liver failure, kidney failure and anemia (Fosmire, 1990).

Chromium metal and chromium (III) compounds are not usually considered health hazards (Ghosh *et al*., 2009); chromium is an essential trace mineral. However, hexavalent

chromium (chromium VI) compounds can be toxic if ingested or inhaled (Ghosh *et al*., 2009). Chromium enhances insulin activity in the body and thus essential to the body. Chromium (VI) is one of the pronounced toxins. It easily permeates biological membrane due to its oxidizing potential and chromium (VI) causes renal damage, cancer in man and disease of central nervous system (Bae *et al.*, 2001). Chromates are often used to manufacture, amongst other things, leather products, paints, cement, mortar and anti-corrosives. Contacts with products containing chromates leads to allergic dermatitis, resulting in ulceration of the skin, sometimes referred to as 'chrome ulcers'.

Copper is one of a relatively small group of metallic elements which are essential to human health. These elements, along with amino and fatty acids as well as vitamins, are required for normal metabolic processes. While copper is an essential micronutrient, exposure to excess Cu has detrimental effect on plant growth. Copper toxicity leads to organs damage in fish which would lead to mortalities. In man, acute copper toxicity causes cardiovascular collapse while chronic toxicity leads to fever, jaundice and diarrhea (Bae *et al.,* 2001).

Recent research with acute Ni exposure is associated with variety of clinical symptoms and signs which include gastrointestinal disturbances (nausea, vomiting, abdominal discomfort and diarrhoea), visual disturbance, headache, giddiness, wheezing and cough. Chronic inhalation of Ni and its compounds is associated with increased risk of lung cancer (Ghosh *et al*., 2009).

2.10 THEORY OF FLAME ATOMIC ABSORPTION SPECTROMETRY

Atomic absorption spectrometry (AAS) is an analytical technique capable of determining trace amounts of elements or metals in different environmental samples. AAS

uses the absorption of light to measure the concentration of gas phase atoms in liquid samples. Atomic absorption spectrometers have four principal components: a light source (usually a hollow cathode, an atom cell (atomizer), a monochromator, and a detector, and output device.

An atom absorbs light at discrete wavelengths. In order to measure this narrow light absorption with maximum sensitivity, it is necessary to use a line source, which emits the specific wavelengths, which can be absorbed by the atom. The common source of light in AAS is a hollow cathode lamp which contains a tungsten anode and a cylindrical hollow cathode made of the element to be determined. These are sealed in a glass tube filled with an inert gas like neon or argon. Each element has its own unique lamp, which must be used for that analysis. Applying a potential difference of about 300- 400 V between the anode and the cathode leads to the ionization of some gas atoms. These gaseous ions bombard the cathode and eject metal atoms from the cathode in a process called sputtering. Some sputtered atoms are in excited states and emit radiation characteristic of the metal as they fall back to the ground state sputtering (PerkinElmer Corporation, 1996). The Sputtered metal atoms are further excited to emit through impact with the filled gas.

Atomic absorption uses this relationship to determine the presence of a specific element based on absorption in a specific wavelength. For example, lead absorbs light with a wavelength of 422.7nm. Since atoms of different elements absorb characteristic wavelengths of light, analyzing a sample to see if it contains a particular element means using light from that element. In the case of lead, a lamp containing lead emits light from excited lead atoms which produce the right mix of wavelengths to be absorbed by any lead atoms from the sample. The greater the number of atoms in the vapour (ground state free atoms), the more radiation is absorbed.

$Pb^* \rightarrow Pb + h\nu$ ---------- (1)

Each element in the periodic table will have a specific change of energy (ΔE) that will absorb a specific wavelength of light. The relationship between the energy transition and the wavelength (λ) can be described by,

$\Delta E = hc/\lambda = h\nu$ ---------- (2)

Where, h is Planck's constant (h = 6.626 x 10^{-34} Joule .second), λ is the absorbed wavelength (in m), and ν is frequency (in Hz).

Absorbance is the most convenient term for characterizing light absorption in absorption spectrophotometry, which simply states that the absorbance is directly proportional to the concentration of the absorbing species for a given set of instrumental conditions. Beer's Law defines this relationship as:

$A = €bc$ ---------- (3)

Where, A, is the measured absorbance by an absorbing element (no units); €, is a wavelength-dependent absorptivity coefficient of the absorbing element (L/molcm); b, is the path length of the light intercepted by the absorbing element in the absorption cell (in cm) ; and c, is the concentration of the absorbing species expressed in mol/L.

The technique of flame atomic absorption spectroscopy (FAAS) requires a liquid sample to be aspirated, aerosolized, and mixed with combustible gases, such as acetylene and air or acetylene and nitrous oxide. The mixture is ignited in a flame whose temperature ranges from 2100 to 2800^0C. During combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb ultraviolet or visible light and make transitions to higher electronic energy levels. Sample solutions are usually introduced into a nebuliser by being sucked up in a capillary tube. In the nebuliser

the sample is dispersed into tiny droplets, which can be readily broken down in the flame. The fine mist of droplets is mixed with fuel (acetylene) and oxidant (nitrous oxide) and burned. The monochromator is an optical system, which separates the spectral line of interest from other spectral lines with different wavelengths emitted by the hollow-cathode lamp. It selects the specific wavelength of light, which is absorbed by the sample, and excludes other wavelengths. The selection of the specific light allows the determination of the selected element in the presence of others.

The light selected by the monochromator is directed onto a detector that is typically a photomultiplier tube, whose function is to convert the light signal into an electrical signal proportional to the light intensity. The signal could be displayed for readout, or further fed into a data station for printout by the requested format. Finally a calibration curve is constructed by running several samples of known concentration under the same conditions as the unknown. The absorbance of each known solution is measured and then a calibration curve of concentration vs. absorbance is plotted.

CHAPTER THREE

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 Apparatus/Equipment

Volumetric flasks, 50cm^3, 100cm^3, 250cm^3 and 100cm^3

Measuring cylinder, 100 cm^3, 10cm^3

Plastic bottle for samples and digest.

Conical flasks, 125cm^3, 250cm^3

Polythene bags

Funnels

Wash bottles

Filter paper Whatman No. 42

Mortar and pestle

Eye goggles

Nose guard

Drying oven Gallenkamp Model No 237887c

Desiccators

Hot plates Bibby Sterlin Ltd. Model No HC500

Analytical balance Mettler Model No 38544

Fume cupboard

Thermometer

pH meter Hanna (Model H1991000)

Steam bath Gallenkamp Model No 587542B

Flask shaker Tamson PMT Model No 5657HAAN

Glass rod

Centrifuge Baird and Tatlock Model No B93129

Pipette

Kjeldahl flask

Teflon cups

Deionizer Zerorif England Model No 5202

Carbolite furnace (Model GLM 3)

Crucible

Butchner funnel

Sieve Endecotts Model No H5369

3.1.2 Reagents

Magnesium nitrate ($Mg(NO_3)_2$) Analar Grade, BDH

Hydrofloric acid, (HF) (1.21, 73%) (Manufactured by Fluka Chemika-BioChemika, Switzerland)

Double distilled water

Hydrogen peroxide (H_2O_2) (1.13, 35%) Analar Grade, BDH

Conc. Nitric acid (HNO_3) (1.41, 70%) Analar Grade, BDH

Sodium ethylenedimethyltetraamine (NaEDTA) Analar Grade, BDH

Ammonium acetate (CH_3COONH_4) Analar Grade, BDH

Hydroxylamine hydrochloride ($NH_2OH.HCl$) (Manufactured by Fluka Chemika-BioChemika, Switzerland)

Deionized water

Conc. Hydrochloric acid (HCl) (1.18, 37%) Analar Analar Grade, BDH

Cadmium nitrate ($Cd(NO_3)_2$)Analar Grade, BDH

Copper nitrate ($Cu(NO)_3$) Analar Grade BDH

Zinc chloride ($ZnCl_2$) Analar Grade, BDH

Perchloric acid ($HClO_4$) Analar Grade BDH

Distilled water

Ammonium chloride (NH_4Cl) Analar Grade, BDH

Sodium chloride ($NaCl_2$) Analar Grade, BDH

Stannous chloride ($SnCl_2$) Analar Grade, BDH

Ammonium floride (NH_4F)Analar Grade,BDH

Devardo's Alloy (Manufactured by Fluka Chemika-BioChemika, Switzerland)

Potassium chloride (KCl) Analar Grade BDH

Conc. Tetraoxosulphate (VI) (H_2SO_4) (1.86, 98%) Analar Grade BDH

Boric Acid (H_3BO_3) (1.50, 48%) (Manufactured by Fluka Chemika-BioChemika, Switzerland)

Potassium tetraoxosulphate (VI) (K_2SO_4) Analar BDH

Potassium heptaoxochromate (VI) ($K_2Cr_2O_7$) Analar grade, BDH

Sodium metaphosphate $(NaPO_3)_6$ Analar Grade, BDH

Acetic acid (HOAc)

Sodium acetate (NaOAc)

3.1.3 Preparation of Solutions

3.1.3.1 Stock Solutions

1000mgdm^{-3} Cadmium solution: prepared by dissolving 2.7500g of $Cd(NO_3)_2.\ 4H_2O$ in a 100cm^3 beaker in a minimum amount of distilled deionized water. The solution was then transferred into a 1000cm^3 standard flask and diluted to mark with distilled deionzed water.

1000mgdm^{-3} Chromium solution: prepared by dissolving 5.6538g $K_2Cr_2O_7$ in a 100cm^3 beaker in a minimum amount of distilled deionized water. The solution was transferred into a 1000cm^3 standard flask and diluted to mark with distilled deionized water.

1000mgdm^{-3} Copper Solution: Prepared by dissolving 1.0000g Cu metal in a 100cm^3 beaker in minimum amount of 1:1 HNO_3. The solution was then transferred into a 1000cm^3 standard flask and diluted to mark with distilled deionized water.

1000mgdm^{-3} Iron solution: Prepared by dissolving 6.6785g $Fe(SO_4)_2.\ 7H_2O$ in a 100cm^3 beaker in a minimum amount of 1:1 HNO_3. The solution was then transferred into 1000cm^3 standard flask and diluted to mark with distilled deionized water.

1000mgdm^{-3} Nickel solution: Prepared by dissolving 4.9322g Ni $(NO_3)_2.6H_2O$ in a 100cm^3 beaker in a minimum amount of distilled deionized water. The solution was transferred into a 1000cm^3 standard flask and diluted to mark with distilled deionized water.

1000mgdm^{-3} Lead Solution: Prepared by dissolving 1.5990g Pb $(NO_3)_2$ in a 100cm^3 beaker in a minimum amount of distilled deionzied water. The solution was then transferred into 1000cm^3 standard flask and diluted to mark with distilled deionized water.

1000mgdm^{-3} Zinc Solution: Prepared by dissolving 1.2461g ZnO in a 100cm^3 beaker in a minimum amount of 1:1 HNO_3. The solution was then transferred into 1000cm^3 standard flask and diluted to mark with distilled deionzied water.

1000mgdm^{-3} Potassium Solution: Prepared by dissolving 2.5897g KNO_3 in a 100cm^3 beaker in minimum amount of distilled deionized water. The solution was then transferred into 1000cm^3 standard flask and diluted to mark with distilled deionized water.

1000mgdm^{-3} Magnesium solution: Prepared by dissolving 10.6667g $Mg(NO_3)_2.6H_2O$ in a 100cm^3 beaker in a minimum amount of distilled water. The solution was then transferred into a 1000cm^3 standard flask and diluted to mark with distilled deionized water.

1000mgdm^{-3} Calcium solution: Prepared by dissolving 2.7750g $CaCl_2$ in a 100cm^3 beaker in minimum amount of distilled deionized water. The solution was then transferred into 1000cm^3 standard flask and diluted to mark with distilled deionized water.

3.1.3.2 Standard Working Solutions

These were prepared using the dilution formula:

$$C_{\text{Stock solution}} \times V_{\text{stock solution required}} = C_{\text{standard working solution}} \times V_{\text{standard working solution}}$$

$$V_{\text{stock solution required}} = \frac{C_{\text{Standard working solution}} \times V_{\text{standard working solution}}}{C_{\text{stock solution}}}$$

Following a range finding test, working standard concentrations were prepared from 1000 mgdm^{-3} of each metal stock solutions by serial dilution as follows; 0.5, 1.0, 1.5, 2.0 and 2.5 mgdm^{-3} Cd; 0.5, 1.0, 2.0, 3.0, and 4.0mgdm^{-3}, Cr, 0.5, 1.0, 1.5, 2.0, and 2.5 mgdm^{-3} Cu; 1.0, 2.5, 5.0, 7.5 and 10.0 mgdm^{-3}, Ni; 1.0, 2.0, 5.0, 20.0 and 50.0 mgdm^{-3} Pb, and 0.5, 1.0, 2.0 3.0 and 5.0 mgdm^{-3} Zn. Distilled deionized water was used for preparing all solutions.

3.1.3.3 Other Solutions

1moldm^{-3} magnesium Nitrate – $Mg(NO_3)_2$, prepared by dissolving 148g $Mg(NO_3)_2$ in a 500cm^3 beaker in a minimum amount of distilled deionized water. The solution was then transferred to a 1000cm^3 standard flask and diluted to mark with distilled deionized water.

8.8moldm^{-3} Hydrogen peroxide, H_2O_2 – Prepared by measuring 756.7cm^3 of 35% H_2O_2 using a measuring cylinder and transferring it into a 1000cm^3 standard flask and diluting to mark with distilled deionized water.

0.02moldm^{-3} Trioxonitrate (v) acid HNO_3 – Prepared by measuring 1.28cm^3 of conc. HNO_3 using a 1cm^3 graduated and transferring it into a 1000cm^3 standard flask and diluting to mark with distilled deionized water.

1moldm^{-3} Ammonium acetate, CH_3COONH_4 – Prepared by dissolving 77g CH_3COONH_4 in a 500cm^3 beaker in a minimum amount of distilled deionized water. The dissolved solution was then transferred to a 1000cm^3 standard flask and diluted to mark with distilled deionized water.

0.04moldm^{-3} Hydroxylamine hydrochloride, $NH_2OH.HCI$ – prepared by dissolving 2.78g $NH_2OH.HCI$ in a 100cm^3 beaker in a minimum amount of distilled deionized water. The solution was then transferred to a 1000cm^3 standard flask and diluted to mark with distilled deionized water.

Ferroin indicator: Prepared by dissolving 7.425g of O-phenanthrolein and 3.475g $FeSO_4$. $7H_2O$ in a separate 100cm^3 beaker in a minimum amount of distilled water. The solution were then transferred quantitatively into 500cm^3 standard flask, mixed thoroughly and diluted to mark with distilled deionized water.

50% w/v Calgon (sodium hexametaphosphate)- prepared by dissolving 500g calgon in a 500cm^3 beaker in a minimum amount of distilled water. $NaHCO_3$ was added to bring the

pH of dissolved solution to 9.0. The solution was then transferred quantitatively into 1000cm^3 standard flask and diluted to mark with distilled deionized water.

0.02moldm^{-3} Potassium dichromate, $K_2Cr_2O_7$ solution – Prepared by dissolving 5.88g $K_2Cr_2O_7$ previously dried at 103^{0}C to constant weight in a 100cm^3 beaker in minimum amount of distilled water. The solution was then transferred quantitatively into a 1000cm^3 standard flask and diluted to mark with distilled deionized water.

0.25moldm^{-3} Ammonium ferrous sulphate ($(NH_4)_2SO_4.FeSO_4.6H_2O$) – prepared by dissolving 97g of ammonium ferrous sulphate in a 200cm^3 beaker in minimum amount of distilled water and 10cm^3 of Conc. H_2SO_4 added. The resulting solution was stirred thoroughly with a glass rod to have homogenous mixture, then transferred into 1000cm^3 standard flask and diluted to mark with distilled deionized water.

3.1.4 The Study Area

Kano metropolis is located at the Central Western part of Kano State between latitude 11^{0}59′59.57 – 12^{0}02′39.57″N of the equator and between longitude 8^{0}33′19.69 – 8^{0}31′59.69″E. It lies in the Northern Central boundary of Nigeria and is located some 840km away from the edge of the Sahara desert and 1,140km from the Atlantic Ocean (Oseiki, 2009). Its population is the second largest in Nigeria after Lagos (TWG, 2010). The Kano Urban area covers approximately 137 sq.km and comprises six Local Government Areas (LGAs) - Kano Municipal, Fagge, Dala, Gwale, Tarauni and Nassarawa.

The climate of Kano metropolis is that of tropical continental which is the Aw type according to Koppen's classification scheme. The dry season lasts from October to May when the tropical continental airmass dominates. During the months of December and

February, the harmattan is at its peak blowing thin dust from the Sahara which creates poor visibility. From March to May, however, the dry cold air turns into searing hot air with temperature rising up to and above 32^0C. Rainfall is concentrated from June to September and the rains are preceded by violent dust storms followed by tornadoes mainly during the month of May and at the close of the rains in September and early October. About 58% of the rain falls in July and August (Oseiki, 2009).

Kano Metropolis attracts substantial number of immigrants being the seat of government and center of commerce, industry and education. In the city, there are various large markets such as the City (Kurmi) Market, Sabongari Market and Katin Kwari (cloth market) which attract people from all over the country. The major form of transportation within Kano Metropolis is by road. Most common transport modes used include cars, buses, motocycles and tricycles (Keke NAPEP).

3.1.5 Sampling Sites Description

Ten sites situated along busy roads originating from the city centre covering the six L.G.A. (as in **section 3.1.4**) was selected. Specifically, the sites selected for the study included the following: Dan Agundi (**Site 1)**, Kofar Nassarawa (**Site 2)**, France Road (**Site 3)**, Zoo Road (**Site 4)**, Sani Abacha Road (**Site 5)**, Ibo Road (**Site 6)**, Aminu Kano Teaching Hospital (**Site 7)**, Kofar Mazugal (**Site 8)**, Zungeru/Airport Road (**Site 9)** and Rimi Market (**Site 10)** as shown in Fig 3.1. The criteria for selection of sampling sites included the following: Presence of a household near a major road, traffic density and area of population exposure and wind direction. One site, farm center was used as control **(Site C)**. A small garden within a residential buildup area of farm center was used as control site,

which is neither closer to any secondary nor main road. Also describe in Table 3.1 below is the geographical locations of the sampling sites as shown on Figure 3.1.

3.1.6 Sample Collection

The air pollutant and metrological data, roadside dust particulate and roadside soils were collected at the eleven sites including control on a seasonal basis between February 2010 and September 2010 as follows:

Seasons

Cold and dry season	-	December – February
Hot and dry season	–	March – May
Warm and wet season	-	June – August
Warm and dry season	-	September – November

3.1.6.1 Road Air Pollutant and other Field Data

Concentrations of gaseous pollutants data; CO, H_2S, SO_2, NO_2, FL (flammable gases) and NH_3 were determined using mobile gas sensors manufactured by Crown Detection Instrument Ltd. Oxon OX14DY England and metrological data: sound level and

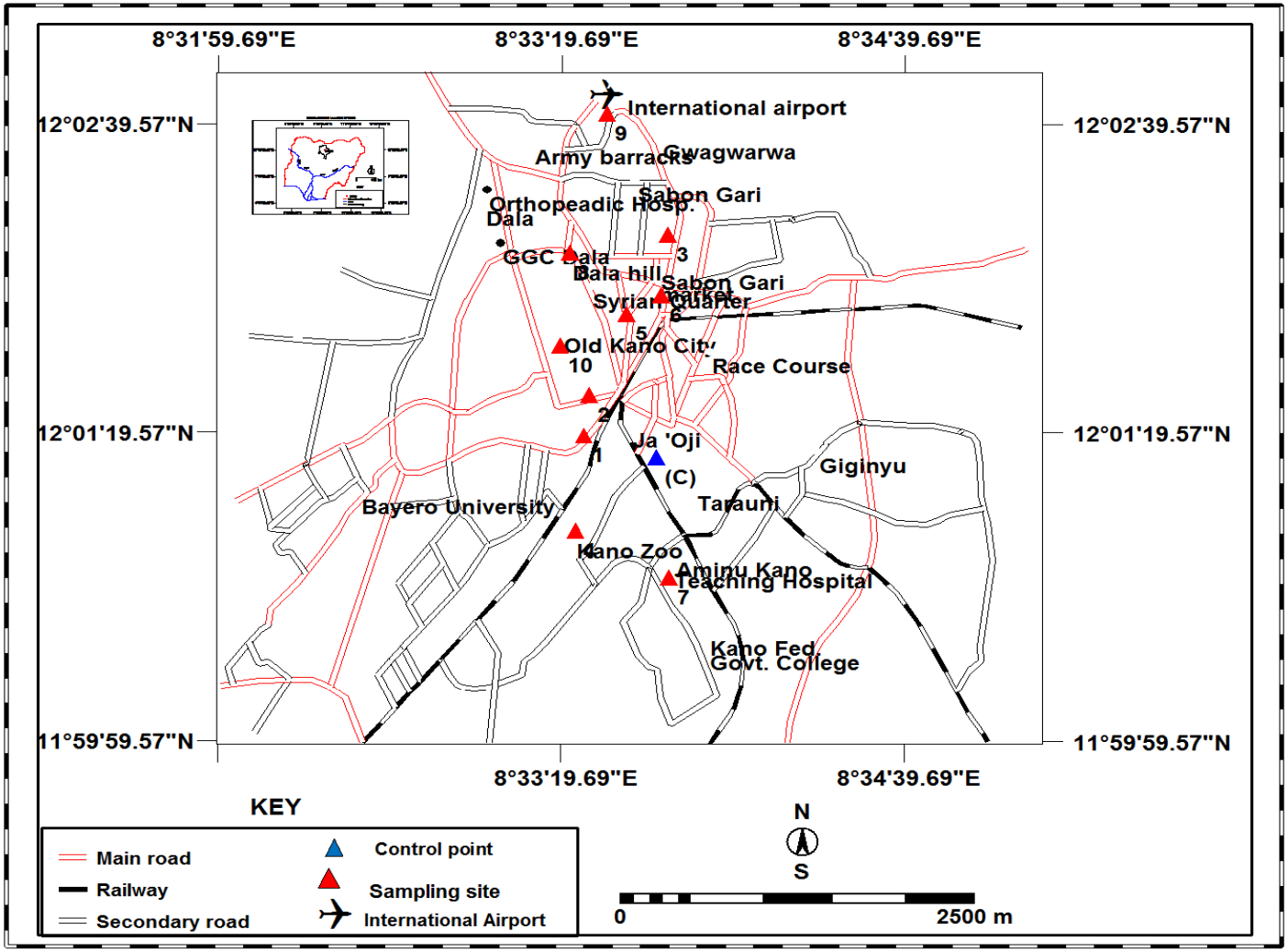


FIGURE 3.1 : KANO METROPOLIS SHOWING THE SAMPLING SITES

Source : Adapted and modified from google map data, 2010

Table 3.1 Geographical Locations of the Sampling Sites

Sampling Site code	Sampling Site	GPS Grid Coordinate		
		Latitude (N)	Longitude (E)	Elevation (m)
1	Aminu Kano Teaching Hospital	11.96828	008.55063	486
2	Zoo Road	11.97815	008.53862	487
3	Dan Agundi	11.98127	008.52328	488
4	Kofar Nassarawa	11.99062	008.53137	486
5	Rimi Market	11.99770	008.52134	482
6	Sani Abacha Road	12.00938	008.54282	488
7	Ibo Road	12.01445	008.53942	480
8	France Road	12.01436	008.53446	478
9	Kofar Mazugal	12.01436	008.51801	479
10	Zungeru/Airport Road	12.02734	008.54070	467
C	Control	11.90128	008.40120	484

temperature were determined using NL-21 Sound Level Meter and In-Out Door Thermometer (Crown Detection Instrument Ltd. Oxon OX14DY England).

3.1.6.2 Road Air Particulates Matter (PM)

Atmospherically deposited particulates from window glass were sampled as an indirect method of air sampling as described by Nabuloa (2004) selected sites. Window glass was use as an inert collector of airborne contaminants because it has the ability to accumulate pollutants from the atmosphere. The glass windows were first washed clean using detergents and tap water then rinsed with distilled and finally deionized water. The windows were left for 1 month at each site to accumulate pollutants and ensure that all windows had uniform exposure period. Samples was collected using inert tissue (Tissue paper) soaked in isopropyl alcohol (2-propanol) solvent.

3.1.6.3 Roadside Soils

Surface samples of soil was taken 3m from the roadway at the studied sites in the four (4) main seasons with the aid of stainless steel spoon (Awofolu, 2005). Approximately 20g of surface (0 – 5cm) roadside soils each were collected from five spot at a distance of 10m apart from each side of the road within a given site with a stainless steel spoon, pooled and homogenized to form a representative sample of 200g for a given road (Onianwa, 2001). Samples were placed in polythene bags and air-dried in the laboratory for 3days. They were then sieved with 1400µm, 355µm and 150µm sieve to achieve different grain sizes. Subsequently, chemical analyses were performed including both strong acid digestion and sequential extraction procedures. The samples for physicochemical analysis were removed from the representative sample before sieving.

3.2 METHODS

3.2.1 Traffic Density

The traffic density was determined by directly observing and counting the traffic (Onianwa, 2001; Nabuloa, 2004) during the usual peak traffic periods 8:00 a.m. - 10.00 a.m, 12:00 p.m - 2.00 p.m, 4:00 p.m – 6:00 p.m each day for three days within week days. The average number of traffic at each site per hour was calculated as shown in Table 3.2.

3.2.2 Quality Assurance

All glassware, polythene tubes and Teflon beakers used in the analyses were precleaned by washing with liquid detergent, rinsed with water and distilled-deionized water, and then soaked in 10% HNO_3 for 24hrs and rinsed with distilled – deionized water and in such a manner that no contamination occurred (Adnan *et al*., 2003). Thereafter, the apparatus were oven-dried for 12hrs at a temperature of 80^0C. All reagents used were of analytical grade.

3.2.3 Determination of Physicochemical Parameters of Soils

3.2.3.1 Determination of pH (Hendershot et al., 1993)

Air dried soil samples of 10g were weighed into a 50cm^3 beaker and 20cm^3 distilled deionized water added. The mixture was allowed to stand for 30 minutes with occasional stirring with glass rod.

Table 3.2 Average Traffic Volume Per Hour on High Traffic Roads in Kano Metropolis

Sampling Site Code	Sampling Site	Average Traffic Volume Per h			
		Number of Motorcycle	Number of other Vehicles	Number of Trucks/Lorry	Total
1	Aminu Kano Teaching Hospital	1902±12	2634±10	196±2	4732
2	Zoo Road	2011±20	1504±8	121±5	3636
3	Dan Agundi	1206±15	1935±12	216±2	2831
4	Kofar Nassarawa	1323±13	1801±19	46±2	3170
5	Rimi Market	3005±10	2008±14	25±2	5038
6	Sani Abacha Road	6857±23	1292±13	207±2	8357
7	Ibo Road	2464±19	1845±19	35±5	4344
8	France Road	2651±18	1041±9	16±2	3708
9	Kofar Mazugal	1995±21	2836±12	149±2	4180
10	Zungeru/Airport Road	1443±11	2366±17	198±3	4007
C	Control	< 1	< 1	<1	< 1

The electrodes of a pre-calibrated HANNA pH meter (model 111991000) were inserted into the partly settled suspension and the pH of the soil solution taken.

3.2.3.2 Determination of Electrical Conductivity (Hendershot et al., 1993)

The electrical conductivities of soil samples were measured as follows: Soil to water ratio was 1:2. 2mm air-dried soil samples of 10g were weighed into plastic containers and 20cm^3 of distilled deionized water added. The mixture was stirred several times for 30 minutes. Then the soil suspension was allowed to stand for 30 minutes more undisturbed. The electrodes of the conductivity meter were immersed into the settled suspension and the electrical conductivity of the soil recorded in $\mu s cm^{-1}$. The electrical conductivity meter was calibrated using 0.1MKCl before use (Bamgbose *et al*., 2005).

3.2.3.3 Determination of Organic Matter (Walkley and Black, 1934)

The organic matter of the soil samples was determined by weighing 1g of the composite soil sample into three 250cm^3 conical flasks. 10cm^3 of 0.20M potassium dichromate was added into each flask and swirled gently to disperse the soil followed by addition of 20cm^3 concentrated H_2SO_4. The flasks were swirled gently until the soil and reagent were thoroughly mixed. The mixture was then allowed to stand for 30minutes on a glass plate. 100cm^3 of distilled water was added followed by the addition of 4 drops of ferroin indicator, after which it was titrated with 0.25M ammonium ferrous sulphate. The processes were repeated for all the samples. Blank titration was similarly carried out.

$$\% \text{ Organic carbon is given by the equation} = \frac{(\text{Blank Titre} - \text{Actual Titre}) \times 0.3 \times m \times f}{\text{Weight of air – dried sediment taken}}$$

Where f = correction factor = 1.33

m = concentration of ammonium ferrous sulphate

Then % Organic matter in soil = % Organic carbon x 1.729

3.2.3.4 Particle Size Distribution (Bauyocos, 1951)

Particle size distribution was determined by the hydrometer method: 50g of 200µm sieved soil samples was weighed into a 250cm^3 plastic beaker. 100cm^3 of 50% calgon was added and then stirred with a glass rod. Then 100cm^3 of distilled water was added and stirred. The beaker was left to stand for about 30minutes with occasional stirring. The mixture was then transferred into 250cm^3 plastic container and shaken on an end-to-end shaker for 10 minutes. The shaken sample was next transferred into a 1000cm^3 measuring cylinder and made to the 1000cm^3 mark with distilled water. Before the hydrometer reading was taken, the suspension in the cylinder was mixed vigorously using a long handle plunger making sure that the soil at the bottom was thoroughly disturbed. Hydrometer readings at 40 seconds and 2 hrs were taken. A blank cylinder was prepared by making 100cm^3 of the 50% calgon solution up to 1000cm^3 mark with distilled water. The blank hydrometer reading was taken at the respective time intervals. The temperature of the suspension and blank was also taken. The corrected hydrometer reading C (g/l) were obtained by subtracting the blank reading R_L (g/l) from the hydrometer readings in the soil suspensions R (g/l) and adding 0.36g/l for every degree above 20^0C.

$C = R - R_L + (0.36T)$

Where T = Room temperature at 20^0C.

$$\text{Clay} = \frac{\text{Corrected 2 hrs reading} - \text{Blank} \times 100}{\text{Weight of soil taken}}$$

$$\text{Silt} = \frac{\text{Corrected 40 secs reading} - \text{Blank} \times 100}{\text{Weight of soil taken}}$$

Sand = 100 – (% Clay + % Silt)

3.2.3.5 Cation Exchangeable Capacity (CEC) (Hendershot et al., 1993)

The Cation Exchanged Capacity (CEC) was determined by the sum of exchangeable cations (Banerjee and Shrivastava, 2004): 2g of soil samples were weighed into 30cm^3 centrifuge tubes. 20cm^3 of 0.1$moldm^{-3}$ $BaCl_2.2H_2O$ was added and shaken for 2hrs. The tubes were removed from the shaker, placed in a centrifuge and centrifuged at about 10000rpm for 30mins, and the supernatant decanted carefully. These were filtered into plastic bottles and taken for AAS and flame photometer determinations, respectively.

3.2.4 Sample Digestion

3.2.4.1 Total Metal Determination

Total metal content of soil and dust particulate was done according to Venkateswaran *et al*. (2007): 1g of soil (grain size 1400, 355 and 150µm) and dust were digested with 8cm^3 of *aqua regia* (HCl and HNO_3, 3:1v/v) for 2hrs at 120^{0}C separately. The mixture was then filtered and diluted to 50cm^3. Total metal determination was done in triplicate.

3.2.4.2 Chemical Fractionation of Soil and Dust Particulate

Chemical fractionation of heavy metal was done on soil and dust particulate using Finzgar *et al*. (2007) method. This method modified the conventional method developed by Tessier *et al*. (1979). The modified method determines fractionation of heavy metals into six (6) geochemical fractions as follows:

FI (fraction soluble in soil solution)

1g of air – dried soil sample (of a particular particle size fraction) was mixed with $10cm^3$ of deionised water with continuous agitation for 1hr, centrifuged and supernant decanted and made up to $50cm^3$ with deionised water prior to analysis.

FII (Exchangeable Fraction)

The residue from **FI** was leached at room temperature with $10cm^3$ of 1M $MgNO_3$ at pH 7.0 with continuous agitation for 1hr, centrifuged and supernatant decanted into $50cm^3$ volumetric flask and made up to the mark with deionized water prior to analysis. $MgNO_3$ displaces ions electrostatically bound in the soil matrix.

FIII (Acid Extractable – Carbonate bound Fraction)

Residue from **FII** was leached at room temperature with $10cm^3$ of 1M NaOAc (pH 5 adjust with HOAc) with continuous agitation for 5hrs and centrifuged. The supernatant was decanted into $50cm^3$ volumetric flask and made up the mark with deionized water prior to analysis. NaOAc solubilises carbonates (calcites, dolomite) and releases entrapped metals.

FIV (Reducible – Fe – Mn Oxides and Hydroxide Fraction)

Residue from **FIII** was leached with $20cm^3$ of 0.04M $NH_2OH.HCl$ (pH adjusted with 25%v/v HOAc) at 96^0C for 6hrs with occasional agitation and centrifugation. The supernatant decanted into $50cm^3$ volumetric flasks and made up the mark with deionized water prior to analysis. $NH_2OH.HCl$ reduces Fe and Mn oxides to soluble forms.

FV (Oxidizable – Organic Matter Bound Fraction)

To the residue from **FIV**, $3cm^3$ of 0.02M HNO_3 and 30%v/v H_2O_2 was added. The mixture was then heated to 85^0C in a water bath for 3hrs. After cooling, 5ml of 1M NaOAc was then used to extract with occasional agitation for 3hrs at 85^0C. Mixture was centrifuged and

supernatant decanted into 50cm^3 volumetric flask and made up the mark with deionized water prior to analysis. HNO_3 and H_2O_2 oxidise organic matter and solubilise sulphides. Oxidized organic matter releases complexed, adsorbed and chelated metals.

FVI (Residual and Inert Fraction)

Residual from **FV** was digested with a mixture of 8cm^3 of 5:1 mixture of HF and $HClO_4$ in acid digestion Teflon cup. Then mixture was dried ashed for 2hrs and evapourated to dryness. The residue was dissolved in little quantity of water in 50cm^3 volumetric flask and diluted to mark with deionized water prior to analysis.

After successive extraction, the sample was centrifuged at 3000rpm for 15mins. The supernatants was removed with pipette and filtered with Whatmann No 42 filter paper. The residue was washed with deionized water followed by vigorous hand shaking and then follows 15mins of centrifugation before next extraction. The volume of rinse water used was left at minimum to avoid excessive solubilization of solid materials. The process was then carried out in triplicate for a particular sample.

3.2.5 Quality Assurance Protocol

This was conducted according to Ogunfowokan *et al*. (2009) to ascertain the precision of the analytical procedures used in this study, since reference soil and dust materials were not available to us when this study was carried out. This was done by spiking the pre-digested soil and dust samples with 50cm^3 of multielemetal metal standard solution (MESS) (5mgdm^{-3} of Cd, Cr, Ni, Pb, Cu and Zn).

3.2.5.1 Preparation of Multielement Standard Solution (MESS)

0.0013g of $Cd(NO_3)_2.4H_2O$ was weighed out, dissolved in $2cm^3$ distilled water in a beaker and transferred into a $1000cm^3$ volumetric flask. The beaker was rinsed thoroughly with distilled water into the flask. 0.0050g of Cu metal and 0.0062g of ZnO were weighed separately and dissolved in 2ml concentrated HNO_3 each in a beaker and transferred into the same 1 litre volumetric flask. The beakers were rinsed with distilled water into the volumetric flask. 0.0282g of $K_2Cr_2O_7$ was dissolved in $2cm^3$ HNO_3 in a beaker and transferred into the volumetric flask. This was followed by separately weighing out 0.0080g of $Pb(NO_3)_2$ and 0.0247g of $Ni(NO_3)_2.6H_2O$ were separately weighed and distilled in distilled water and quantitatively transferred into the same volumetric flask. The flask was made up to mark with distilled water to give $5mgdm^{-3}$ of the MESS Cd, Cr, Ni, Pb, Cu and Zn. Aliquot of this solution was used in the spiking experiment.

3.2.5.2 Spiking Experiment

$50cm^3$ of the multi-element standard solution was drawn with graduated pipette and used to spike quantity one of the soil and dust particulate samples. These were then digested using the method already described in Section **3.2.3.1**. The digests were run on atomic absorption spectrometry (AAS). Also, a $50cm^3$ of $5mgdm^{-3}$ of the MESS Cd, Cr, Ni, Pb, Cu and Zn was taken for AAS analysis. The results obtained were compared with those of the spiked soil and dust samples to obtain the recovery of the analysis. Triplicate analysis was carried out to further check the reproducibility of the methods used in this study.

Amount of metal used to spike a sample

$$= \frac{\text{Volume of MESS used x conc. of metal in MESS}}{1000}$$

= X mg of metal used to spike a sample (calculated)

Amount of metal in unspiked sample

$$= \frac{\text{Vol. of digest of unspiked sample x conc. of metal in digest of unspiked sample}}{1000}$$

$$= Y_0 \text{mg of metal in Zg of unspiked sample}$$

Amount of metal in spiked sample

$$= \frac{\text{Volume of digest of spiked sample x conc. of metal in digest of spiked sample}}{1000}$$

$$= Y_1 \text{mg of metal in Zg of sample spiked.}$$

Estimate of amount of metal used to spike a sample

= Amount of metal in spiked sample (Y_1) – Amount of metal in unspiked sample (Y_0)

$$= X' \text{ mg of metal used to spike a sample (determined)}$$

$$\% \text{ Recovery of metal} = \frac{\text{Amount of metal used to spike a sample determined}}{\text{Amount of metal used to spike a sample calculated}} \times 100$$

$$= \frac{X'}{X} \times 100$$

3.2.6 Calibration Curve

A calibration curve of absorbance against concentration for each metal ion was prepared as shown in Appendices I – VI for Cd, Cr, Ni, Pb, Cu and Zn respectively which yielded a good linearity. This implies that the instrument responded very well to the standard analyte of interest and therefore would respond to analyte in the samples. The calibration curves were used for the determination of metal concentrations in samples. The actual concentration of the metal in the sample was determined as follows:

$$\text{Amount of metal in volume of digested solution} = \text{Vol. of digest solution} \times \frac{\text{Conc. of Metal in sample solution from calibration curve}}{1000}$$

$$= X \text{ mg}$$

$$\text{Amount of metal in mgkg}^{-1} \text{ of soil sample} = \frac{\text{Amount of metal in volume of digested solution}}{\text{Weight of sample digested (kg)}}$$

$$= \frac{X}{\text{Weight of sample digested (kg)}}$$

3.2.7 Statistical Analysis

The results of this study were analyzed using Pearson Correlation analysis and ANOVA single factor analysis of variance. Pearson correlation coefficient, r is an index without dimension that has a range -1.0 to +1.0 inclusive. The index indicates the extent of linear relationship between two variables X and Y. The coefficient is always 1 when there is a perfect linear relationship which gives a positive slope between the two variables. A coefficient of -1 is obtained when there is a perfect linear relationship which gives a negative slope between data of the two variables. A +1 coefficient is obtained when one variable has a high value and so does the other. While a -1 coefficient is obtained when one Variable has a high value while the other has low value.

A correlations coefficient is 0 when there is no linear relationship between two variables. An ANOVA is an analysis of the variation present in a given experiment. It is a test of the hypothesis of that the variation in an experiment is no greater than that due to normal variation of individual's characteristics and error in their measurement. The tests in an ANOVA are based on the F – ratio: the variation due to an experimental treatment or effect directed by the variation due to experimental error. ANOVA puts all the data into one number (F) and gives us one P for the null hypothesis.

The t –test tells us if the variation between two groups is "significant" P reports the significance level.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 QUALITY ASSURANCE

Quality assurance test such as the spiking experiment is usually conducted to ascertain the accuracy and reliability of the analytical procedure. Table 4.1 shows the results obtained for the spiked samples and the MESS. The percentage recoveries obtained for the metals under investigation (Cd, Cr, Ni, Pb, Cu and Zn) varied from 90.4 – 103.2 for soil samples. The highest percentage recovery for the metal was found for Ni – 103.2%. The pattern of recovery for soil samples followed the decreasing order: Ni > Zn > Cr > Cu > Pb > Cd. While for dust samples, percentage recoveries of metals varied from 91.6 – 105.0. Similar to soil samples, highest percentage recoveries for the metals were found for Ni – 105.0%. The pattern of recoveries followed the order: Ni > Zn > Cr > Pb > Cd > Cu.

Analysis of difference between the samples and MESS recoveries showed no significant difference between the MESS value and either the spiked soil result or particulate dust result. Similarly, regression analysis showed high positive r^2 value for the metals (Cd; 0.890; Cr; 0.703; Ni; 0.973; Pb; 0.999; Zn;1.000) except for Cu (0.154). This means that accurate and precise results were obtained by the acid digestion method. Similar percentage recoveries have been reported by others who have also used MESS in roadside soils spiking experiments: 91 – 94% with profile Pb > Cd > Zn (Onianwa, 2001); 90.0 – 103.3% with profile Ni > Zn > Cr > Cu > Pb > Cd (Lee *et al*., 2005); > 85% for As, Cd, Cr and Pb (Melaku *et al*., 2008); 85.38 – 94.70% with profile Mn > Pb (Ogunfowokan *et al*., 2009), and 63- 98% with profile Cu> Pb > Zn > Cr > Ni > Fe (Yahaya *et al*., 2010). Also, a range of 95.3 – 97.1% recoveries were reported for Pb, Cu, Zn, Cr, Cd, As and Hg using standard reference materials (SRM) (Christoforidis and Stamatis, 2009).

Table 4.1. Percentage recovery of heavy metal in studied samples

Metal	MESS	Soil	particulate Dust
Cd	96.75±0.35	90.40±0.50	91.60±1.30
Cr	98.05±0.07	96.10±1.20	96.40±1.23
Ni	100.55±0.78	103.20±0.90	105.00±3.56
Pb	94.00±1.41	93.20±0.56	95.00±1.20
Cu	96.75±1.78	93.40±1.00	90.20±0.15
Zn	104.50±0.71	101.20±1.00	102.60±2.00

Although slight changes especially in the profile of metal were observed for the spiked samples compared to other studies, the results however lies within the acceptable range with high recoveries for spiked and MESS. This validates the experimental protocol and the efficiency of the atomic absorption spectrophotometer.

4.2 PHYSICOCHEMICAL PARAMETERS

4.2.1 Results

Statistical analysis of roadside soils physico-chemical parameters across the seasons, including the mean, standard deviation and student t-test analysis of means for the study sites and control are summarized in Tables 4.2 – 4.5. The results of the particle size distribution for study site clay fraction range from 3.00 (Site 4) – 7.00% (Site 8), 5.33 (Site 6) – 8.33% (Site 9), 4.67 (Site 4) – 7.67% (Site 3), and 4.00 (Site 6) – 7.33% (Site 3) for cool and dry season, hot and dry season, warm and wet season, and warm and dry season respectively. For the control site, the clay fraction was 10.00, 8.00, 9.00 and 6.00 in the same order of seasons. Silt fraction for the study site revealed 4.00 (Site 5 and 6) – 22.33% (Site 1), 2.00 (Site 7) – 8.00% (Site 2), 3.67 (Site 7) – 8.67% (Site 2, 4 and 5), and 5.33 (Site 9) – 9.33% (site 4) for cool and dry season, hot and dry season, warm and wet season, and warm and dry season respectively. Again for the control site, the silt fraction was found to be 10.00, 6.00, 6.00 and 6.00% across the seasons in the same order as the study sites. The sand fraction across the seasons, cool and dry, hot and dry, warm and wet, and warm and dry revealed the range: 71.33 (Site 1) – 91.00 (Site 5 and 6), 84.00 (Site 2) – 92.33 (Site 7), 84.67 (Site 2) – 91.00 (Site 7), and 85.33 (Site 5) – 88.33 (Site 9) for the seasons respectively, 80.00, 85.00, 85.00 and 88.00% were the % sand values for the control site across the seasons in the same order.

Table 4.2. Physicochemical parameters of roadside soil in Cool and Dry season

	Particle size distribution corrected to 20^0C (%)						
SITE	**CLAY**	**SILT**	**SAND**	**pH**	**EC(dSm^{-1})**	**OM (%)**	**CEC (Cmolkg^{-1})**
1	6.67±0.58^{a}	22.33±0.58^{a}	71.33±0.58^{a}	6.60±0.10^{c}	1.30±0.10^{c}	1.47±0.01^{d}	5.10±0.10^{f}
2	4.67±0.58^{b}	4.67±0.58^{b}	90.67±0.58^{b}	7.07±0.15^{e}	1.10±0.10^{ab}	1.47±0.01^{d}	3.70±0.10^{b}
3	5.00±1.00^{b}	8.00±1.00^{c}	87.00±0.00^{c}	6.70±0.10c^{d}	1.00±0.10^{a}	2.14±0.01^{e}	3.80±0.10^{b}
4	3.00±1.00^{c}	8.00±1.00^{c}	89.00±0.00^{d}	7.00±0.10^{e}	1.00±0.10^{a}	0.99±0.01^{a}	4.30±0.10^{d}
5	5.00±1.00^{b}	4.00±1.00^{b}	91.00±2.00^{b}	6.20±0.10^{a}	3.00±0.00^{d}	5.79±0.02^{i}	5.60±0.00^{g}
6	5.00±1.00^{b}	4.00±0.00^{b}	91.00±1.00^{b}	6.50±0.10^{bc}	1.30±0.02^{c}	4.36±0.01^{h}	4.63±0.06^{e}
7	5.00±0.00^{b}	14.00±1.00^{e}	81.00±1.00^{e}	6.90±0.20^{de}	1.10±0.00^{ab}	1.40±0.02^{c}	5.60±0.10^{g}
8	7.00±1.00^{a}	8.00±0.00^{c}	85.00±1.00^{f}	6.90±0.00^{de}	1.40±0.02^{c}	2.66±0.01^{g}	4.00±0.00^{c}
9	5.00±0.00^{b}	8.00±0.00^{c}	87.00±0.00^{c}	6.40±0.00^{b}	1.10±0.10^{ab}	1.26±0.01^{b}	3.30±0.10^{a}
10	5.00±1.00^{b}	10.00±1.00^{d}	85.00±0.00^{f}	6.70±0.10^{cd}	1.15±0.01^{b}	2.18±0.01^{f}	5.80±0.00^{h}
******	10.00±1.00	10.00±1.00	80.00±1.00	8.30±0.40	1.18±0.03	2.51±0.92	3.61±0.48

Values are Mean±SD triplicate analysis of samples from each site.

Mean values in the same column followed by the same superscript letters are not significantly different ($p > 0.05$)

*** Control*

Table 4.3. Physicochemical parameters of roadside soil in Hot and Dry season

	Particle size distribution corrected to 20^0C (%)						
SITE	**CLAY**	**SILT**	**SAND**	**pH**	**EC(dSm^{-1})**	**OM (%)**	**CEC ($Cmolkg^{-1}$)**
1	8.00 ± 1.00^{b}	4.33 ± 0.58^{bc}	88.00 ± 0.00^{bc}	6.80 ± 0.10^{a}	1.70 ± 0.20^{c}	3.85 ± 0.00^{c}	6.80 ± 0.10^{c}
2	8.00 ± 0.00^{b}	8.00 ± 0.00^{f}	84.00 ± 0.00^{a}	7.70 ± 0.10^{ef}	1.40 ± 0.00^{b}	2.39 ± 0.54^{a}	7.00 ± 0.20^{c}
3	8.00 ± 0.00^{b}	4.00 ± 0.00^{b}	88.00 ± 0.00^{bc}	7.90 ± 0.10^{f}	2.20 ± 0.10^{d}	4.45 ± 0.02^{d}	8.00 ± 0.20^{d}
4	5.67 ± 0.58^{a}	$7.67\pm0.58e^{f}$	87.00 ± 1.00^{b}	$7.50\pm0.10d^{e}$	2.10 ± 0.00^{d}	5.33 ± 0.01^{e}	10.60 ± 0.20^{f}
5	5.67 ± 0.58^{a}	6.00 ± 1.00^{d}	88.33 ± 0.58^{c}	7.00 ± 0.30^{ab}	3.20 ± 0.10^{f}	7.76 ± 0.06^{b}	8.80 ± 0.10^{e}
6	5.33 ± 1.15^{a}	5.00 ± 1.73^{bcd}	89.67 ± 0.58^{d}	7.10 ± 0.00^{bc}	1.40 ± 0.10^{b}	3.03 ± 0.03^{g}	5.40 ± 0.20^{b}
7	5.67 ± 0.58^{a}	2.00 ± 1.00^{a}	92.33 ± 0.58^{e}	7.30 ± 0.10^{cd}	2.50 ± 0.00^{e}	3.57 ± 0.01^{c}	7.80 ± 0.10^{d}
8	5.67 ± 0.58^{a}	$6.33\pm0.58d^{e}$	88.00 ± 0.00^{bc}	7.30 ± 0.10^{cd}	4.00 ± 0.00^{g}	6.24 ± 0.02^{f}	9.00 ± 1.00^{e}
9	8.33 ± 0.58^{b}	2.00 ± 1.00^{a}	89.67 ± 1.53^{d}	7.00 ± 0.10^{ab}	0.75 ± 0.01^{a}	5.19 ± 0.01^{e}	7.40 ± 0.00^{cd}
10	6.00 ± 0.00^{a}	5.67 ± 0.58^{cd}	88.33 ± 0.58^{c}	7.10 ± 0.00^{bc}	0.75 ± 0.00^{a}	2.43 ± 0.01^{a}	4.60 ± 0.10^{a}
**	8.00±1.40	6.00±1.00	85.00±0.00	8.15±0.24	1.25±0.00	2.56±0.11	3.10±0.01

Values are Mean±SD triplicate analysis of samples from each site.

Mean values in the same column followed by the same superscript letters are not significantly different ($p > 0.05$)

*** Control*

Table 4.4. Physicochemical parameters of roadside soil in Warm and Wet season

	Particle size distribution corrected to 20^0C (%)						
SITE	**CLAY**	**SILT**	**SAND**	**pH**	**EC(dSm^{-1})**	**OM (%)**	**CEC ($Cmolkg^{-1}$)**
1	6.33 ± 0.58^{bcd}	7.67 ± 0.58^{cd}	86.00 ± 1.00^{ab}	6.47 ± 0.06^{a}	1.83 ± 0.06^{c}	3.92 ± 0.03^{d}	6.87 ± 0.15^{c}
2	6.67 ± 0.58^{cd}	8.67 ± 0.58^{d}	84.67 ± 0.58^{a}	7.30 ± 0.17^{d}	1.43 ± 0.06^{b}	2.46 ± 0.47^{a}	7.07 ± 0.23^{c}
3	7.67 ± 0.58^{d}	5.67 ± 0.58^{b}	86.67 ± 1.15^{b}	8.03 ± 0.06^{f}	2.30 ± 0.00^{e}	4.49 ± 0.01^{e}	8.13 ± 0.12^{e}
4	4.67 ± 1.15^{a}	8.67 ± 0.58^{d}	86.67 ± 0.58^{b}	6.43 ± 0.06^{a}	2.14 ± 0.05^{d}	5.42 ± 0.03^{f}	10.67 ± 0.12^{h}
5	5.33 ± 0.58^{abc}	8.67 ± 0.58^{d}	86.00 ± 0.00^{ab}	7.07 ± 0.15^{c}	3.17 ± 0.12^{g}	7.87 ± 0.11^{h}	8.90 ± 0.00^{f}
6	5.00 ± 1.00^{ab}	5.67 ± 0.58^{b}	89.33 ± 0.58^{d}	7.03 ± 0.06^{c}	1.47 ± 0.06^{b}	3.07 ± 0.23^{b}	5.53 ± 0.12^{b}
7	5.33 ± 1.15^{abc}	3.67 ± 0.58^{a}	91.00 ± 1.00^{e}	6.80 ± 0.10^{b}	2.57 ± 0.12^{f}	3.59 ± 0.01^{c}	$7.93\pm0.12d^{e}$
8	5.33 ± 0.58^{abc}	7.33 ± 0.58^{c}	87.33 ± 1.15^{bc}	7.10 ± 0.10^{c}	4.50 ± 0.10^{h}	6.50 ± 0.00^{g}	9.33 ± 0.58^{g}
9	7.33 ± 0.58^{d}	4.00 ± 0.00^{a}	88.67 ± 0.58^{cd}	7.73 ± 0.06^{e}	0.76 ± 0.01^{a}	5.19 ± 0.01^{f}	7.53 ± 0.15^{d}
10	5.33 ± 0.58^{abc}	8.33 ± 0.58^{d}	86.33 ± 0.58^{b}	7.03 ± 0.12^{c}	0.80 ± 0.01^{a}	2.39 ± 0.08^{a}	5.00 ± 0.30^{a}
**	9.00±0.10	6.00±1.00	85.00±0.00	8.05±0.10	1.23±0.02	2.56±0.11	3.10±0.10

Values are Mean±SD triplicate analysis of samples from each site.

Mean values in the same column followed by the same superscript letters are not significantly different ($p > 0.05$)

*** Control*

Table 4.5. Physicochemical parameters of roadside soil in Warm and Dry season

	Particle size distribution corrected to 20C (%)						
SITE	**CLAY**	**SILT**	**SAND**	**pH**	**EC(dSm^{-1})**	**OM (%)**	**CEC ($Cmolkg^{-1}$)**
1	4.67 ± 0.58^{a}	7.67 ± 0.58^{cd}	87.67 ± 1.15^{bc}	6.33 ± 0.12^{a}	1.93 ± 0.06^{c}	3.27 ± 0.06^{d}	5.33 ± 0.12^{b}
2	4.67 ± 1.15^{a}	8.33 ± 0.58^{def}	87.00 ± 1.00^{abc}	6.97 ± 0.12^{cd}	1.67 ± 0.06^{b}	2.43 ± 0.06^{b}	6.60 ± 0.17^{c}
3	7.33 ± 0.58^{c}	5.67 ± 0.58^{ab}	87.00 ± 1.00^{abc}	7.23 ± 0.15^{e}	2.40 ± 0.10^{e}	4.73 ± 0.12^{f}	7.37 ± 0.12^{d}
4	4.67 ± 1.15^{a}	9.33 ± 0.58^{f}	86.00 ± 1.00^{ab}	6.17 ± 0.06^{a}	2.23 ± 0.06^{d}	4.73 ± 0.06^{f}	8.30 ± 0.10^{e}
5	5.00 ± 1.00^{ab}	9.00 ± 0.00^{ef}	85.33 ± 0.58^{a}	6.97 ± 0.12^{cd}	3.27 ± 0.06^{g}	7.74 ± 0.12^{h}	$8.00\pm0.10d^{e}$
6	4.00 ± 0.00^{a}	6.67 ± 1.15^{bc}	89.33 ± 1.15^{d}	$7.07\pm0.06d^{e}$	1.62 ± 0.03^{b}	2.47 ± 0.06^{b}	4.93 ± 0.12^{b}
7	4.33 ± 0.58^{a}	6.00 ± 0.00^{ab}	89.67 ± 0.58^{d}	6.60 ± 0.17^{b}	2.80 ± 0.10^{f}	2.86 ± 0.06^{c}	6.63 ± 1.01^{c}
8	5.00 ± 1.00^{ab}	8.00 ± 0.00^{de}	87.00 ± 1.00^{abc}	6.90 ± 0.00^{cd}	4.80 ± 0.10^{h}	5.83 ± 0.06^{g}	7.37 ± 0.38^{d}
9	6.33 ± 0.58^{bc}	5.33 ± 1.15^{a}	88.33 ± 0.58^{cd}	7.57 ± 0.12^{f}	0.90 ± 0.01^{a}	4.47 ± 0.06^{e}	5.27 ± 0.12^{b}
10	5.00 ± 1.00^{ab}	9.00 ± 1.00^{ef}	86.00 ± 0.00^{ab}	6.80 ± 0.10^{c}	0.80 ± 0.01^{a}	1.83 ± 0.21^{a}	4.13 ± 0.06^{a}
**	6.00±0.00	6.00±1.00	88.00±0.10	7.60±0.23	0.95±0.10	2.12±0.56	3.00±0.00

Values are Mean±SD triplicate analysis of samples from each site.
Mean values in the same column followed by the same superscript letters are not significantly different ($p > 0.05$)
*** Control*

From the results, highest % mean clay fractions of 8.33 (Site 9) was recorded for the Hot and Dry season, highest % mean silt fraction of 22.33 (Site 1) was recorded in Cool and Dry Season and highest % mean sand fraction of 91.00 (Site 5) was recorded in Cool and Dry Season. Also variations ($p < 0.05$) in soil particle distribution were obtained across the seasons per sites. This could be due to rate of deposition of suspended particles across the sites.

Seasonal variation in hydrogen ion (H^+) concentration and the variations between sampling sites were observed. The pH varied between 6.20 (Site 5) – 7.07 (Site 2), 6.80 (Site 1) – 7.90 (Site 3), 6.43 (Site 4) – 8.03 (Site 3), and 6.17 (Site 4) – 7.57 (Site 9) for cool and dry season, hot and dry season, warm and wet season, and warm and dry season, respectively for study sites. However, 8.30, 8.15, 8.05 and 7.60 were observed for the control site across the seasons. Analysis of variation between the study and control sites, and among the study sites across the seasons showed significant differences ($p<0.05$). The rate of emitted particles deposition across the seasons could be a possible reason. Comparing the pH of study and control sites, pH at the control site is alkaline across the seasons.

The electrical conductivity (EC) varied between 1.00 (Site 3 and 4) – 3.00dSm^{-1} (Site 5) for Cool and Dry Season, 0.75 (Site 9and 10) - 3.20dSm^{-1} (Site 5) for Hot and Dry Season, 0.76 (Site 9) – 4.50dSm^{-1} (Site 8) for Warm and Wet Season, and 0.80 (Site 10) – 4.80dSm^{-1} (Site 8) during Warm and Dry Season. Across the seasons highest EC was recorded at site 8 (4.80dSm^{-1}) during Warm and Dry season. For the control Site, EC(dSm^{-1}) were observed to be 1.18, 1.25, 1.23, 6.00 and 0.95 for cool and dry season, hot and dry season, warm and wet season, and warm and dry season, respectively. There were significant differences ($p<0.05$) in EC among the various sites with exception of Sites 9 and 10. Highest values of EC were recorded across all sites during Warm and Dry season. Analysis of variation also indicated that mean values of EC did vary between and within seasons, and did show seasonal pattern.

Percentage (%) OM fluctuated between 0.99 (Sites 4) – 5.79 (Site 5), 2.39 (Site 2) – 7.76 (Site 5), 2.39 (Site 10) – 6.50 (Site 8), and 1.83 (Site 10) – 5.83 (Site 8) during the cool and dry season, hot and dry season, warm and wet season, and warm and dry season, respectively. Also, across the season highest % OM was recorded for Site 5 (7.76) during Hot and Dry Season. For control site, % OM values were 2.51, 2.56, 2.56 and 2.12% for Cool and Dry Season, Hot and Dry Season, Warm and Wet Season, and Warm and Dry Season, respectively. Analysis of variance among the various sampling sites showed significant differences ($p < 0.05$). Also, there was marked variation ($p < 0.05$) observed in seasonal pattern in % OM. Generally, highest concentration of organic matter in soils were revealed during Warm and Wet season with exception of Site 3.

CEC also varied between 3.30 (Site 9) – 5.80Cmolkg^{-1} (Site 10), 4.60 (Site 10) – 10.60 Cmolkg^{-1} (Site 4), 5.00 (Site 10) – 10.67Cmolkg^{-1} (Site 4), and 4.13 (Site 10) – 8.00 (Site 5) for Cool and Dry Season, Hot and Dry Season, Warm and Wet Season, and Warm and Dry Season, respectively. Significantly, there were variations ($p < 0.05$) among sites across seasons with lowest mean value of CEC recorded in the Cool and Dry Season and the highest mean value recorded in the Warm and Wet Season. Similar to percentage organic matter content, highest CEC were obtained during Warm and Wet season across all sites. Analysis of variation showed significant differences ($p<0.05$) in the value of CEC recorded among the sites across the seasons. Comparing the study and control sites, high values were obtained in study sites, implying increase in cations in the soils as a result of

contamination.

Multivariate correlation analysis between various soil physicochemical parameters across the seasons is presented in Tables 4.6 – 4.9 below. Some of the parameters were found to bear statistically significant correlation with each other indicating close association of the parameters. In the Cool and Dry Season (Table 4.6), for example, data showed high significant positive correlation between the EC from one side and each of the OM ($p < 0.01$) and CEC ($p < 0.05$) from the other side.

On the other hand, the correlation coefficient becomes negative in the case of sand: clay and silt content ($p<0.01$), OM: silt ($p<0.01$) and pH: EC and OM ($p<0.01$). In Hot and Dry Season (Table 4.7), significant positive correlation ($p < 0.01$) was observed between EC: OM and CEC. Negative correlation was also observed between clay content: EC ($p<0.05$), and sand content: silt content and pH ($p<0.01$). On the contrary, during Warm and Wet Season (Table 4.8), significant positive correlations ($p < 0.01$) were observed between: pH: Clay content, and OM: EC and CEC. However, for silt: sand content and pH, negative correlations were observed for Warm and Wet Season. Lastly, in Warm and Dry Season (Table 4.9), significant positive correlations were observed between: pH and clay content ($p < 0.05$), OM: EC and CEC ($p < 0.01$).

While significant negative correlations were revealed between sand content: pH and OM, and silt content: clay content, results with positive correlations imply that increase in any one would increase the other.

Soil parameters on traffic using Pearson's correlation as shown in Tables 4.6 – 4.9 were found to be negatively correlated and significant in case of EC (during Warm and Wet, Warm and Dry Season) with few exceptions (clay content and pH). Also, the results revealed decrease in positive correlations between Silt: traffic across the seasons, and traffic: clay content and pH during Warm and Wet to Warm and Dry season.

Table 4.6. Correlation matrix among physicochemical parameters in Cool and Dry season

Parameters	Clay	Silt	Sand	pH	EC	OM	CEC
Clay	1						
Silt	0.336	1					
Sand	-0.515**	-0.980**	1				
pH	-0.047	0.073	-0.057	1			
EC	0.145	-0.276	0.224	-0.605**	1		
OM	0.119	-0.486**	0.419*	-0.627**	0.833**	1	
CEC	0.050	0.321	-0.302	-0.202	0.417*	0.360	1
Traffic	0.020	0.350	-0.320	0.112	-0.438	-0.612	-0.216

** Correlation is significant at the 0.05 level (2-tailed)*
*** Correlation is significant at the 0.01 level (2-tailed)*

Table 4.7. Correlation matrix among physicochemical parameters in Hot and Dry season

Parameters	Clay	Silt	Sand	pH	EC	OM	CEC
Clay	1						
Silt	-0.293	1					
Sand	-0.310	-0.811**	1				
pH	0.140	0.317	-0.407*	1			
EC	-0.400*	0.187	0.063	0.141	1		
OM	-0.196	0.041	0.084	-0.149	0.682**	1	
CEC	-0.089	0.194	-0.113	0.294	0.642**	0.714**	1
Traffic	-0.532	0.129	-0.006	-0.494	-0.300	-0.499	-0.524

** Correlation is significant at the 0.05 level (2-tailed)*

*** Correlation is significant at the 0.01 level (2-tailed)*

Table 4.8. Correlation matrix among physicochemical parameters in Warm and Wet season

Parameters	Clay	Silt	Sand	pH	EC	OM	CEC
Clay	1						
Silt	-0.309	1					
Sand	-0.305	-0.812**	1				
pH	0.629**	-0.364*	-0.022	1			
EC	-0.258	0.134	0.024	-0.135	1		
OM	-0.097	0.130	-0.070	0.021	0.671**	1	
CEC	-0.105	0.141	-0.076	-0.138	0.644**	0.734**	1
Traffic	0.507	0.106	-0.389	0.132	-0.693*	-0.473	-0.548

** Correlation is significant at the 0.05 level (2-tailed)*

*** Correlation is significant at the 0.01 level (2-tailed)*

Table 4.9. Correlation matrix among physicochemical parameters in Warm and Dry season

Parameters	Clay	Silt	Sand	pH	EC	OM	CEC
Clay	1						
Silt	-0.423*	1					
Sand	-0.298	-0.713**	1				
pH	0.436*	-0.528**	0.189	1			
EC	-0.066	0.139	-0.125	-0.162	1		
OM	0.251	0.150	-0.429*	0.131	0.646**	1	
CEC	0.086	0.219	-0.331	-0.194	0.671**	0.705**	1
Traffic	0.249	0.001	-0.114	0.088	-0.687*	-0.473	-0.548

** Correlation is significant at the 0.05 level (2-tailed)*

*** Correlation is significant at the 0.01 level (2-tailed)*

The decrease in positive correlation between these parameters and traffic could be due to the fact that topsoil is regularly eroded by precipitation runoff into public drains and water bodies.

4.2.2 Discussion

As presented above, the roadside soils composition was dominated by sand. Also, comparing the study and control sites, high percentage fractions of clay were observed to be higher in control site across the seasons. This could be attributed to source of top soil formation at the study site being due to vehicular emissions. Also, clay content were found to increase s between Cool and Dry Season and Hot and Dry Season (with exception of Site 8) then decreases down in the other seasons at all the sites. However, variation in silt and sand contents were not consistent for the sites across the seasons. The decrease in the clay fraction could be due to surface runoff during rains which deplete the properties of the surface soil.

The textural class for sampling sites across the seasons as identified according to USDA soil classification scheme (USDA, 1986) were dominated by high % sand fractions followed by % silt (with few exception) and then % clay. This is similar to Mohammed *et al*. (2006), that soils closest to the road are usually dominated by sand fractions, constituting an average range from 84 – 92%. According to Nyles and Ray (1999), soil with low clay content has usually high pollutant leaching potentials. It could therefore be deduced that underground water and farmland along the roadside could suffer from pollution, though the situation seem ameliorated as % clay content increased in Hot and Dry season. Also, Ericksson (1989) found that for a given total Cd concentration, Cd was more soluble and plant available in sandy soil than in clay soil. This suggests that soil solution might be enriched with metals, though might not be readily available due to seasonal decrease in % sand content. Soil pH generally plays an important role in metal bioavailability, toxicity and leaching capability to the surrounding environment especially hot and dry seasons when the moisture contents of soils are low.

From the results, pH varies between slightly acidic to moderately alkaline between seasons, with highest pH value across the season recorded at Site 3 (8.03) in Warm and Wet Season. Change in pH between these sites could result from vehicular emissions of CO_2 which is converted to H_2CO_3 through absorption of moisture and sorbed in soils making the soil slightly acidic which is more pronounced after rains. The pH values obtained were generally within pH 5.09 – 8.57 and 6.34 – 7.65 reported by Mohammed *et al*. (2005) and Yahaya *et al*. (2010), respectively for roadside soils. Most metals in the pH range 6.0 – 9.0 are not always in the free form (Porteus, 1985). From the results it could imply that some metal ions may not exist in the free form and hence could not be leached into subsoil and subsequently into ground water. According to Brandy and Weil (1996), such pH values are common to areas that receive low rainfall (a common phenomenon in the study area) where leaching tends not to be very intense and the base forming cation are left to dominate the exchange complex in the place of Al^{3+} and H^{+}. In line with the trends in pH, Yaron (1995) states that a decrease in soil pH from 7.7 – 5.5 causes an increase in conductivity because many more ions, especially those of metals go into solution. This is also supported by negative correlation observed between pH and EC in all the seasons.

In general, the EC which measures the salinity of the soil were found high in some of the study sites than the control area. The reason could be due to activities within these sites releasing metal ion in either sulphate or chloride form into the soil. By comparison,

Boulding (1994) classified EC of soils (in dSm^{-1}) as: non-saline < 2; moderately saline 2 – 8; very saline 8 – 16; extremely saline > 16. Across the seasons EC < 1 for Sites 9 and 10 which indicated no acute problems with soil salinity. Also from the results, gradual increase in salinity was found across the seasons for all sites with highest of $4.80dSm^{-1}$ at Site 8. This suggests that soil in Site 8 had higher concentrations of salts in Warm and Dry Season when compared to the other Sites. This could probably be explained by anthropogenic rather than pedologic forces. Compared to literature studies, values were higher than 0.128 – $0.158dSm^{-1}$ (Mohammed *et al*., 2006) and 0.5 – $2.0dSm^{-1}$ (Li *et al*., 2007) in roadside soils. With negative correlation between traffic and EC, it suggests other sources such as metal scraps and automobile engine oils responsible for the increase.

Also from the results, the soils showed no distinct difference in percentage organic matter between the study and control sites, decomposition of biomaterials such as vegetable, litter and animal droppings in these sites could be responsible (Hassett and Banwart, 1992). At Site 5 high OM up to 7.76% was found, which could be the location of this site along the Market. However, highest of 6.5% (Site 8) during rains in this study was higher than 3.7% reported for roadside soils of Kaduna metropolis during the same season (Okunola *et al*., 2007). This means the soil organic matter contains humic materials with highly complex functional groups, which have the ability to complex metals thereby retaining them in the topsoil (Evans, 1989). The more organic matter is present in soil, the more functional groups available for complexation with the metals, hence, the more the retention. The organic matter of soils in the present study indicated high retention of metals, thereby making them unavailable for plant uptake.

The CEC of studied soils generally revealed an increase from Cool and Dry season to Hot and Dry Season, then decreases across the Warm and Wet Season to Warm and Dry season. The increase across the seasons could be due to increase in percentage clay content that is capable of accumulating large quantities of metals in the soil matrix, thereby increasing the cation exchange surfaces. With negative correlation between traffic and CEC, it could be concluded that other factors than vehicular emission is responsible. Other than the highest value obtained during warm and wet season (10.67), the value of CEC obtained in this study is lower than range of 10.20 – $27.2Cmolkg^{-1}$ reported in a similar study (Mohammed *et al*., 2006). The retention of metals by CEC or non-specific adsorption mechanisms is complex because it is dependent on various factors like pH, concentration of metal ion etc (Adie and Osibanjo, 2009).

However, CEC of any soil is an important parameter that could assist in explaining the retention capacity of many metals especially metals in the soil. Metals bound by cation exchange mechanism are via electrostatic forces resulting in the formation of outer-sphere complexes. The ions in solution are always in equilibrium with counter ions that balance the surface charge of the colloids. As observed from the results, the more the CEC of soil, the more the active sites available for cation exchange. The affinity of soil colloid surfaces for cations increases as the valency increases. For cations of the same valence, the adsorption strength is usually determined by the hydrated radius of the ions (Ji and Li, 1997). Cation exchange capacity normally ranges from 1.0 – $100Cmolkg^{-1}$. It is low for sandy soils and high for clayey soils. The CEC of soil samples in the present study was low probably because of the sandy nature of the soils. The same trend was observed by Okunola *et al*. (2007), Adie and Osibanjo (2009) and Mashal *et al*. (2009). This also explains why negative correlations were observed between CEC and % sand content.

4.3 TOTAL METAL CONTAMINATION OF ROADSIDE SOILS

4.3.1 Results

The totals metal concentrations as shown in Tables 4.10 – 4.15 describes that there was a distinct change in the contents of heavy metals among different grain size of roadside soils samples across the seasons. The concentration of Cd as shown in Table 4.10 varied between 1.13 (Site 1) – 7.01mgkg^{-1} (Site 8), 2.00 (Site 3) – 8.12mgkg^{-1} (Site 8) and 2.11 (Site 3) – 11.03mgkg^{-1} (Site 8) across Cool and Dry Season for grain sizes 1400µm, 355µm and 150µm, respectively, 1.42 (Site 1) – 8.08mgkg^{-1} (Site 8), 2.45 (Site 3) – 9.44mgkg^{-1} (Site 8) and 2.77 (Site 3) – 13.86mgkg^{-1} (Site 8) in Hot and Dry Season for grain size 1400µm, 355µm and 150µm, respectively. Also, in Warm and Wet Season, 0.88 (Site 1) – 5.86mgkg^{-1} (Site 8), 1.55 (Site 3) – 6.06 (Site 8), and 1.63 (Site 3) – 9.15mgkg-1 (Site 8) for grain size 1400µm, 355µm and 150µm, respectively. In Warm and Dry Season, 1.25 (Sites 1 and 3) – 6.50mgkg^{-1} (Site 8), 2.00 (Site 3) – 7.25 (Site 8) for grain size 1400µm, 355µm and 150µm, respectively.

Generally, highest concentration of Cd was obtained at Site 8 in samples of grain size 150µm across all seasons and lowest concentration at Site 3 with exception of grain size 1400µm. For control site the concentration of Cd is generally less than 1mgkg^{-1}except for 1.51mgkg^{-1} in grain size 150µm in Warm and Dry Season.

The average Cr concentrations in Cool and Dry season ranged between 2.50 (Site 1) – 34.27 mgkg^{-1} (Site 9), 14.42 (Site 5) – 28.61 mgkg^{-1} (Site 8) and 18.52 (Site 1) – 103.26 mgkg^{-1} (Site 8) for grain sizes 1400µm, 355µm and 150µm, respectively. For Hot and Dry Season, the range is between 2.46 (Site 1) – 41.88mgkg^{-1} (Site 9), 13.95 (Site 5) – 31.11 mgkg^{-1} (Site 9) and 23.54 (Site 1) – 136.77 mgkg^{-1} (Site 8) for grain size 1400µm, 355µm and 150µm, respectively.

Table 4.10. Distribution of Cd ($mgkg^{-1}$) in various particle sizes across roadside soils from Kano Metropolis

	SEASON											
	Cool and Dry			Hot and Dry			Warm and Wet			Warm and Dry		
	Grain size			Grain size			Grain size			Grain size		
Site	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150
1	1.13±0.01^{a}	2.76±0.04^{b}	3.74±0.01^{b}	1.42±8.90^{a}	3.23±0.19^{b}	4.77±0.16^{b}	0.88±0.01^{a}	2.15±0.04^{b}	2.91±0.06^{b}	1.25±0.01^{a}	2.50±0.01^{b}	3.25±
2	1.23±0.02^{a}	4.10±0.07^{d}	4.50±0.07^{c}	1.91±0.01^{a}	4.37±0.09^{c}	5.49±0.36^{c}	0.97±0.01^{a}	3.30±0.07^{c}	3.65±0.25^{c}	2.00±0.08^{b}	3.00±0.01^{c}	3.50±
3	1.21±0.01^{a}	2.00±0.00^{a}	2.11±0.06^{a}	1.45±0.01^{a}	2.45±0.04^{a}	2.77±0.16^{a}	0.92±0.01^{a}	1.55±0.04^{a}	1.63±0.26^{a}	1.25±0.00^{a}	2.00±0.07^{a}	2.00±
4	3.32±0.01^{d}	6.80±0.07^{i}	8.92±0.01^{g}	4.16±0.11^{a}	6.75±0.18^{e}	10.59±0.29^{f}	2.56±0.01^{c}	5.27±0.02^{e}	7.16±0.24^{g}	3.75±0.73^{d}	4.25±0.01^{e}	6.75±
5	3.40±0.07^{e}	6.10±0.00^{g}	7.80±0.14^{f}	3.78±0.16^{a}	6.85±0.11^{e}	10.48±0.37^{f}	2.77±0.16^{c}	5.06±0.04^{e}	6.48±0.37^{f}	3.00±0.06^{cd}	5.00±0.13^{f}	7.50±
6	2.30±0.07^{b}	3.50±0.00^{c}	7.20±0.57^{f}	2.55±0.32^{a}	3.68±0.23^{b}	8.84±0.11^{e}	1.94±0.04^{b}	2.97±0.02^{c}	6.05±0.32^{f}	2.00±0.01^{b}	2.50±0.07^{b}	5.75±
7	3.01±0.01^{c}	4.66±0.04^{f}	5.30±0.14^{d}	3.27±0.16^{a}	5.18±0.58^{d}	6.36±0.45^{d}	2.50±0.35^{c}	3.98±0.01^{d}	4.48±0.01^{d}	2.50±0.18^{c}	3.75±0.04^{d}	4.00±
8	7.01±0.06^{g}	8.12±0.01^{j}	11.02±0.01^{i}	8.08±0.30^{a}	9.44±0.40^{g}	13.86±0.10^{h}	5.86±0.10^{e}	6.06±0.66^{f}	9.15±0.11^{i}	6.50±0.14^{f}	7.25±0.04^{h}	9.28
9	3.28±0.01^{d}	4.50±0.00^{e}	6.60±0.07^{e}	3.71±0.21^{a}	5.83±0.12^{d}	8.53±0.33^{e}	2.67±0.23^{c}	3.75±0.18^{d}	5.38±0.08^{e}	3.00±0.14^{cd}	5.00±0.14^{f}	5.90±
10	4.35±0.04^{f}	6.30±0.07^{h}	9.85±0.04^{h}	5.39±0.43^{a}	7.84±0.11^{f}	12.76±0.17^{g}	3.54±0.33^{d}	5.24±0.18^{e}	8.16±0.11^{h}	4.75±0.04^{e}	6.50±0.28^{g}	9.08
**	0.07±0.00	0.09±0.00	0.21±0.01	0.07±0.00	0.15±0.00	0.23±0.00	0.21±0.01	0.75±0.01	0.90±0.02	0.50±0.02	0.95±0.02	1.51

Maximum Allowable Limit used in different countries for Cd in soils (Kabata-Pendias, 1995)

Austria	Canada	Poland	Japan	Great Britain	Germany
5	8	3	-	3	2

Values are mean±SD of triplicate determinations of a sample mixed from three simultaneous soil collections at each site.
Mean values in the same column followed by the same superscript letters are not significantly different ($p > 0.05$)
*** Control*

Table 4.11. Distribution of Cr (mgkg^{-1}) in various particle sizes across roadside soils from Kano Metropolis

	SEASON											
	Cool and Dry			Hot and Dry			Warm and Wet			Warm and Dry		
	Grain size			Grain size			Grain size			Grain size		
Site	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm
1	2.50±0.00^{a}	16.30±0.14^{b}	18.52±0.01^{a}	2.46±0.38^{a}	20.07±0.30^{b}	23.54±0.04^{a}	1.97±0.02^{a}	12.93±0.05^{b}	14.76±0.17^{a}	1.63±0.05^{a}	16.00±0.07^{b}	15.50±0.07^{a}
2	22.60±0.07^{f}	24.10±0.64^{d}	39.53±0.33^{g}	26.27±0.16^{i}	28.95±0.04^{e}	52.89±0.08^{f}	17.09±0.64^{f}	18.30±0.42^{d}	32.17±0.59^{f}	21.58±0.01^{h}	23.30±0.14^{g}	36.35±0.04^{c}
3	13.02±0.01^{cd}	16.29±0.01^{b}	25.47±0.02^{c}	14.58±0.30^{d}	19.75±0.18^{b}	57.63±3.27^{f}	10.69±0.22^{cd}	13.39±0.28^{b}	21.38±0.44^{c}	11.30±0.07^{d}	15.75±0.04^{b}	58.00±0.35^{d}
4	13.27±0.01^{d}	26.46±0.25^{e}	29.20±0.57^{e}	11.52±0.34^{c}	29.19±0.22^{e}	43.30±0.00^{e}	10.47±1.08^{d}	21.29±0.21^{e}	23.44±0.40^{d}	6.25±0.04^{c}	21.00±0.71^{e}	34.00±0.42^{c}
5	10.92±0.06^{b}	14.42±0.13^{a}	24.55±0.32^{c}	9.50±0.35^{b}	13.95±0.04^{a}	33.39±0.01^{c}	9.00±0.71^{b}	12.08±0.06^{a}	20.76±0.17^{c}	5.00±0.07^{b}	8.03±0.05^{a}	24.00±0.49^{b}
6	18.44±0.40^{e}	22.64±0.18^{c}	26.15±0.60^{d}	21.01±0.01^{f}	27.49±0.36^{d}	29.25±0.32^{b}	14.54±0.33^{e}	17.68±0.23^{c}	20.59±0.29^{c}	17.00±0.07^{f}	22.25±0.04^{f}	16.75±0.18^{a}
7	11.70±0.14b^{c}	23.50±1.77^{c}	23.40±0.42^{b}	19.01±0.35^{e}	25.23±0.54^{c}	30.65±0.25^{b}	9.58±0.30^{bc}	18.89±0.08^{d}	18.89±0.08^{b}	20.50±0.07^{g}	17.75±0.04^{c}	22.00±0.35^{b}
8	21.37±0.16^{f}	28.61±0.36^{f}	103.26±0.18^{i}	21.94±0.04^{g}	31.00±0.71^{f}	136.77±0.16^{h}	16.77±0.16^{f}	84.04±0.33^{h}	84.04±0.68^{h}	15.75±0.07^{e}	21.75±0.00^{ef}	95.25±3.36^{f}
9	34.27±0.52^{g}	28.03±0.05^{f}	99.21±0.15^{h}	41.88±0.08^{j}	31.11±0.08^{f}	129.37±0.45^{g}	28.03±0.69^{g}	81.32±0.13^{g}	81.32±0.48^{g}	35.75±0.03^{i}	22.75±0.18^{g}	86.50±0.35^{e}
10	22.87±0.02^{f}	27.22±0.08^{ef}	35.52±0.34^{f}	23.55±0.32^{h}	28.05±0.67^{de}	39.13±0.62^{d}	17.97±0.02^{f}	27.92±0.06^{e}	27.92±0.06^{e}	17.00±0.00^{f}	18.55±22.13^{d}	0.32±0.01^{b}
**	ND	ND	ND	ND	0.01	0.01±0.00	ND	ND	ND	ND	ND	ND

Maximum Allowable Limit used in different countries for Cr in soils (Kabata-Pendias, 1995)

Austria	Canada	Poland	Japan	Great Britain	Germany
100	75	100	-	50	200

Values are mean±SD of triplicate determinations of a sample mixed from three simultaneous soil collections at each site.
Mean values in the same column followed by the same superscript letters are not significantly different (p > 0.05)
*** Control*

Table 4.12. Distribution of Ni (mgkg^{-1}) in various particle sizes across roadside soils from Kano Metropolis

Site	SEASON

	Cool and Dry			Hot and Dry			Warm and Wet			Warm and Dry		
	Grain size			Grain size			Grain size			Grain size		
	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm
1	224.78±0.16^{i}	279.75±0.18^{i}	331.75±0.18^{j}	263.30±0.07^{h}	340.43±0.40^{j}	450.87±0.09^{i}	184.61±0.28^{h}	233.65±0.25^{h}	272.63±0.45^{i}	221.50±0.35^{e}	274.00±0.71^{h}	330.00±1.41^{i}
2	27.34±0.01^{a}	37.32±0.48^{a}	52.92±0.06^{c}	35.15±0.60^{b}	42.30±0.49^{a}	71.81±0.13^{b}	21.46±0.38^{a}	29.36±0.45^{a}	42.90±0.00^{b}	32.00±0.71^{ab}	31.75±0.04^{a}	52.00±2.12^{b}
3	35.58±0.01^{d}	46.81±0.13^{e}	60.78±0.16^{d}	40.60±0.28^{d}	54.14±0.^{61d}	80.34±0.47^{c}	28.97±0.02^{d}	38.14±0.25^{d}	50.39±0.43^{c}	33.00±0.35^{ab}	41.50±0.35^{c}	57.50±0.35^{c}
4	34.95±0.04^{d}	39.20±0.57^{b}	50.72±0.20^{b}	37.62±0.27^{c}	43.69±0.22^{b}	66.67±0.23^{a}	28.85±0.11^{d}	32.22±0.16^{b}	41.53±0.33^{b}	28.50±0.35^{a}	32.00±0.71^{a}	47.00±0.71^{a}
5	31.95±0.04^{c}	47.30±0.49^{e}	65.40±0.28^{e}	38.13±0.62^{c}	61.10±0.64^{g}	90.39±0.43^{d}	26.13±0.62^{c}	38.59±0.29^{d}	53.01±0.70^{d}	32.25±0.53^{ab}	51.75±0.18^{e}	66.75±0.18^{d}
6	28.20±0.57^{b}	41.45±0.39^{c}	48.45±0.25^{a}	33.65±0.25^{a}	57.56±0.31^{e}	79.63±0.26^{c}	22.91±0.06^{b}	233.84±0.11^{h}	39.64±0.25^{a}	28.25±0.53^{a}	51.75±0.18^{e}	67.75±0.18^{d}
7	42.60±0.28^{f}	93.52±0.34^{g}	220.53±0.33^{h}	50.25±0.18^{e}	116.95±0.04^{h}	308.98±0.01^{h}	34.48±0.37^{e}	75.02±0.69^{f}	184.36±1.16^{g}	42.25±0.53^{bc}	96.75±0.18^{f}	232.00±0.71^{h}
8	45.96±0.03^{g}	150.65±0.25^{h}	228.00±0.35^{i}	55.01±0.70^{f}	171.09±0.64^{i}	303.29±0.50^{g}	37.37±0.45^{f}	122.36±0.45^{g}	187.03±0.69^{h}	46.25±0.18^{c}	126.50±0.35^{g}	216.25±2.65^{g}
9	37.78±0.16^{e}	42.96±0.03^{d}	135.46±0.38^{g}	41.15±0.60^{d}	49.08±0.65^{c}	184.77±0.16^{f}	28.89±0.08^{d}	35.14±0.10^{c}	105.36±1.16^{f}	31.75±14.32^{bc}	36.75±0.18^{b}	134.50±0.35^{f}
10	71.10±0.64^{h}	52.05±0.67^{f}	92.80±0.14^{f}	82.61±0.28^{g}	58.99±0.71^{f}	120.28±1.22^{e}	61.02±0.69^{g}	42.52±0.34^{e}	75.64±0.25^{e}	67.25±0.18^{d}	44.00±0.71^{d}	86.75±0.18^{e}
**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Maximum Allowable Limit used in different countries for Ni in soils (Kabata-Pendias, 1995)

Austria	Canada	Poland	Japan	Great Britain	Germany
100	100	100	100	50	100

Values are mean±SD of triplicate determinations of a sample mixed from three simultaneous soil collections at each site.
Mean values in the same column followed by the same superscript letters are not significantly different (p > 0.05)
*** Control*

Table 4.13. Distribution of Pb (mgkg^{-1}) in various particle sizes across roadside soils from Kano Metropolis

Site	SEASON

	Cool and Dry			Hot and Dry			Warm and Wet			Warm and Dry		
	Grain size			Grain size			Grain size			Grain size		
	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm
1	55.73±1.74^{b}	61.86±0.10^{e}	93.46±0.38^{a}	60.68±0.93^{e}	82.91±0.06^{e}	133.42±0.41^{a}	45.72±0.20^{f}	50.38±0.27^{e}	76.22±0.55^{a}	45.75±0.18^{f}	71.50±0.35^{e}	98.75±0.18^{a}
2	11.61±0.28^{a}	21.81±0.13^{a}	121.40±0.42^{f}	10.39±0.43^{a}	19.78±0.16^{a}	166.99±0.01^{d}	9.33±0.47^{a}	17.60±0.28^{a}	94.92±0.06^{d}	6.05±0.67^{a}	10.78±0.16^{a}	122.48±0.37^{bc}
3	30.04±0.03^{ab}	53.08±0.01^{c}	143.24±0.18^{g}	33.62±0.27^{c}	75.60±0.28^{d}	188.09±0.64^{e}	22.97±0.02^{c}	42.63±0.26^{c}	112.95±0.04^{f}	26.50±0.35^{c}	69.50±0.35^{d}	130.00±0.71^{c}
4	20.90±0.07^{ab}	52.89±0.08^{c}	176.78±0.16^{i}	21.70±0.21^{b}	59.33±0.47^{c}	233.51±0.35^{h}	17.17±0.59^{b}	43.28±0.20^{c}	141.65±0.25^{h}	16.00±0.71^{b}	44.00±0.71^{c}	166.50±0.35^{d}
5	80.51±0.35^{ab}	115.19±0.71^{i}	896.18±0.58^{j}	91.35±0.46^{g}	150.47±1.08^{i}	1174.22±0.55^{i}	65.56±0.31^{h}	93.04±0.03^{i}	711.13±0.62^{i}	73.25±0.53^{h}	130.00±0.71^{j}	866.00±13.44^{f}
6	31.75±0.18^{ab}	27.90±0.07^{b}	108.66±0.24^{b}	34.02±0.69^{c}	31.94±0.04^{b}	156.54±1.03^{b}	25.23±0.54^{d}	22.27±0.19^{b}	86.14±0.61^{b}	25.75±0.18^{c}	24.50±0.35^{b}	121.25±0.53^{bc}
7	126.12±0.08^{ab}	107.63±0.26^{h}	117.64±0.25^{e}	98.37±0.45^{h}	139.88±0.08^{f}	214.79±0.15^{f}	100.99±0.71^{j}	81.94±0.04^{g}	90.29±0.50^{c}	41.00±0.71^{e}	120.00±1.41^{g}	197.50±0.35^{e}
8	47.76±0.17^{ab}	56.31±0.49^{d}	115.02±0.27^{c}	48.19±0.93^{d}	111.22±0.55^{f}	213.52±0.34^{f}	38.06±0.66^{e}	44.80±0.14^{d}	90.50±0.35^{c}	33.50±0.35^{d}	125.75±0.53^{i}	199.00±0.00^{e}
9	64.63±0.26^{ab}	80.37±0.45^{f}	116.17±0.02^{d}	74.73±0.19^{f}	94.21±0.56^{c}	160.46±0.38^{c}	53.10±0.64^{g}	64.98±0.01^{f}	96.87±0.09^{e}	62.25±0.53^{g}	73.75±0.18^{f}	119.25±0.18^{b}
10	86.50±0.35^{ab}	106.20±0.57^{g}	145.05±0.67^{h}	106.52±0.34^{i}	141.08±0.65^{g}	219.03±0.69^{g}	71.13±0.09^{i}	86.10±0.07^{h}	117.10±0.64^{g}	93.00±0.71^{i}	123.25±0.53^{h}	174.75±0.18^{d}
**	20.11±0.60	20.00±0.62	32.50±2.02	21.11±0.60	22.00±0.83	30.50±0.60	2.00±0.83	3.56±0.60	5.56±2.02	20.88±2.11	22.30±0.40	32.20±2.93

Maximum Allowable Limit used in different countries for Pb in soils (Kabata-Pendias, 1995)

Austria	Canada	Poland	Japan	Great Britain	Germany
100	200	100	400	100	500

Values are mean±SD of triplicate determinations of a sample mixed from three simultaneous soil collections at each site.

Mean values in the same column followed by the same superscript letters are not significantly different ($p > 0.05$)

*** Control*

Table 4.14. Distribution of Cu (mgkg^{-1}) in various particle sizes across roadside soils from Kano Metropolis

	SEASON											
	Cool and Dry			Hot and Dry			Warm and Wet			Warm and Dry		
	Grain size			Grain size			Grain size			Grain size		
Site	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm
1	9.90±0.07^{g}	13.31±0.49^{e}	19.64±0.25^{a}	12.45±0.04^{g}	10.53±0.33^{d}	26.02±0.01^{a}	8.02±0.69^{ab}	10.62±0.27^{e}	16.06±0.31^{a}	11.08±0.06^{cd}	3.75±0.00^{b}	18.25±0.53^{a}
2	4.55±0.32^{e}	7.19±0.01^{d}	36.36±0.45^{e}	4.84±0.11^{c}	7.42±0.41^{c}	50.43±0.30^{d}	3.74±0.40^{b}	5.84±0.11^{d}	29.56±0.31^{e}	3.53±0.05^{abc}	4.75±0.00^{c}	38.48±0.06^{g}
3	3.62±0.06^{d}	16.02±0.06^{f}	32.98±0.01^{d}	3.06±0.31^{b}	21.53±0.33^{e}	44.01±0.01^{c}	2.86±0.10^{ab}	13.19±0.57^{f}	26.92±0.06^{d}	1.53±0.23^{bcd}	19.18±0.13^{e}	32.83±0.12^{e}
4	11.06±0.10^{h}	29.51±0.35^{i}	155.50±0.35^{i}	11.65±0.25^{f}	35.32±0.48^{h}	203.73±0.90^{h}	9.33±0.33^{ab}	24.31±0.22^{i}	127.27±0.52^{i}	8.53±1.36^{abcd}	28.43±0.05^{g}	154.53±0.33^{j}
5	0.50±0.07^{a}	4.68±0.23^{b}	49.37±0.45^{f}	6.58±0.30^{d}	23.14±0.10^{f}	55.72±0.20^{e}	0.38±0.08^{a}	3.89±0.08^{b}	40.67±0.23^{f}	10.75±0.04^{cd}	33.55±0.04^{i}	34.08±0.01^{f}
6	3.31±0.06^{c}	6.56±0.31^{c}	54.78±0.86^{g}	1.94±0.04^{a}	6.86±0.10^{b}	72.09±0.64^{f}	2.61±0.06^{ab}	5.26±0.18^{c}	45.20±0.57^{g}	0.00±0.00^{a}	4.53±0.05^{c}	52.75±0.04^{h}
7	16.75±0.04^{i}	22.70±0.21^{h}	104.50±0.35^{h}	18.59±0.29^{h}	29.89±0.08^{g}	133.27±1.22^{g}	13.62±0.27^{ab}	18.30±0.42^{h}	85.14±0.61^{h}	14.80±0.00^{d}	26.20±0.07^{f}	94.78±0.16^{i}
8	3.58±0.06^{cd}	19.30±0.28^{g}	27.38±0.44^{b}	2.86±0.10^{b}	29.60±0.28^{g}	37.42±0.41^{b}	2.98±0.01^{ab}	15.89±0.08^{j}	22.35±0.46^{b}	1.25±0.01^{ab}	29.25±0.53^{h}	28.75±0.18^{d}
9	8.06±0.04^{f}	19.00±0.00^{g}	27.50±0.35^{b}	8.39±0.22^{e}	22.04±0.03^{e}	37.17±0.12^{b}	6.33±0.05^{ab}	15.40±0.42^{g}	22.09±0.06^{b}	6.03±0.01^{abc}	17.00±0.00^{d}	27.53±0.33^{c}
10	2.82±0.13^{b}	3.20±0.28^{a}	28.75±0.18^{c}	1.68±0.23^{a}	2.29±0.15^{a}	37.88±0.08^{b}	2.24±0.03^{ab}	2.57±0.30^{a}	23.24±0.54^{c}	0.00±0.00^{a}	0.53±0.01^{a}	26.25±0.53^{b}
**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Maximum Allowable Limit used in different countries for Cu in soils (Kabata-Pendias, 1995)

Austria	Canada	Poland	Japan	Great Britain	Germany
100	100	100	125	100	50

Values are mean±SD of triplicate determinations of a sample mixed from three simultaneous soil collections at each site.
Mean values in the same column followed by the same superscript letters are not significantly different ($p > 0.05$)
*** Control*

Table 4.15. Distribution of Zn ($mgkg^{-1}$) in various particle sizes across roadside soils from Kano Metropolis

	SEASON											
	Cool and Dry			Hot and Dry			Warm and Wet			Warm and Dry		
	Grain size			Grain size			Grain size			Grain size		
Site	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm	1400 µm	355µm	150µm
1	798.94±10.30^{h}	1043.62±0.56^{h}	331.28±0.81^{b}	507.36±0.28^{i}	282.52±0.53^{b}	331.28±6.47^{b}	651.09±0.05^{i}	846.45±0.30^{g}	258.44±0.38^{b}	447.45±0.39^{e}	585.20±3.39^{d}	782.00±0.71^{b}
2	483.15±1.06^{d}	703.00±0.64^{c}	1896.00±0.68^{h}	317.64±0.38^{e}	1389.09±0.76^{h}	1896.00±0.68^{h}	393.17±0.17^{e}	572.68±0.78^{c}	1543.16±0.25^{h}	470.75±0.18^{g}	548.50±0.35^{c}	947.50±0.35^{d}
3	447.24±1.71^{c}	743.11±0.59^{e}	290.50±3.53^{a}	303.85±0.31^{c}	267.09±0.77^{a}	290.50±3.53^{a}	365.11±0.59^{d}	603.39±0.74^{e}	219.14±0.42^{a}	602.73±0.19^{i}	811.00±0.00^{i}	998.75±0.18^{e}
4	74.72±1.27^{g}	1001.69±0.06^{g}	1727.24±1.84^{g}	483.12±0.53^{h}	1277.41±0.60^{g}	1727.24±1.84^{g}	609.47±0.19^{h}	809.82±1.22^{f}	1395.08±3.64^{g}	593.50±4.60^{h}	689.50±0.35^{g}	1170.25±0.53^{g}
5	493.96±0.28^{e}	754.45±0.39^{f}	1336.09±0.74^{f}	322.84±0.42^{g}	983.59±1.42^{f}	1336.09±2.16^{f}	397.48±0.13^{f}	600.82±1.23^{d}	1059.00±1.36^{f}	462.75±0.18^{f}	617.50±0.35^{e}	847.25±0.53^{c}
6	388.41±4.12^{b}	680.21±0.60^{b}	1128.80±0.70^{d}	257.70±0.68^{b}	879.10±0.68^{e}	1128.80±1.41^{d}	340.94±0.38^{b}	547.41±0.62^{b}	894.67±0.21^{d}	429.00±0.71^{d}	723.75±1.24^{h}	1405.75±0.18^{i}
7	445.34±2.43^{c}	544.61±1.30^{a}	948.71±1.30^{c}	315.51±0.57^{d}	786.25±0.35^{c}	948.71±2.01^{c}	358.65±2.43^{c}	439.59±1.48^{a}	767.21±1.33^{c}	819.25±0.53^{j}	1242.25±0.18^{j}	1801.00±0.71^{j}
8	871.54±3.25^{i}	1534.40±0.69^{i}	3269.98±0.13^{j}	537.34±0.36^{j}	2284.86±0.93^{j}	3269.98±0.13^{j}	692.26±0.25^{j}	1232.72±1.23^{i}	2634.90±0.68^{j}	270.75±0.88^{c}	629.75±0.18^{f}	1035.00±0.71^{f}
9	52.24±0.37^{a}	1547.96±0.26^{j}	2409.37±0.92^{i}	45.71±1.99^{a}	1755.01±6.99^{i}	2409.37±0.92^{i}	40.88±0.13^{a}	1226.26±0.23^{h}	1905.28±1.49^{i}	245.75±0.18^{b}	427.75±1.59^{b}	1212.00±0.71^{h}
10	516.15±0.30^{f}	708.02±1.94^{d}	1198.17±0.91^{e}	319.05±2.45^{f}	861.17±5.81^{d}	1198.17±1.22^{e}	417.92±0.56^{g}	1905.28±0.08^{j}	968.04±0.40^{e}	170.00±0.00^{a}	256.00±0.71^{a}	381.25±0.53^{a}
**	30.03±1.40	30.00±0.17	48.20±3.40	32.00±5.20	34.12±0.20	56.10±2.10	22.00±0.20	20.00±0.30	30.20±0.90	37.00±2.30	38.14±1.40	64.14±0.68

Maximum Allowable Limit used in different countries for Zn in soils (Kabata-Pendias, 1995)

Austria	Canada	Poland	Japan	Great Britain	Germany
300	400	300	250	300	300

Values are mean±SD of triplicate determinations of a sample mixed from three simultaneous soil collections at each site.
Mean values in the same column followed by the same superscript letters are not significantly different ($p > 0.05$)
*** Control*

In Warm and Wet Season, mean concentration of Cr ranged from 1.97 (Site 1) – 28.03 $mgkg^{-1}$ (Site 9), 12.08 (Site 5) – 84.04 $mgkg^{-1}$ (Site 8), and 14.76 (Site 1) – 84.04 $mgkg^{-1}$ (Site 8) for grain size 1400µm, 355µm and 150µm, respectively. Similarly in Warm and Dry Season, details of the Cr concentration were as follows: for grain size 1400µm: 1.63 (Site 1) – 35.75 $mgkg^{-1}$ (Site 9), for 355µm: 8.08 (Site 5) – 23.30$mgkg^{-1}$ (Site 2), and for 150µm: 15.50 (Site 1) – 95.25$mgkg^{-1}$ (Site 8). With exception of grain size 355 and 150µm in hot and dry season, no Cr was detected in samples of control site.

Also, Ni varied between 27.34 (Site 2) – 224.78$mgkg^{-1}$ (Site 1), 37.32 (Site 2) – 279.75$mgkg^{-1}$ (Site 1) and 48.45 (Site 6) – 331.75$mgkg^{-1}$ (Site 1) in Cool and Dry seasons for grain sizes 1400µm, 355µm and 150µm, respectively. Also, for Hot and Dry Season the mean concentrations of Ni ranged from 33.65 (Site 6) – 263.30$mgkg^{-1}$ (Site 1), 42.30 (Site 2) – 340.43$mgkg^{-1}$ (Site 1) and 66.67 (Site 4) – 450.87$mgkg^{-1}$ (Site 1) for grain size 1400µm, 355µm and 150µm, respectively. Similarly, for Warm and Wet season the average concentration of Ni ranged from 22.91 (Site 6) – 184.61 $mgkg^{-1}$ (Site 1), 29.36 (Site 2) – 233.65 $mgkg^{-1}$ (Site 1), and 39.64 (Site 6) – 272.63 (Site 1) for grain size 1400µm, 355µm and 150µm, respectively. Lastly, in Warm and Dry Season the mean concentration ranged from 28.25 (Site 6) – 221.50 $mgkg^{-1}$ (Site 1), 31.75 (Site 2) – 274.00 $mgkg^{-1}$ (Site 1), and 52.00 (Site 2) – 330.00 $mgkg^{-1}$ (Site 1) for the same grain sizes in the same order, respectively. Similar to Cr, Ni was not detected in any of the samples of the control site in all the seasons.

The concentration of Pb varied between 11.61 (Site 2) – 126.12$mgkg^{-1}$ (Site 7), 21.81 (Site 2) – 107.63$mgkg^{-1}$ (Site 7) and 93.46 (Site 1) – 896.18$mgkg^{-1}$ (Site 5) in Cool and Dry Season for grain sizes 1400µm, 355µm and 150µm, respectively. The ranges were 10.39 (Site 2) – 106.52$mgkg^{-1}$ (Site 10), 19.78 (Site 2) – 150.47$mgkg^{-1}$ (Site 5) and 133.42 (Site 1) – 1174.22$mgkg^{-1}$ (Site 5) in Hot and Dry Season for grain size 1400µm, 355µm and 150µm, respectively. In Warm and Wet Season, mean concentration of Pb ranged from 9.33 (Site 2) – 100.99 $mgkg^{-1}$ (Site 7), 17.60 (Site 2) – 93.04 $mgkg^{-1}$ (Site 5), and 76.22 (Site 1) – 711.13 $mgkg^{-1}$ (Site 5) for grain size 1400µm, 355µm and 150µm, respectively. Similarly in Warm and Dry Season, details of the Pb concentration were as follows: for grain size 1400µm: 6.05 (Site 1) – 73.25 $mgkg^{-1}$ (Site 5), for 355µm: 10.78 (Site 2) – 130.00$mgkg^{-1}$ (Site 5), and for 150µm: 98.75 (Site 1) – 866.00$mgkg^{-1}$ (Site 5). For the control site the mean of Pb levels ranged from 2.00 – 5.56$mgkg^{-1}$ for the same grain size in the same order.

Cu concentrations across Cool and Dry Season ranged from 0.50 (Sites 5) – 16.75 $mgkg^{-1}$ (Site 7), 3.20 (Site 10) – 29.51 $mgkg^{-1}$ (Site 4) and 27.38 (Site 8) – 155.50 $mgkg^{-1}$ (Site 4) for grain size 1400µm, 355µm and 150µm, respectively, and Hot and Dry Season ranged between 1.68 (Site 10) – 18.59$mgkg^{-1}$ (Site 7), 6.86 (Site 6) – 35.32 $mgkg^{-1}$ (Site 4) and 26.02 (Site 1) – 203.73$mgkg^{-1}$ (Site 4) for grain size 1400µm, 355µm and 150µm, respectively. In Warm and Wet Season, mean concentration of Cu ranged from 0.38 (Site 5) – 13.62 $mgkg^{-1}$ (Site 7), 3.89 (Site 5) – 18.30 $mgkg^{-1}$ (Site 7), and 16.06 (Site 1) – 127.27 $mgkg^{-1}$ (Site 4) for grain size 1400µm, 355µm and 150µm, respectively. Similarly in Warm and Dry Season, details of the Cu concentration are as follows: for grain size 1400µm: ND (Site 1) – 14.80 $mgkg^{-1}$ (Site 7), for 355µm: 0.53 (Site 10) – 33.55$mgkg^{-1}$ (Site 5), and for 150µm: 18.25 (Site 1) – 154.53$mgkg^{-1}$ (Site 4). Similar to Ni, Cu was not detected in any of the samples from the control site in the seasons.

Also, Zn varied between 52.24 (Site 9) – 798.94$mgkg^{-1}$ (Site 1), 544.61 (Site 7) – 1547.96$mgkg^{-1}$ (Site 9) and 290.50 (Site 3) – 3269.98$mgkg^{-1}$ (Site 8) in Cool and Dry

Season for grain sizes 1400µm, 355µm and 150µm, respectively. The range for this metal was 45.71 (Site 9) – 537.34mgkg^{-1} (Site 8), 267.07 (Site 3) – 2284.86mgkg^{-1} (Site 8) and 290.50 (Site 3) – 3269.98mgkg^{-1} (Site 8) in Hot and Dry season for grain size 1400µm, 355µm and 150µm respectively. In Warm and Wet Season, mean concentration of Zn ranged from 40.88 (Site 9) – 692.26 mgkg^{-1} (Site 8), 439.59 (Site 7) – 1905.28 mgkg^{-1} (Site 10), and 219.14 (Site 3) – 2634.90 mgkg^{-1} (Site 8) for grain size 1400µm, 355µm and 150µm, respectively. Similarly in Warm and Dry Season, details of the Zn concentration are as follows: for grain size 1400µm: 170.00 (Site 10) – 819.25 mgkg^{-1} (Site 7), for 355µm: 256.00 (Site 10) – 1242.25 mgkg^{-1} (Site 7), and for 150µm: 381.25 (Site 10) – 1801.00mgkg^{-1} (Site 7). Also, from the Tables, the values obtained from the study area were generally higher than the control site, an indication of pollution of the roadside soils. The trend of concentration of different heavy metals studied was found to be in the following decreasing order across the seasons: Zn > Pb > Ni > Cu > Cr > Cd.

Generally, the results show decrease in concentration of all studied heavy metals during wet season. This was supported by statistical analysis which revealed significant variation ($p < 0.05$) in the seasons. This could implies that metal concentrations in soils, are greatly affected by precipitation.

Correlation coefficients between the levels of metals and physicochemical parameters of roadside soils as shown in Tables 4.16 – 4.19 revealed that in the Cool and Dry Season, significant positive correlations were observed between $Ni_{(1400\mu m)}$: silt and sand ($p<0.01$), $Ni_{(355\mu m)}$: silt and sand ($p<0.01$), $Ni_{(150\mu m)}$: clay, silt and sand ($p<0.05$) and $Pb_{(150\mu m)}$: EC. In the Hot and Dry Season, significant positive correlations were observed between: Cd: EC and OM, $Cr_{(1400\mu m)}$: silt and sand, $Cr_{(355\mu m)}$: sand, $Ni_{(1400\mu m)}$ and $Ni_{(355\mu m)}$: silt and sand, $Ni_{(150\mu m)}$: silt, and $Pb_{(1400\mu m)}$: CEC. In the Warm and Wet Season, significant positive correlations were found: $Pb_{(150\mu m)}$: OM, and $Cu_{(355\mu m)}$: OM and CEC.

Table 4.16. Correlation matrix between physicochemical parameters and metals concentration in different grain sizes of roadside soil (Cool and Dry Season)

Parameters	CLAY	SILT	SAND	pH	EC	OM	CEC
CdA	0.043	-0.397	0.370	0.166	0.854**	0.830**	0.628
CdB	0.213	-0.440	0.378	0.156	0.686*	0.639*	0.544
CdC	0.339	-0.501	0.405	0.312	0.794**	0.665*	0.587
CrA	-0.422	-0.698*	0.756*	0.1730	0.211	0.205	-0.056
CrB	-0.264	-0.612	0.651*	0.008	0.595	0.581	0.342
CrC	-0.378	-0.288	0.353	-0.132	0.410	0.497	0.064
NiA	0.050	0.886**	-0.859**	-0.467	-0.126	-0.307	-0.170
NiB	-0.003	0.876**	-0.837**	-0.442	0.116	0.038	0.038
NiC	-0.168	0.742*	-0.670*	-0.343	0.234	0.223	0.247
PbA	-0.049	0.084	-0.064	0.390	0.287	0.253	0.657*
PbB	0.065	0.017	-0.028	0.279	0.151	0.087	0.468
PbC	0.479	0.000	-0.112	0.414	-0.199	-0.209	0.043
CuA	-0.061	0.279	-0.234	-0.224	-0.051	0.134	0.314
CuB	-0.007	0.052	-0.032	-0.469	0.058	0.372	0.181
CuC	0.465	-0.247	0.153	0.069	0.034	0.218	0.378
ZnA	0.238	0.382	-0.413	-0.401	0.359	0.283	0.163
ZnB	-0.130	0.082	-0.054	-0.405	0.242	0.326	-0.086
ZnC	-0.140	-0.473	0.481	0.047	0.503	0.576	0.204

A, B, C: Grain size 1400µm, 355µm and 150µm respectively.

** Correlation is significant at the 0.05 level (2-tailed)*

*** Correlation is significant at the 0.01 level (2-tailed)*

Table 4.17. Correlation matrix between physicochemical parameters and metals concentration in different grain sizes of roadside soil (Hot and Dry Season)

Parameter	CLAY	SILT	SAND	pH	EC	OM	CEC
CdA	-0.484	0.163	0.094	-0.135	0.497	0.397	0.272
CdB	-0.530	0.311	-0.034	-0.226	0.411	0.437	0.312
CdC	-0.670*	0.332	0.022	-0.292	0.277	0.351	0.129
CrA	0.318	-0.452	0.293	0.556	-0.386	-0.202	-0.254
CrB	-0.113	-0.168	0.235	-0.003	-0.227	-0.355	-0.072
CrC	0.319	-0.252	0.084	0.472	0.259	0.374	0.287
NiA	0.102	0.172	-0.235	-0.456	-0.098	-0.164	-0.245
NiB	0.009	0.053	-0.061	-0.469	0.258	0.023	-0.045
NiC	0.028	-0.240	0.231	-0.384	0.271	0.028	-0.017
PbA	-0.168	-0.240	0.339	-0.091	-0.042	0.115	-0.268
PbB	-0.214	-0.098	0.217	-0.078	0.319	0.408	0.084
PbC	-0.246	0.346	-0.223	-0.038	0.368	0.684*	0.294
CuA	-0.125	-0.326	0.408	-0.500	0.047	0.053	0.345
CuB	-0.170	-0.213	0.315	-0.098	0.616	0.678*	0.913**
CuC	-0.547	0.003	0.299	-0.504	0.080	0.067	0.542
ZnA	-0.459	0.578	-0.347	-0.637*	0.607	0.174	0.394
ZnB	-0.169	0.051	0.039	0.079	0.315	0.358	0.353
ZnC	-0.166	0.081	0.006	0.080	0.325	0.366	0.348

A, B, C: Grain size 1400µm, 355µm and 150µm respectively.

** Correlation is significant at the 0.05 level (2-tailed)*

*** Correlation is significant at the 0.01 level (2-tailed)*

Table 4.18. Correlation matrix between physicochemical parameters and metals concentration in different grain sizes of roadside soil (Warm and Wet Season)

Parameters	CLAY	SILT	SAND	pH	EC	OM	CEC
CdA	-0.137	0.260	-0.186	0.030	0.539	0.338	0.103
CdB	-0.343	0.601	-0.426	-0.209	0.389	0.337	0.243
CdC	-0.384	0.530	-0.305	-0.115	0.277	0.206	-0.001
CrA	0.286	-0.260	0.103	0.709*	-0.320	-0.108	-0.320
CrB	0.246	-0.231	0.102	0.433	0.219	0.228	-0.087
CrC	0.290	-0.214	0.046	0.502	0.235	0.271	-0.025
NiA	-0.147	0.098	0.025	-0.478	-0.123	-0.210	-0.360
NiB	-0.457	-0.134	0.490	-0.225	0.065	-0.259	-0.407
NiC	-0.177	-0.171	0.334	-0.352	0.297	-0.061	-0.182
PbA	-0.148	-0.155	0.225	-0.055	0.051	-0.007	-0.229
PbB	0.074	0.095	-0.226	-0.031	0.040	0.291	-0.041
PbC	-0.011	0.392	-0.545	0.070	0.290	0.724*	0.436
CuA	-0.243	-0.269	0.510	-0.512	-0.047	-0.288	0.070
CuB	0.137	-0.216	0.185	-0.332	0.294	0.194	0.492
CuC	-0.351	0.221	0.018	-0.580	0.095	0.044	0.494
ZnA	-0.384	0.612	-0.357	-0.765**	0.562	0.129	0.341
ZnB	0.143	0.264	-0.341	0.084	-0.253	-0.160	-0.497
ZnC	-0.088	0.183	-0.123	0.235	0.356	0.287	0.186

A, B, C: Grain size 1400µm, 355µm and 150µm respectively.

** Correlation is significant at the 0.05 level (2-tailed)*

*** Correlation is significant at the 0.01 level (2-tailed)*

Table 4.19. Correlation matrix between physicochemical parameters and metals concentration in different grain sizes of roadside soil (Warm and Dry Season)

Parameters	CLAY	SILT	SAND	pH	EC	OM	CEC
CdA	0.180	-0.211	0.155	0.202	0.078	0.045	0.050
CdB	0.207	-0.165	0.109	-0.009	0.226	0.097	0.151
CdC	0.069	-0.310	0.268	-0.136	0.332	0.336	0.255
CrA	-0.059	-0.297	0.276	0.031	-0.379	-0.288	-0.455
CrB	-0.099	-0.136	0.140	0.556	-0.766**	-0.559	-0.599
CrC	0.285	-0.232	0.157	0.075	-0.180	-0.213	-0.727*
NiA	0.549	0.878**	-0.893**	-0.092	-0.049	-0.225	0.300
NiB	0.718*	0.856**	-0.904**	-0.033	0.009	-0.150	0.260
NiC	0.729*	0.855**	-0.909**	0.027	-0.097	-0.287	0.228
PbA	0.199	0.153	-0.177	-0.619	0.416	0.291	0.569
PbB	0.400	0.212	-0.269	-0.276	0.442	0.254	0.556
PbC	-0.046	-0.333	0.313	-0.559	0.965**	0.763*	0.443
CuA	-0.095	0.491	-0.430	-0.079	0.279	-0.126	0.386
CuB	-0.131	-0.225	0.225	-0.041	0.426	0.209	-0.025
CuC	-0.726*	-0.072	0.193	0.463	-0.239	-0.289	0.057
ZnA	-0.348	0.164	-0.088	0.307	-0.078	-0.141	0.150
ZnB	-0.078	0.153	-0.129	0.252	-0.082	-0.046	0.147
ZnC	-0.186	-0.054	0.079	0.162	-0.212	-0.112	-0.156

A, B, C: Grain size 1400µm, 355µm and 150µm respectively.

** Correlation is significant at the 0.05 level (2-tailed)*

*** Correlation is significant at the 0.01 level (2-tailed)*

Also, in the Warm and Dry season, significant positive correlations were observed between $Cr_{(1400\mu m)}$: pH, and PbC: OM. Positive correlation between metal and physicochemical parameters suggests significant effect of physicochemical parameters on the amount of metal in the soil. This is evident that the mobility and bioavailability of metals present in soils depend on physicochemical properties of both the metal and the soil (McEldowney *et al*., 1993).

Heavy metals in soils usually have complicated relationships among them. It was noted that numerous factors control their relative abundance like original contents of heavy metals in rocks and parent materials, various processes of soil formation, and anthropogenic factors such as the contamination by human activities (Li *et al*., 2008). As shown in Tables 4.20 – 4.23, the correlation of heavy metals in different grain sizes revealed positive correlation among different grain sizes for Cd, Cr, Ni, Pb, Cu and Zn and Cd: Cr, Pb, Cu (with exception of grain size 1400µm) and Zn across the seasons. Negative correlation was also observed between metals.

The high correlations between soil heavy metals may reflect that these heavy metals had similar pollution level and similar pollution sources (Li *et al*., 2009). Overall, all the heavy metals, Cd, Cr, Cu, Pb and Zn are group together, indicating that the anthropogenic sources of these heavy metals are closely related in the soil of the study area which was consistent with what Onianwa (2001), Romic and Romic (2003), Li *et al*. (2009), Sun *et al*. (2010) reported. However, some of the correlations were poor, possibly due to varied nature of the sources of the contamination. Open burning of municipal solid waste, which can contribute to soil metal levels, is a common feature on many street corners of Nigeria, couple with other ancillary work such as vulcanizer, mechanics, and lubricating oil vendors among others miscellaneous sources from which random metal pollution could occur.

Table 4.20. Correlation matrix among metal concentration in different grain sizes of roadside soil (Cool and Dry Season)

Parameter	CdA	CdB	CdC	CrA	CrB	CrC	NiA	NiB	NiC	PbA	PbB	PbC	CuA	CuB	CuC	ZnA	ZnB	ZnC
CdA	1.000																	
CdB	0.889**	1.000																
CdC	0.884**	0.922**	1.000															
CrA	0.355	0.253	0.349	1.000														
CrB	0.593	0.564	0.616	0.727*	1.000													
CrC	0.653*	0.453	0.449	0.740*	0.648*	1.000												
NiA	-0.261	-0.299	-0.266	-0.538	-0.340	-0.232	1.000											
NiB	-0.003	-0.119	-0.147	-0.535	-0.245	-0.009	0.899**	1.000										
NiC	0.148	-0.026	-0.087	-0.345	-0.043	0.175	0.757*	0.919**	1.000									
PbA	0.271	0.171	0.130	-0.099	-0.022	-0.056	0.108	0.142	0.411	1.000								
PbB	0.323	0.314	0.239	-0.086	-0.111	-0.052	0.046	0.001	0.200	0.890**	1.000							
PbC	0.085	0.255	0.161	-0.242	-0.531	-0.215	-0.195	-0.216	-0.282	0.229	0.504	1.000						
CuA	-0.159	-0.106	-0.234	-0.245	0.186	-0.133	0.238	0.281	0.480	0.368	0.141	-0.419	1.000					
CuB	0.174	0.184	0.020	-0.070	0.324	0.243	-0.061	0.107	0.254	-0.022	-0.060	-0.349	0.716*	1.000				
CuC	0.022	0.284	0.178	-0.251	0.184	-0.322	-0.309	-0.295	-0.239	0.030	0.045	0.024	0.578	0.636*	1.000			
ZnA	0.291	0.382	0.276	-0.592	-0.070	-0.141	0.432	0.591	0.400	-0.191	-0.162	-0.036	0.032	0.193	0.164	1.000		
ZnB	0.516	0.363	0.359	0.439	0.440	0.871**	0.123	0.289	0.364	-0.172	-0.094	-0.183	-0.025	0.396	-0.248	0.080	1.000	
ZnC	0.741*	0.726*	0.674*	0.669*	0.725*	0.867**	-0.415	-0.166	-0.025	-0.151	-0.118	-0.043	-0.157	0.223	-0.027	0.048	0.699*	1.000

A, B, C: Grain size 1400µm, 355µm and 150µm respectively.

** Correlation is significant at the 0.05 level (2-tailed)*

** *Correlation is significant at the 0.01 level (2-tailed)*

Table 4.21. Correlation matrix among metal concentration in different grain sizes of roadside soil (Hot and Dry Season)

Parameter	CdA	CdB	CdC	CrA	CrB	CrC	NiA	NiB	NiC	PbA	PbB	PbC	CuA	CuB	CuC	ZnA	ZnB	ZnC
CdA	1.000																	
CdB	0.952**	1.000																
CdC	0.902**	0.927**	1.000															
CrA	0.249	0.218	0.193	1.000														
CrB	0.443	0.362	0.377	0.689*	1.000													
CrC	0.582	0.471	0.346	0.650*	0.537	1.000												
NiA	-0.255	-0.258	-0.255	-0.512	-0.286	-0.273	1.000											
NiB	-0.051	-0.121	-0.165	-0.508	-0.225	-0.077	0.910**	1.000										
NiC	0.096	0.015	-0.100	-0.240	-0.049	0.114	0.755**	0.913**	1.000									
PbA	0.275	0.349	0.297	0.061	-0.261	-0.083	0.157	0.120	0.320	1.000								
PbB	0.469	0.527	0.395	-0.090	-0.337	0.052	0.066	0.127	0.310	0.907**	1.000							
PbC	0.100	0.272	0.254	-0.315	-0.681*	-0.197	-0.197	-0.183	-0.249	0.365	0.502	1.000						

CuA	-0.232	-0.142	-0.299	-0.248	-0.119	-0.257	0.291	0.348	0.513	0.252	0.227	-0.031	1.000						
CuB	0.335	0.324	0.143	-0.105	0.016	0.339	-0.307	-0.061	0.104	-0.035	0.261	0.187	0.492	1.000					
CuC	0.026	0.100	0.097	-0.212	0.181	-0.293	-0.317	-0.287	-0.228	-0.186	-0.102	-0.027	0.540	0.595	1.000				
ZnA	0.282	0.247	0.195	-0.727*	-0.113	-0.176	0.430	0.569	0.383	-0.237	0.015	-0.014	0.111	0.225	0.216	1.000			
ZnB	0.739*	0.724*	0.646*	0.593	0.667*	0.805**	-0.434	-0.219	-0.047	-0.135	-0.008	-0.024	-0.195	0.338	0.014	-0.017	1.000		
ZnC	0.755*	0.740*	0.661*	0.578	0.656*	0.811**	-0.414	-0.203	-0.041	-0.131	0.004	-0.017	-0.223	0.324	-0.013	0.006	0.999**	1.000	

A, B, C: Grain size 1400µm, 355µm and 150µm respectively.

** Correlation is significant at the 0.05 level (2-tailed)*

*** Correlation is significant at the 0.01 level (2-tailed)*

Table 4.22. Correlation matrix among metal concentration in different grain sizes of roadside soil (Warm and Wet Season)

Parameter	**CdA**	**CdB**	**CdC**	**CrA**	**CrB**	**CrC**	**NiA**	**NiB**	**NiC**	**PbA**	**PbB**	**PbC**	**CuA**	**CuB**	**CuC**	**ZnA**	**ZnB**	**ZnC**
CdA	1.000																	
CdB	0.857**	1.000																
CdC	0.882**	0.924**	1.000															
CrA	0.358	0.267	0.343	1.000														
CrB	0.699*	0.435	0.487	0.716*	1.000													
CrC	0.652*	0.405	0.436	0.744*	0.986**	1.000												

NiA	-0.254	-0.321	-0.271	-0.541	-0.183	-0.245	1.000												
NiB	-0.097	-0.325	-0.065	-0.391	-0.099	-0.162	0.580	1.000											
NiC	0.158	-0.065	-0.092	-0.353	0.230	0.154	0.750*	0.508	1.000										
PbA	0.282	0.264	0.162	-0.062	0.036	-0.053	0.122	-0.078	0.414	1.000									
PbB	0.318	0.401	0.262	-0.043	0.022	-0.043	0.066	-0.339	0.184	0.873**	1.000								
PbC	0.080	0.301	0.169	-0.221	-0.247	-0.198	-0.189	-0.275	-0.282	0.233	0.524	1.000							
CuA	-0.157	-0.081	-0.226	-0.241	-0.059	-0.142	0.226	0.044	0.477	0.348	0.097	-0.416	1..000						
CuB	0.164	0.137	0.010	-0.048	0.301	0.248	-0.080	-0.165	0.242	-0.042	-0.084	-0.342	0.714*	1.000					
CuC	0.000	0.296	0.168	-0.251	-0.278	-0.326	-0.307	-0.224	-0.229	0.022	0.024	0.025	0.595	0.637*	1.000				
ZnA	0.257	0.273	0.250	-0.635*	-0.151	-0.177	0.444	0.340	0.398	-0.213	-0.183	-0.048	0.054	0.187	0.175	1.000			
ZnB	0.551	0.471	0.576	0.478	0.512	0.455	0.166	-0.153	0.100	0.192	0.338	-0.192	-0.254	-0.160	-0.344	0.032	1.000		
ZnC	0.741*	0.695*	0.673*	0.649*	0.826**	0.857**	-0.420	-0.237	-0.037	-0.149	-0.119	-0.046	-0.146	0.230	-0.022	0.035	0.341	1.000	

A, B, C: Grain size 1400µm, 355µm and 150µm respectively.

** Correlation is significant at the 0.05 level (2-tailed)*

*** Correlation is significant at the 0.01 level (2-tailed)*

Table 4.23. Correlation matrix among metal concentration in different grain sizes of roadside soil (Warm and Dry Season)

Parameter	CdA	CdB	CdC	CrA	CrB	CrC	NiA	NiB	NiC	PbA	PbB	PbC	CuA	CuB	CuC	ZnA	ZnB	ZnC
CdA	1.000																	
CdB	0.945**	1.000																
CdC	0.895**	0.906**	1.000															
CrA	0.124	0.204	0.041	1.000														
CrB	0.208	0.050	0.035	0.606	1.000													
CrC	0.477	0.445	0.218	0.491	0.366	1.000												
NiA	-0.258	-0.204	-0.240	-0.460	-0.207	-0.310	1.000											
NiB	-0.126	-0.123	-0.190	-0.442	-0.185	-0.150	0.920**	1.000										
NiC	0.021	0.055	-0.120	-0.121	-0.056	0.037	0.755*	0.907**	1.000									
PbA	0.284	0.537	0.500	0.068	-0.470	-0.089	0.170	0.042	0.123	1.000								
PbB	0.533	0.669*	0.508	-0.099	-0.546	0.150	0.063	0.184	0.358	0.718*	1.000							
PbC	0.113	0.264	0.336	-0.352	-0.795**	-0.177	-0.199	-0.152	-0.213	0.421	0.497	1.000						
CuA	-0.284	-0.166	-0.267	-0.245	-0.450	-0.330	0.299	0.371	0.460	0.066	0.251	0.340	1.000					
CuB	0.338	0.316	0.233	-0.157	-0.365	0.360	-0.413	-0.168	-0.034	-0.057	0.458	0.551	0.432	1.000				
CuC	0.055	-0.095	0.011	-0.165	0.174	-0.229	-0.323	-0.279	-0.225	-0.412	-0.210	-0.078	0.374	0.414	1.000			
ZnA	-0.512	-0.595	-0.622	-0.275	-0.237	-0.375	-0.094	0.021	0.052	-0.500	-0.139	0.040	0.608	0.373	0.593	1.000		
ZnB	-0.305	-0.408	-0.461	-0.105	-0.141	-0.172	-0.155	0.091	0.229	-0.435	0.057	0.000	0.517	0.453	0.472	0.901**	1.000	
ZnC	-0.214	-0.307	-0.317	0.322	0.257	0.053	-0.349	-0.101	0.131	-0.468	-0.165	-0.163	0.388	0.376	0.506	0.655*	0.822**	1.000

A, B, C: Grain size 1400µm, 355µm and 150µm respectively.

** Correlation is significant at the 0.05 level (2-tailed)*

*** Correlation is significant at the 0.01 level (2-tailed)*

The dependence of metal concentrations on traffic volume was evaluated by calculation using Pearson's correlation coefficient (SPSS Version 17) as shown in Table 4.24. The correlations were found to be significant for CdB, CrB and CuB (during cool and dry season) ($p < 0.05$), and Pb throughout the study. Positive correlation between Pb and traffic density for all the seasons confirm the fact that Pb concentration in roadside soil is a function of traffic, an indication that leaded fuel are still in use in Nigeria. This may be due to the fact that other sources of heavy metals contribute significant fractions to the soil burden. The results compared with other research that traffic density is not only a contributory factor to soil along roadside, other factor such as waste disposal could be responsible (Lau and Wong, 1982; Onianwa, 2001; Okunola *et al*., 2007). Also, the topsoil is regularly eroded by precipitation runoff into public drains and water bodies, so that some amount of accumulated metals is removed during rains. Contrary to this study, Ward *et al*. (1977) found significant correlations between traffic density and Pb, Cu, Zn, Cd, Cr and Ni in surface soils. Though their studies were not seasonal, variation in their correlation values across the seasons revealed effect of season on the rate of metal deposition.

Apart from traffic volume, many other factors also govern the release and/or dispersion of these contaminants along the roads. Open burning of municipal solid waste, which may contribute to soil metal levels, is a common feature on many roadside in Kano Metropolis. The city also hosts many road artisans such as vulcanizers, automechanics and lubricating oil sellers among so many others.

4.3.2 Discussion

Generally from the results, Cd, Cr, Ni, Pb, Cu and Zn levels in different grain sizes from the study areas are high compared to control Site (used as background).

Table 4.24. Correlation matrix between traffic volume and heavy metals in roadside soil

Parameters	Cool and Dry Season	Hot and Dry Season	Warm and Wet Season	Warm and Dry Season
	Traffic			
CdA	0.216	0.312	-0.045	0.325
CdB	0.388	0.378	0.381	0.407
CdC	0.464*	0.359	0.420	0.388
CrA	-0.166	-0.071	-0.125	-0.045
CrB	0.714*	-0.331	-0.531	-0.126
CrC	-0.182	-0.122	-0.156	-0.117
NiA	-0.336	-0.334	-0.331	-0.326
NiB	-0.289	-0.322	-0.305	-0.265
NiC	-0.271	-0.278	-0.273	-0.274
PbA	0.586**	-0.091	0.580**	0.494**
PbB	0.602**	0.684**	0.659**	0.691**
PbC	0.935**	0.905**	0.922**	0.904**
CuA	0.146	-0.393	-0.085	-0.386
CuB	0.472*	-0.391	0.118	-0.388
CuC	-0.091	0.021	-0.032	0.023
ZnA	-0.044	-0.161	-0.167	-0.173
ZnB	-0.002	-0.233	0.016	-0.021

ZnC	-0.105	0.019	0.019	0.014

A, B, C: Grain size 1400µm, 355µm and 150µm respectively.
** Correlation is significant at the 0.05 level (2-tailed)*
*** Correlation is significant at the 0.01 level (2-tailed)*

This is an indication that activities on the road and along the roadsides are a potential source of heavy metal deposition to the roadside environment. This agreed with studies of Facchinelli *et al*. (2001) and Han *et al*. (2005) that Cd, Pb, Zn, Cr, Cd, and Ni concentrations in the soils were generally controlled by anthropogenic activities including traffic and industrial activities. Also, lower concentration of all studied metals were observed during the Warm and Wet Season, this corroborate to the to the fact that soils are sink for all kinds of pollutants including metals, during rains, runoffs can dissolve and washed away these metals thereby reducing the concentration of metals in soil (Okunola *et al*., 2007; Yahaya *et al*., 2010). However, after rainy season (Warm and Dry Season), concentration of metal increases, though decrease in concentrations were observed for CrB, PbA, PbB, and ZnB for some of the sites. The reason is that metal concentrations in roadside surface soils represent a more long-term and recent accumulation of pollutants (Chon *et al*., 1998) and during the rainy season not only decreasing the rate of deposition but also flushing away of metals with rains causes relatively lower concentration of metal.

As observed in Table 4.1, Cd was found in all different fractions of particle sizes with concentration increasing as the grain sizes decreases. Hence, the influence of particle size on metal levels varies from one site to another depending on the nature, the type of traffic involved and the wind direction. This is supported by report that heavy metals are concentrated in the small dense particles with possible source from traffic emitted particles (Fergusson and Kim, 1991). Also, variation in behaviour of metals with grain sizes is also largely attributed to differences in their relative potential for sorption onto clay materials, hydrous oxides and organic matter surfaces, all which tend to be concentrated in the smaller grain sizes. This is indicative with positive correlation with % OM, which implies that Cd is bound to organic matter making it unavailable to the environment especially during the Hot and Dry Season when the % OM was high. Contrary to this, negative correlation was observed between % clay content, though positive during the Cool and Dry Season, and Warm and Dry Season. Positive correlation is an indication of % OM controlling the sorption and availability of Cd in these seasons. Furthermore, positive correlation between Cd and, EC and CEC in the grain sizes explains the variation in Cd concentration among different grain sizes.

However, the highest Cd concentration (13.86mgkg^{-1}) in the samples was found at Site 8, a low elevation region and comparatively low traffic volume (3708 h^{-1}) compared to Site 6 (8357 h^{-1}). High Cd concentration in Site 8 can be closely related to the fact that, this

road is flagged by electronic, stationary, paints dealers and other road ancillary work such as vulcanizers. This is also supported with non-significant correlations between traffic and Cd concentrations except CdC (Cool and Dry Season). Compared to literature studies, Aksoy (1996) found mean Cd concentrations for urban roadside soils and rural roadside soils as 2.44mgkg^{-1} and 1.04mgkg^{-1}, respectively, which is lower than highest concentration reported in this study. Cd in this study especially at Site 8 is higher than all the soil criteria from other countries (as shown in metals Tables), background level in Kavala's region, Greece – 1.4 (Christoforidis and Stamatis, 2009) and 0.14 – 7.0mgkg^{-1} (Yahaya *et al*., 2010). However, the range of Cd is within the range 0.1 – 14.6mgkg^{-1} reported in a similar study in Turkey (Tokalioglu and Kartal, 2006). Existence of Cd in roadside soils could be derived from attrition of automobile tires (Akhter and Madany, 1993). Surface area could be an implication for high Cd concentration in this study, since concentration increases with increase in grain size. This could explain reasons for high concentration in this study compared to the literature.

Similar to Cd, the highest concentration of Cr and Zn was found in 150µm samples from Site 8 during Hot and Dry Season. This is supported with strong positive correlation between the Cd, Cr and Zn during Cool and Dry, Hot and Dry, and Warm and Wet Seasons. This indicates that source of these metals during these seasons were similar. Relationship between traffic volume and these metals revealed that traffic may not be the source of these metals, suggesting that other sources such as tires attritions, printing plates, deposition associated with chrome plating of vehicle parts (Al-Shayep and Seaward, 2001) coupled with traffic (for grain size 150µm samples) releases these metals at the Sites. Also, high concentration of Cr and Zn recorded in Site 8 appear to have originated from poorly maintained city taxis, especially during minor mechanical repairs undertaken at this Site. However, relationships between the metals were observed bad during Warm and Dry Season. This could be related to the fact dust concentration and wind speed during this period is high, hence particles from different source are possible (Li *et al*., 2007).

Values of Cr in this study was generally low compared to 200mgkg^{-1} maximum allowable limits in Germany (Kabata-Pendias, 1995), while the levels of Zn were found exceptionally higher compared to those in the range 200 – 480mgkg^{-1} (Christofordis and Stamatis, 2009) and 79.6 – 202.4mgkg^{-1} (Yahaya *et al*., 2011) reported in a similar study. However, the levels of Zn were found within the range 160 – 3725mgkg^{-1} in Lancaster, UK (Harrison, 1979). Abundance of Zn compared to other metals is in agreement with the fact Zn in soil is mainly associated with Fe and Al oxides (Kabata-Pendia and Pendias, 1991) which is revealed in a later chemical fractionation study. Also, coupled with this, contributions from sources such as lubricating oil, tyres, waste cans disposed along the roadside, wood burning and different kind of waste like electronic waste, anticorrosive, plastics, batteries (Jaradat and Momani, 1999; Awofolu, 2005; Okunola *et al*., 2007) along these roads is a major contribution to Zn level.

Like Fe, Ni is a very abundant element. In this study, Ni was the third highest metal in abundance (after Zn and Pb) with the highest concentration in 150µm samples. The highest concentration was obtained in sample from Site 1 during Hot and Dry Season. This corroborate with other studies that source of Ni in roadside environment could not be attributed to vehicular emission alone (Ramakrishaiah and Somashekar, 2002; Bai *et al*., 2008) rather sources such as tobacco smoke, fertilizer and industrial waste, residual oil (Paola, 2005; Odat and Alshammari, 2011) among others were the major sources of Ni. This is supported with negative correlation between traffic volume and Ni. With exception

of Sites 1, 7, 8, 9 and 10, the level of Ni in this study is within 100mgkg^{-1} the maximum allowable limit for Ni in soils (Kabata-Pendias, 1995). Hence, it can be concluded that roadside soils in Kano Metropolis were enriched with Ni though contents did not exceed allowable limits.

Pb is of most concern in environmental heavy metal pollution. Results on Pb contents in soils Kano Metropolis (study and control area) indicate the presence of Pb. The reason is that Pb is emitted from different sources such as glass, waste cans, paints, batteries, PVC-products, and cables (Paola, 2005). Similar to other metals, Pb level is highest in 150µm grain size sample from Site 5 (1174.32mgkg^{-1}) during Hot and Dry Season. The main source of Pb contamination is traffic, usually the highest concentration of this metal is found close to roads with high traffic density (Mohammed *et al*., 2006; Saeedi *et al*., 2009). This is due to the fact that Pb is too heavy to be transported by the air. In the case of this study, the highest concentration was found in the samples from Site 5, as mentioned before not in the samples taken from Site 6, the road with the highest traffic density in Kano Metropolis. This can be explained by the fact that Site 5 is last bus-stop for most intra-city buses or taxes, located along this road is local market specialized in plates and local foodstuff. As common feature along market roads, the traffic in this part of the city has always been quite intense coupled with the fact that automobile flow would be slower and hence, lengthier time is spent by automobile which subsequently leads to more emissions of particle especially from the exhaust compared to other roads. Since Pb is known to be use as antiknock in petrol (Jaradat and Momani, 1999), it is clear from the results that Pb in this Site is due to automobile emissions. This is also supported with strong positive correlation between traffic volume and Pb in soils.

Pb concentrations determined in this study are quite similar to those from previous surveys of roadside soils in Seoul, Korea (Chon *et al*., 1998). Also, levels of Pb from this work is higher than 0.14mgkg^{-1} as background level of Pb in roadside surface soil from "uncontaminated area" in Lagos, Nigeria (Adeniyi and Afolabi, 2002), and 0.01 – 0.23mgkg^{-1} reported by Awofolu (2005). However, the levels of Pb are lower than 2466mgkg^{-1} found in Kuala Lumpar, Malaysia (Ramlan and Badri, 1989). In the absence of knowledge regarding industrial activities in the various cities or countries comments on the cause of the differences between Pb levels are unjustified. However, according to Christoforidis and Stamatis (2009) it is generally agreed that automobile exhaust emission accounted for the elevated Pb levels as all samples were collected at major roads. Also, other researchers in Nigeria (Onianwa, 2001; Awofolu *et al*., 2005; Okunola *et al*., 2007 and Abechi *et al*., 2010) have reported that metal disposal and ancillary work such as metal working and motor repairs could have a stronger influence on the accumulation of the metal in roadside soils.

Also, like all the metals reported in this study, highest level of Cu was found in 150µm grain size sample from Site 4 (203.73mgkg^{-1}) during Hot and Dry Season. This is a road along the old City gate that links Emir's Palace, Government House and G.R.A, and the high Cu contents could be associated with historical activities that have taken place there which could discharge Cu into the soils. However, Cu levels in this study are within 467mgkg^{-1} in Birmingham, U.K. (Charlesworth *et al*., 2003), 47 – 407mgkg^{-1} in Instanbul, Turkey (Sezgin *et al*., 2003), 38mgkg^{-1} in Luanda, Angola (Baptista and De Miguel, 2005), and 124mgkg^{-1} in Kavala, Greece (Christoforidis and Stamatis, 2009) reported in roadside soils. In comparative, non-evidence of Cu in control Site indicates anthropogenic sources are the main source of Cu in Kano Metropolis roadside soil.

4.4 ASSESSMENT OF POTENTIAL ECOLOGICAL RISK

According to the toxicity of metals and the response of the environment, ecological risk index (RI) was introduced by Hakanson (1980) to assess the degree of metal pollution in water. In this study, modified method of Hakanson (1980) according to Sun *et al*. (2010) was used.

$RI = \sum E_i$ ----------4

where $E_i = T_i F_i$ ----------5

and $F_i = C_i/B_i$. ----------6

RI is the sum of all risk factors for metals (Pb, Cd and Zn) in soils,

E_i is the monomial potential ecological risk factor,

T_i is the metal toxicity factor, for Pb and Cu 5, for Cd 30, and for Zn 1,

F_i is the metal pollution factor,

C_i is the concentration of metal in soil, and

B_i is the reference value for the respective metal; in this study, the solid concentrations at the control site were used as reference values.

Classification of metal pollution was done according to Sun *et al*. (2010) as follows:

$RI \leq 50$ (low contamination)

$50 < RI \leq 100$ (moderated contamination)

$100 < RI \leq 200$ (considerable contamination)

$RI > 200$ (high contamination)

As shown in Tables 4.25 – 4.28, variation of E_i was observed across 1400µm, 355µm and 150µm grain sizes for Cd, Pb and Zn and used to evaluate the RI.. The RI range from 674.97 (Site 3) – 3306.38 (Site 8), 927.64 (Site 3) – 3232.21 (Site 8), and 383.73 (Site 3) – 2270.40 (Site 8) for grain size 1400µm, 355µm and 150µm respectively during Cool and Dry Season. In Hot and Dry Season, RI ranges in 1400µm, 355µm and 150µm were 724.35 (Site 3) – 3642.19 (Site 8), 585.46 (Site 3) – 2582.93 (Site 8), and 443.92 (Site 3) – 2425.71 (Site 8), respectively. The RI value during Warm and Wet Season ranged from 340.61 (Site 2) – 1246.96 (Site 8), 423.57 (Site 3) – 1283.17 (Site 10), and 228.47 (Site 3) – 1258.87 (Site 8) in 1400µm, 355µm and 150µm, respectively, and in Warm and Dry Season, RI ranged from 97.64 (Site 3) – 405.34 (Site 8), 99.50 (Site 3) – 272.75 (Site 8), and 75.49 (Site 3) – 231.41 (Site 8) for 1400µm, 355µm and 150µm, respectively. In all the grain sizes studied, highest RI was found at Site 8 (except in 355µm during Warm and Wet Season). Also, from the results, high pollution degree was observed for all Sites during the Cool and Dry, Hot and Dry and Warm and Wet Seasons, with the highest RI obtained during Hot and Dry Season for 1400µm and 150µm grain sizes, and Cool and Dry Season for 355µm grain size. High RI in all studied Sites could be related to activities such as lubricating oil vendors, printing plates, refuse burning and vehicular emission releasing metals in the environment.

RI represents the sensitivity of various biological communities to toxic substances and illustrates the potential ecological risk caused by heavy metals.

Table 4.25. Heavy metal potential ecological risk indexes of roadside soils of Kano Metropolis during Cool and Dry Season

Site	Grain Size	E_i			RI	Pollution Degree
		Cd	Pb	Zn		
1	1400µm	484.29	13.86	266.05	764.19	High
	355µm	920.00	15.47	347.87	1283.34	High
	150 µm	534.29	14.38	68.73	617.40	High
2	1400µm	527.14	2.89	160.89	690.92	High
	355µm	1366.67	5.45	234.34	1606.46	High
	150 µm	642.86	18.68	393.36	1054.90	High
3	1400µm	518.57	7.47	148.93	674.97	High
	355µm	666.67	13.27	247.71	927.64	High
	150 µm	301.43	22.04	60.27	383.74	High
4	1400µm	1422.86	5.20	248.82	1676.88	High
	355µm	2266.67	13.22	333.90	2613.79	High
	150 µm	1274.29	27.20	358.35	1659.83	High
5	1400µm	1457.14	20.02	164.49	1641.65	High
	355µm	2033.33	28.80	251.49	2313.62	High
	150 µm	1114.29	137.87	277.20	1529.36	High
6	1400µm	985.71	7.89	129.34	1122.95	High
	355µm	1166.67	6.98	226.74	1400.38	High
	150 µm	1028.57	16.72	234.19	1279.48	High
7	1400µm	1290.00	31.36	148.30	1469.66	High
	355µm	1553.33	26.91	181.54	1761.78	High
	150 µm	757.14	18.10	196.83	972.07	High
8	1400µm	3004.29	11.87	290.22	3306.38	High
	355µm	2706.67	14.08	511.47	3232.21	High
	150 µm	1574.29	17.70	678.42	2270.40	High
9	1400µm	1405.71	16.07	17.40	1439.18	High
	355µm	1500.00	20.09	515.99	2036.08	High
	150 µm	942.86	17.87	499.87	1460.60	High
10	1400µm	1864.29	21.51	171.88	2057.67	High
	355µm	2100.00	26.55	236.01	2362.56	High
	150 µm	1407.14	22.32	248.58	1678.04	High

Table 4.26. Heavy metal potential ecological risk indexes of roadside soils of Kano Metropolis during Hot and Dry Season

Site	Grain Size	E_i			RI	Pollution Degree
		Cd	Pb	Zn		
1	1400µm	608.57	14.37	158.55	781.49	High
	355µm	646.00	18.84	82.80	747.65	High
	150 µm	622.17	21.87	59.05	703.10	High
2	1400µm	818.57	2.46	99.26	920.30	High
	355µm	874.00	4.50	407.12	1285.62	High
	150 µm	716.09	27.38	337.97	1081.43	High
3	1400µm	621.43	7.96	94.96	724.35	High
	355µm	490.00	17.18	78.28	585.46	High
	150 µm	361.30	30.83	51.78	443.92	High
4	1400µm	1782.86	5.14	150.98	1938.97	High
	355µm	1350.00	13.48	374.39	1737.87	High
	150 µm	1381.30	38.28	307.89	1727.47	High
5	1400µm	1620.00	21.64	100.89	1742.52	High
	355µm	1370.00	34.20	288.28	1692.47	High
	150 µm	1366.96	192.50	238.16	1797.61	High
6	1400µm	1092.86	8.06	80.53	1181.45	High
	355µm	736.00	7.26	257.65	1000.91	High
	150 µm	1153.04	25.66	201.21	1379.92	High
7	1400µm	1401.43	23.30	98.60	1523.33	High
	355µm	1036.00	31.79	230.44	1298.23	High
	150 µm	829.57	35.21	169.11	1033.89	High
8	1400µm	3462.86	11.41	167.92	3642.19	High
	355µm	1888.00	25.28	669.66	2582.93	High
	150 µm	1807.83	35.00	582.88	2425.71	High
9	1400µm	1590.00	17.70	14.29	1621.99	High
	355µm	1166.00	21.41	514.36	1701.78	High
	150 µm	1112.61	26.30	429.48	1568.39	High
10	1400µm	2310.00	25.23	99.70	2434.93	High
	355µm	1568.00	32.06	252.40	1852.46	High
	150 µm	1664.35	35.91	213.58	1913.83	High

Table 4.27. Heavy metal potential ecological risk indexes of roadside soils of Kano Metropolis during Warm and Wet Season

Site	Grain Size	E_i			RI	Pollution Degree
		Cd	Pb	Zn		
1	1400µm	125.71	114.30	295.95	535.97	High
	355µm	86.00	70.76	423.23	579.99	High
	150 µm	97.00	68.54	85.58	251.12	High
2	1400µm	138.57	23.33	178.72	340.61	High
	355µm	132.00	24.72	286.34	443.06	High
	150 µm	121.67	85.36	510.98	718.01	High
3	1400µm	131.43	57.43	165.96	354.82	High
	355µm	62.00	59.87	301.70	423.57	High
	150 µm	54.33	101.57	72.56	228.47	High
4	1400µm	365.71	42.93	277.03	685.67	High
	355µm	210.80	60.79	404.91	676.50	High
	150 µm	238.67	127.38	461.95	828.00	High
5	1400µm	395.71	163.90	180.67	740.29	High
	355µm	202.40	130.67	300.41	633.49	High
	150 µm	216.00	639.51	350.66	1206.17	High
6	1400µm	277.14	63.08	154.98	495.19	High
	355µm	118.80	31.28	273.71	423.78	High
	150 µm	201.67	77.46	296.25	575.38	High
7	1400µm	357.14	252.48	163.03	772.64	High
	355µm	159.20	115.08	219.80	494.08	High
	150 µm	149.33	81.20	254.04	484.57	High
8	1400µm	837.14	95.15	314.67	1246.96	High
	355µm	242.40	62.92	616.36	921.68	High
	150 µm	305.00	81.38	872.48	1258.87	High
9	1400µm	381.43	132.75	18.58	532.76	High
	355µm	150.00	91.26	613.13	854.40	High
	150 µm	179.33	87.11	630.89	897.34	High
10	1400µm	505.71	177.83	189.96	873.50	High
	355µm	209.60	120.93	952.64	1283.17	High
	150 µm	272.00	105.31	320.54	697.85	High

Table 4.28. Heavy metal potential ecological risk indexes of roadside soils of Kano Metropolis during Warm and Dry Season

Site	Grain Size	E_i			RI	Pollution Degree
		Cd	Pb	Zn		
1	1400µm	75.00	10.96	12.09	98.05	Moderate
	355µm	78.95	15.52	15.34	109.81	Considerable
	150 µm	64.57	15.33	12.19	92.10	Moderate
2	1400µm	120.00	1.45	12.72	134.17	Considerable
	355µm	94.74	2.34	14.38	111.46	Considerable
	150 µm	69.54	19.02	14.77	103.33	Considerable
3	1400µm	75.00	6.35	16.29	97.64	Moderate
	355µm	63.16	15.08	21.26	99.50	Moderate
	150 µm	39.74	20.19	15.57	75.49	Moderate
4	1400µm	225.00	3.83	16.04	244.87	High
	355µm	134.21	9.55	18.08	161.84	Considerable
	150 µm	134.11	25.85	18.25	178.21	Considerable
5	1400µm	180.00	17.54	12.51	210.05	High
	355µm	157.89	28.21	16.19	202.30	High
	150 µm	149.01	134.47	13.21	296.69	High
6	1400µm	120.00	6.17	11.59	137.76	Considerable
	355µm	78.95	5.32	18.98	103.24	Considerable
	150 µm	114.24	18.83	21.92	154.98	Considerable
7	1400µm	150.00	9.82	22.14	181.96	Considerable
	355µm	118.42	26.04	32.57	177.03	Considerable
	150 µm	79.47	30.67	28.08	138.22	Considerable
8	1400µm	390.00	8.02	7.32	405.34	High
	355µm	228.95	27.29	16.51	272.75	High
	150 µm	184.37	30.90	16.14	231.41	High
9	1400µm	180.00	14.91	6.64	201.55	High
	355µm	157.89	16.00	11.22	185.11	Considerable
	150 µm	117.22	18.52	18.90	154.63	Considerable
10	1400µm	285.00	22.27	4.59	311.86	High
	355µm	205.26	26.75	6.71	238.72	High
	150 µm	180.40	27.14	5.94	213.48	High

As shown in Table 4.25 – 4.28, Cd (except for Warm and Wet Season) followed by Zn and Pb pose potential risk in that order. Similar trend was also reported in literature (Sun *et al*., 2010), though RI was not as high as in this study. The reason could be due to strict

pollution control system in Shenyang, China compared to Nigeria. After rains moderate – considerable – high potential risk was recorded. The lower values of RI after rains at all sites originate from low concentrations of Cd, Zn and Pb obtained during this period. This indicates Cd, Zn and Pb content of the soils attain the strong pollution level before the rains. The ecological risk index, accounting for the contamination caused by Cd, Pb and Zn indicated that roadside of Kano Metropolis was suffering from high contamination due to these metals in Dry Season, though ameliorated during Wet Season to moderate/considerable level of contamination.

4.5 CHEMICAL PARTITIONING OF METALS IN ROADSIDE SOILS

4.5.1 Results

The sequential extraction procedure and analysis measures the mobility and availability of heavy metals in soils depending on how the metals are associated with the components of the soils. The mobility and availability of metals serve to predict the behaviour of heavy metals in the soils. The chemical fractionation ($mgkg^{-1}$) patterns of Cd, Cr, Ni, Pb, Cu and Zn in the roadside soils of different grain sizes across the seasons are presented in Figs 4.1 – 4.24a-c (raw results are presented in Appendix I – XXIV). The results illustrated seasonal variations which are graphed as leaching percentage, reflecting individual fraction removal relative to the sum of all fractions from any given sample.

Statistical analysis revealed significant differences in fractions of metals ($p < 0.05$) among the sites across the seasons. A satisfactory agreement was found between the total of metals obtained by single determination and the summed totals of the sequential extraction. For most samples, a recovery judged comparing the summed total with the independent total metal analysis falls within 95 – 105%, and is similar to other reports (Chen *et al*., 1998; Lee *et al*., 2005). For all the studied metals across the seasons, high concentration were found in grain size 1400µm compared to 355µm and 150µm in soil fractions IV – VI (FIV – FVI) for all samples.

As shown in Fig. 4.1 – 4.4a-c, Cd exhibits a partitioning pattern (in percent) that varied from site-site across the seasons. For grain size 1400µm, range of ND (FI, FII, FIV-FVI) – 49.59% (FIII), ND (FI, FII, FIII - FVI) – 54.50% (FIII), ND (FI, FII, FIV - FVI) – 49.13% (FIII), and ND (FI, FVI) – 60.00% (FIII, FIV) were observed for Cool and Dry, Hot and Dry, Warm and Wet and Warm and Dry Seasons, respectively. The range ND (FI, FII, FVI) – 42.92% (FII), ND (FI, FII) – 44.90% (FIV), ND (FI, FII, FVI) – 45.19% (FII), and ND (FI - FVI) – 52.94% (FIII) was obtained for the same metal for 355µm across the four seasons, respectively. As for 150µm grain size, the ranges were ND (FI, FII, FVI) – 41.51% (FII), ND (FI, FII, FVI) – 44.46% (FIII), ND (FI, FII, FIII) – 44.18% (FII), and ND (FI, FII, FIV - FVI) – 50.00% (FIV) for Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons, respectively.

Generally, the results for Cd show no clear trend among the fractions as the surface area of samples increases. However, the dominant fractions for Cd across the seasons were carbonate bound (Site 3, 4, 5, 7, 9 and 10), Fe-Mn Oxide bound (Site 1, 2 and 8), organic bound (Site 6) and residual (control) for samples with grain size 1400µm. For samples of grain size 355µm, dominant fractions were exchangeable (Site 7), organic bound (Site 6 and 10), Fe-Mn oxide bound (Site 3), carbonate bound (Site 4 and 5), water soluble (Site 9) and residual (Site 8 and control).

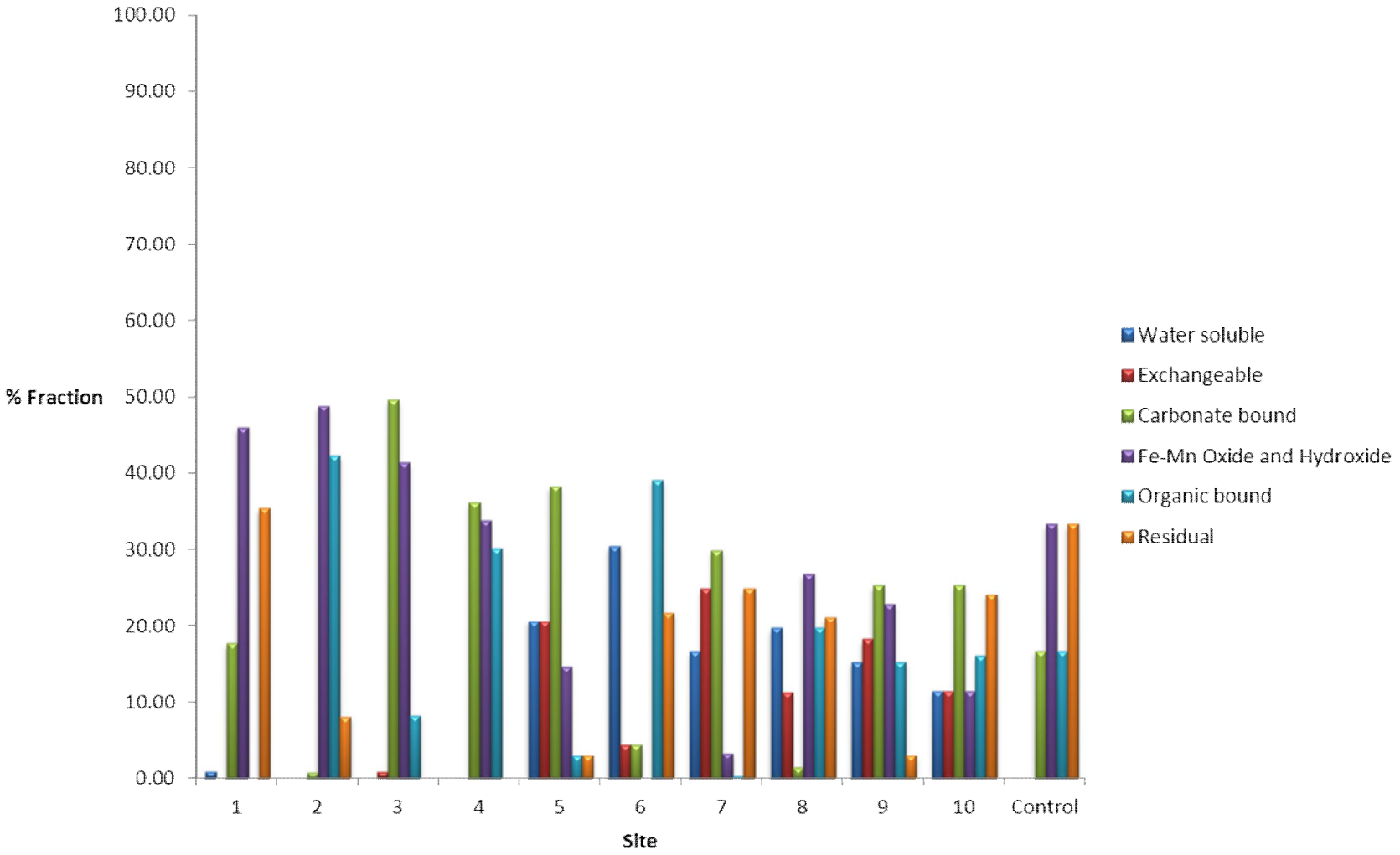


Fig. 4.1a. Percentage Cd in each operationally fraction of roadside soils particle size 1400µm (Cool and Dry Season).

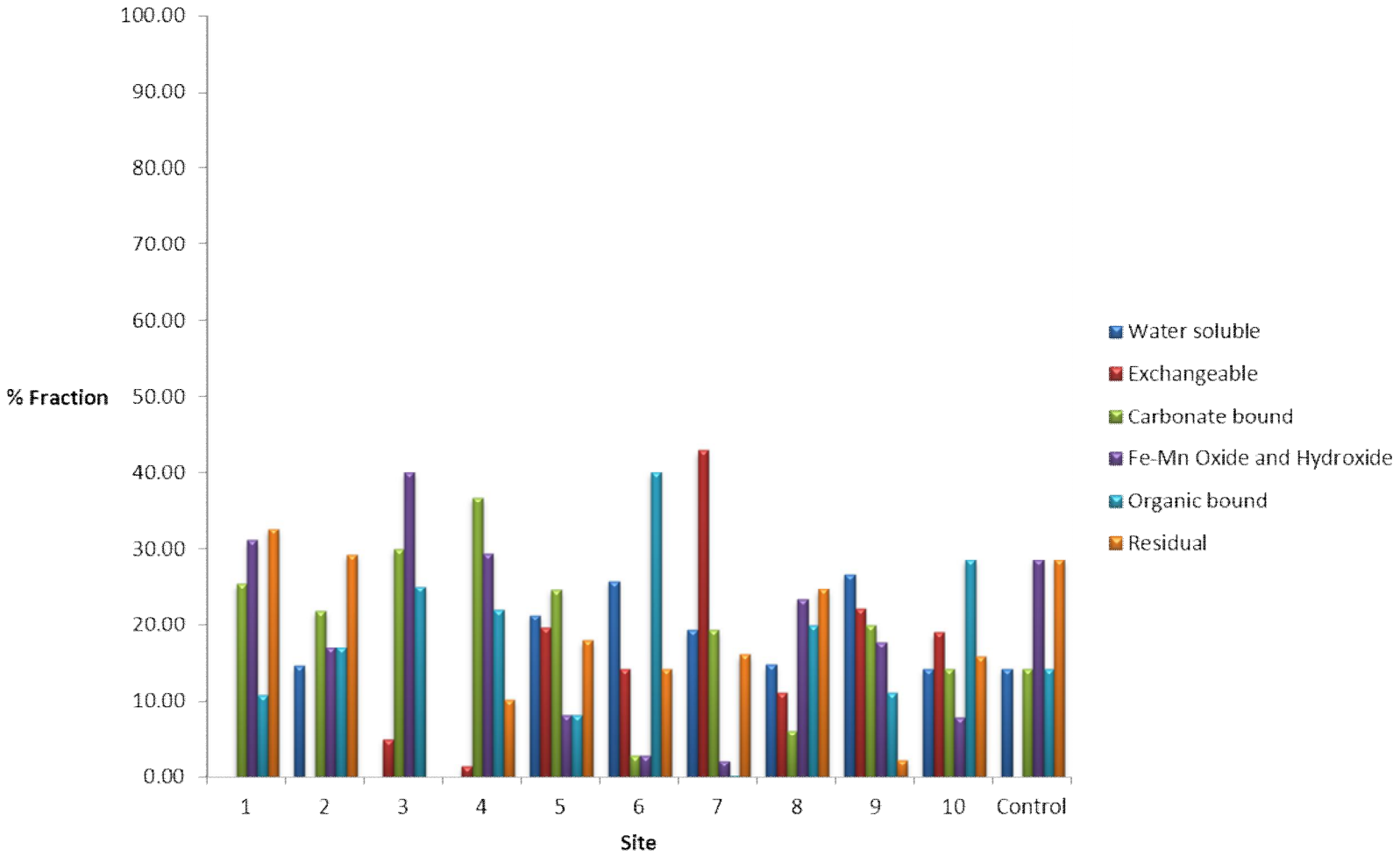


Fig. 4.1b. Percentage Cd in each operationally fraction of roadside soils particle size 355µm (Cool and Dry Season).

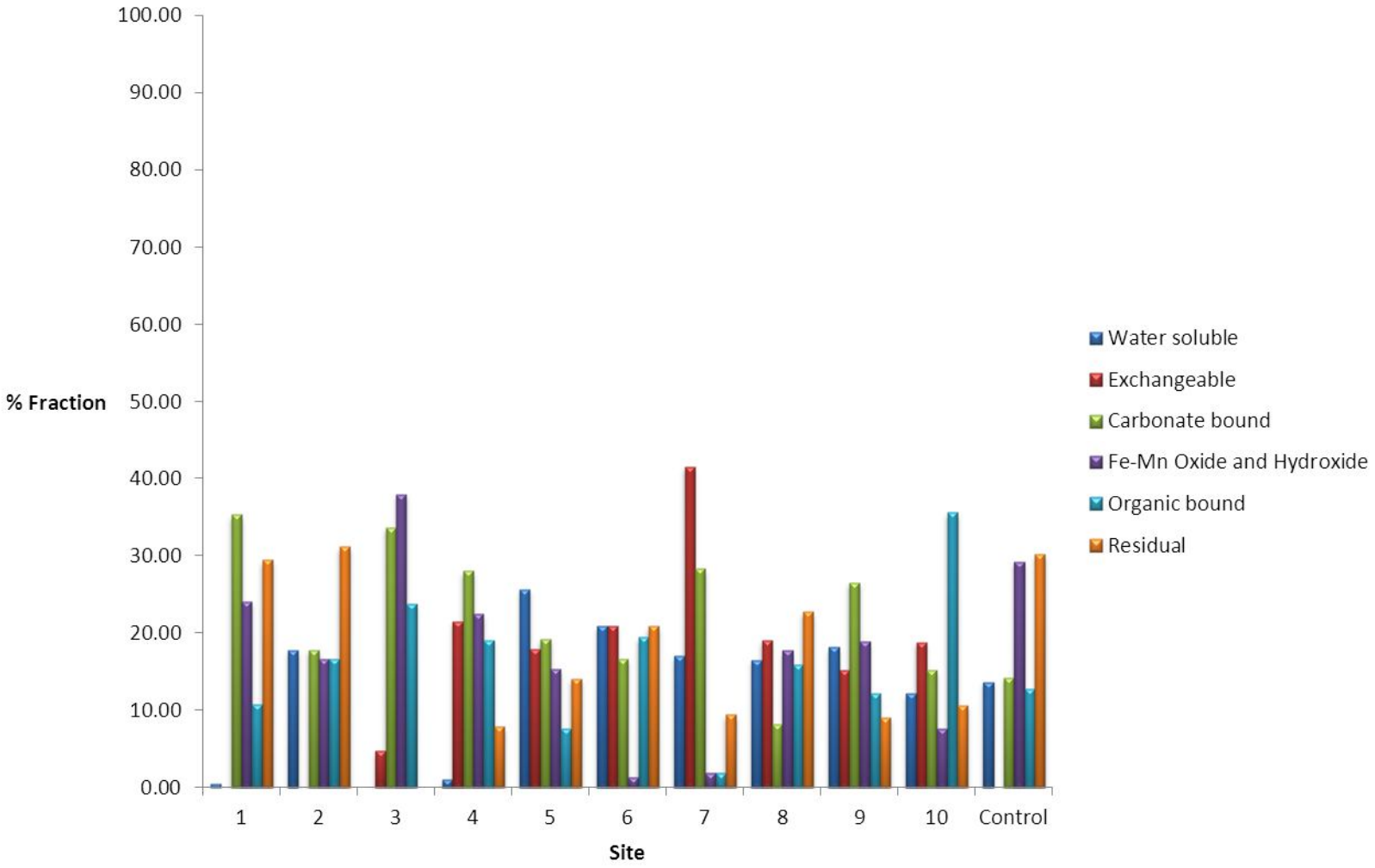


Fig. 4.1c. Percentage Cd in each operationally fraction of roadside soils particle size 150µm (Cool and Dry Season).

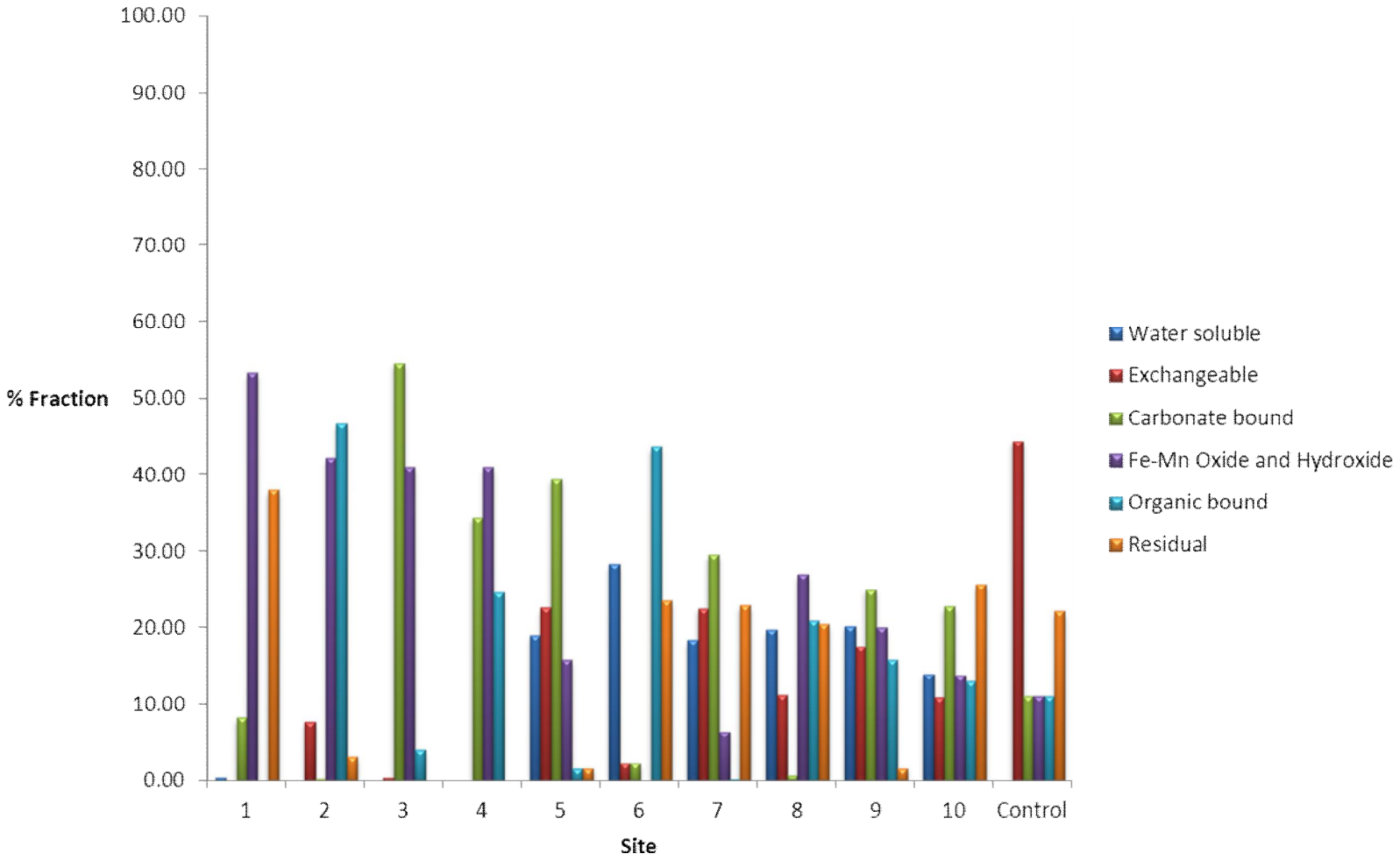


Fig. 4.2a. Percentage Cd in each operationally fraction of roadside soils particle size 1400µm (Hot and Dry Season).

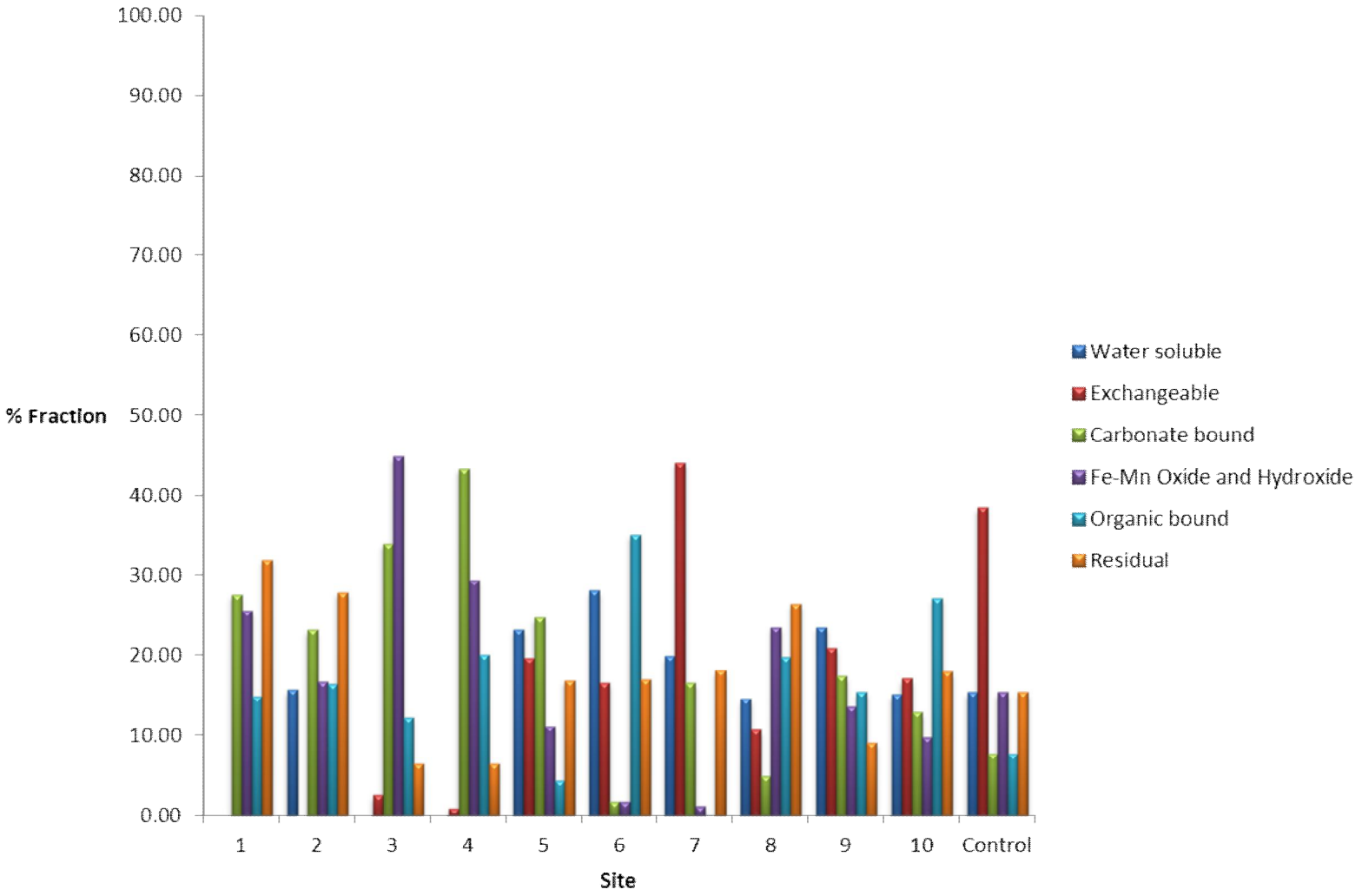


Fig. 4.2b. Percentage Cd in each operationally fraction of roadside soils particle size 355µm (Hot and Dry Season).

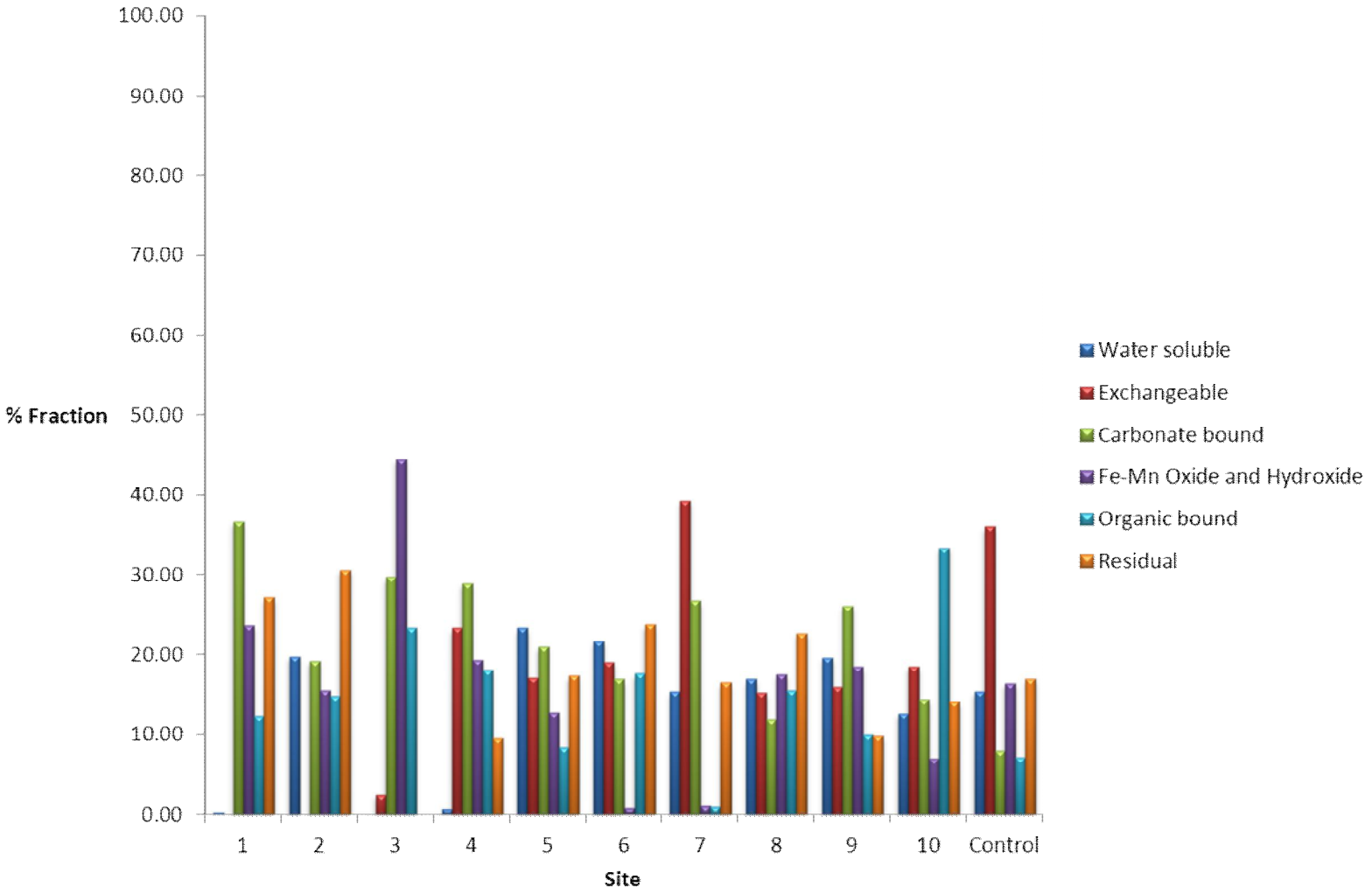


Fig. 4.2c. Percentage Cd in each operationally fraction of roadside soils particle size 150µm (Hot and Dry Season).

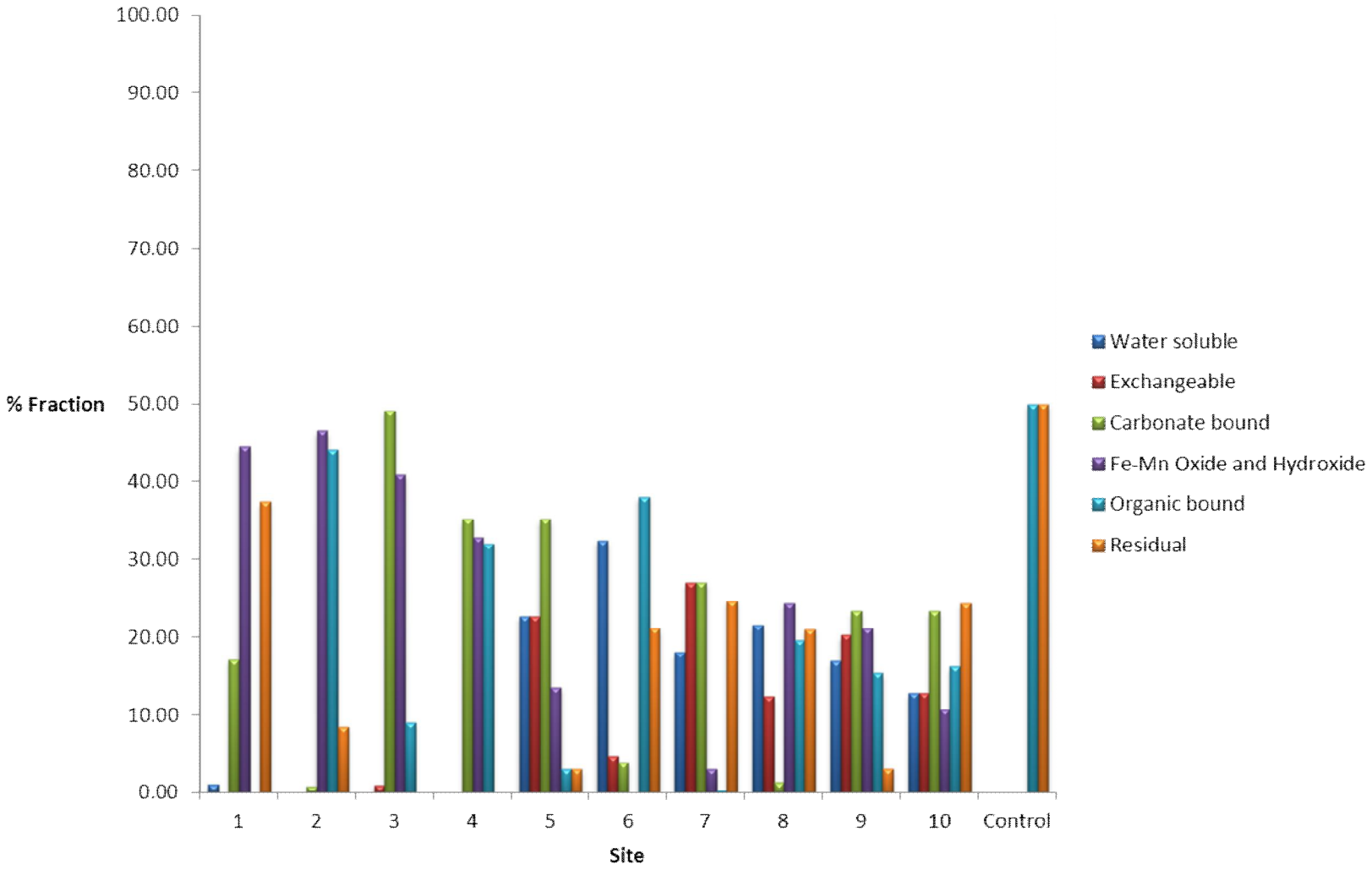


Fig. 4.3a. Percentage Cd in each operationally fraction of roadside soils particle size 1400µm (Warm and Wet Season).

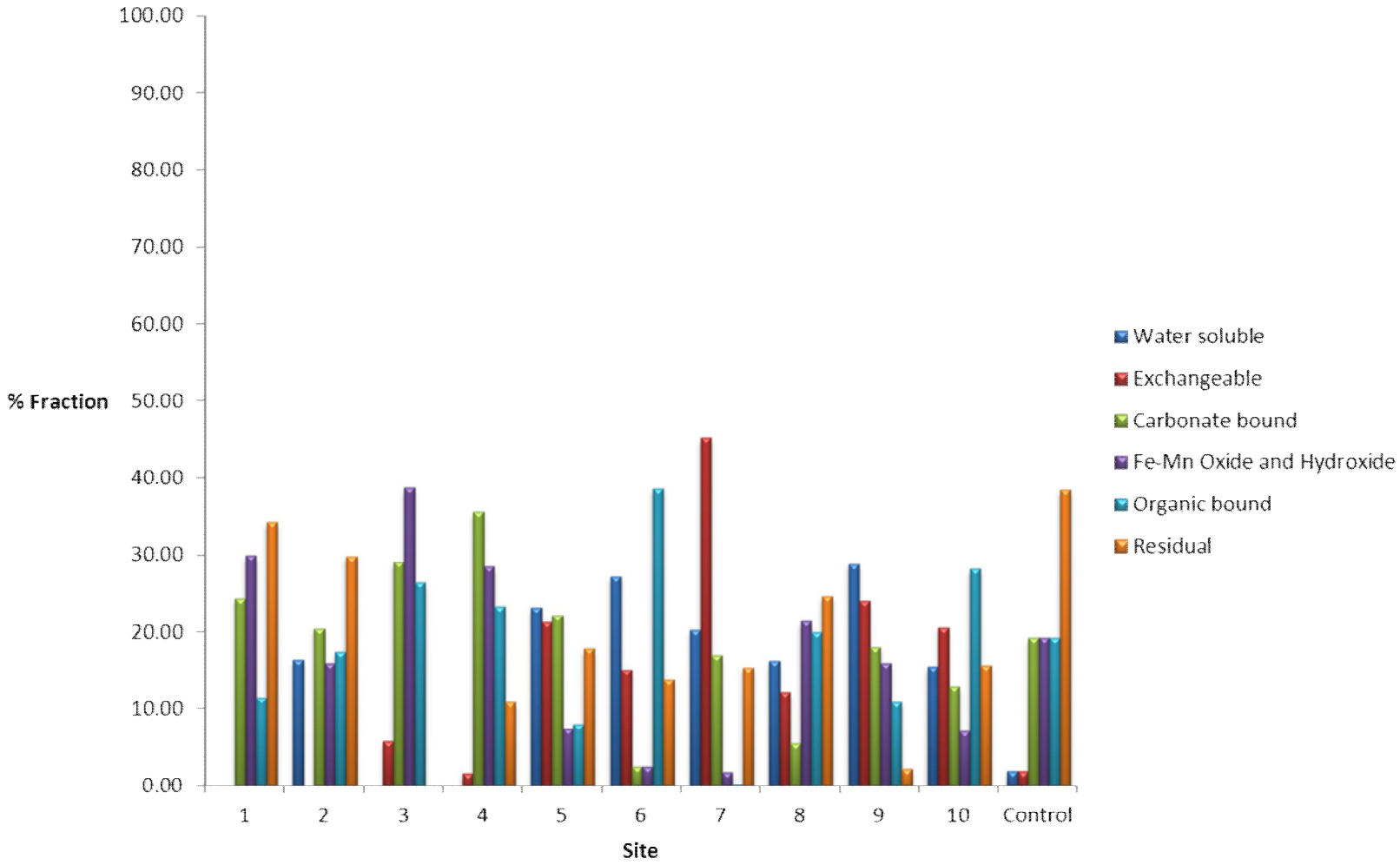


Fig. 4.3b. Percentage Cd in each operationally fraction of roadside soils particle size 355µm (Warm and Wet Season).

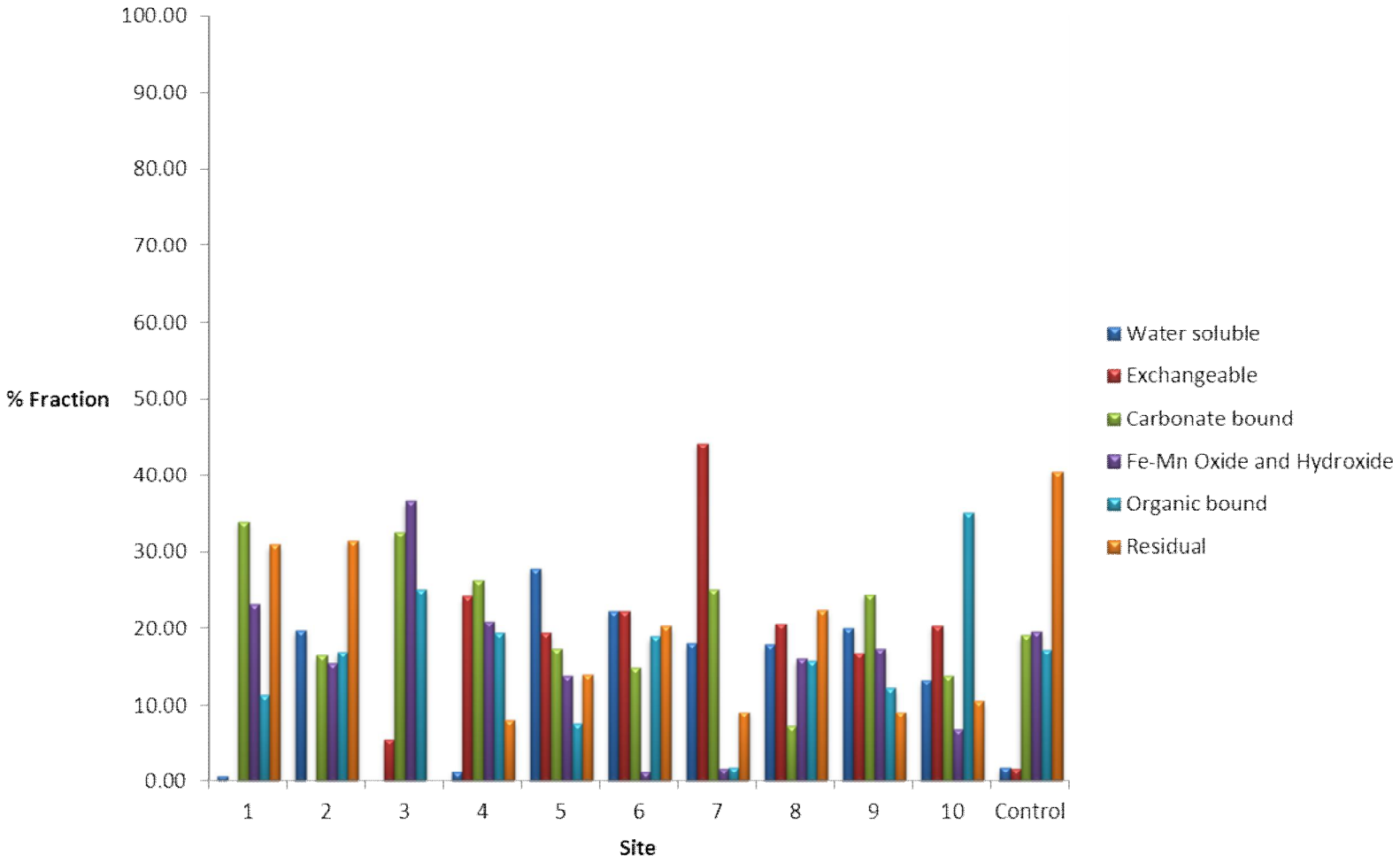


Fig. 4.3c. Percentage Cd in each operationally fraction of roadside soils particle size 150µm (Warm and Wet Season).

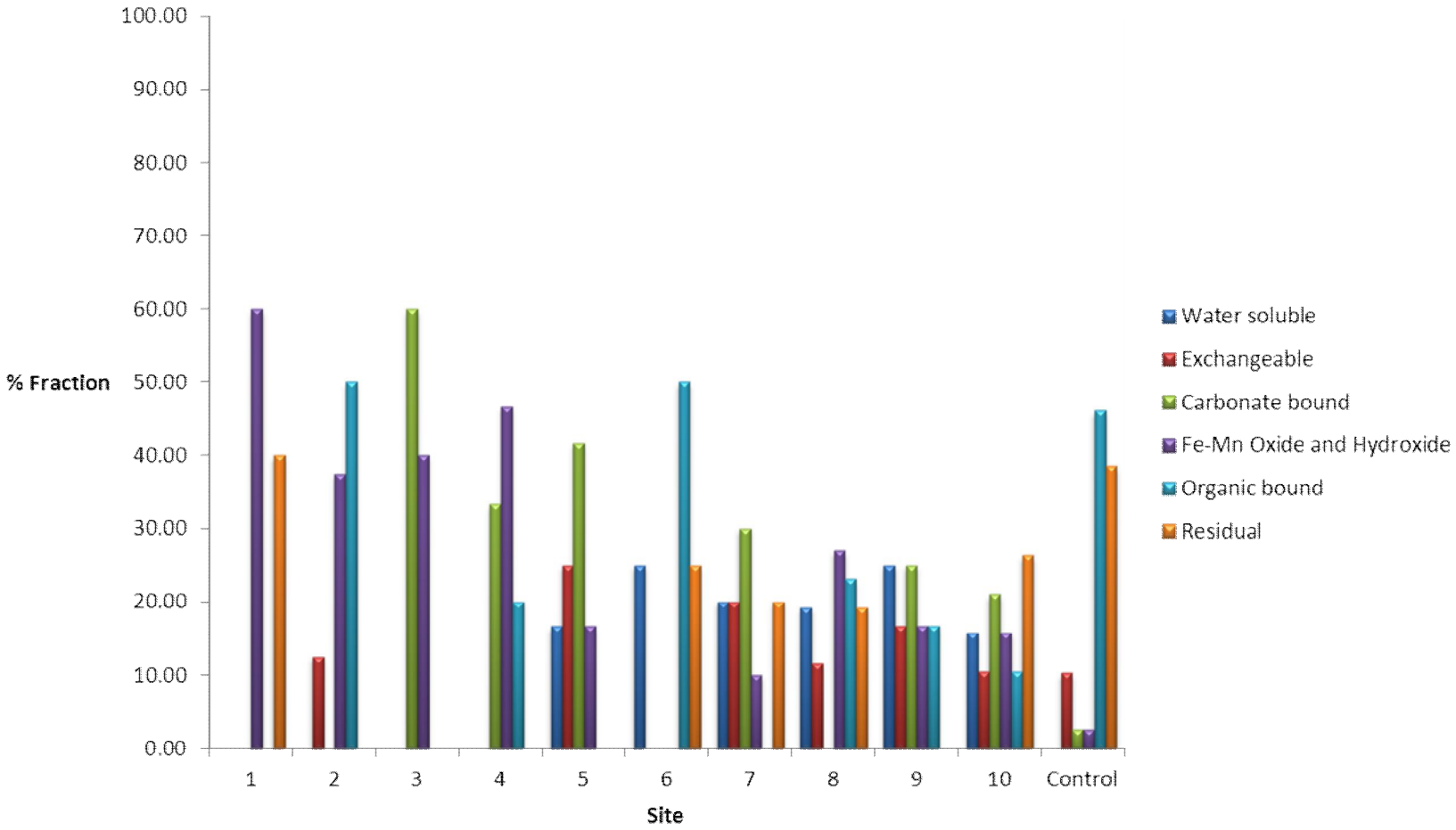


Fig. 4.4a. Percentage Cd in each operationally fraction of roadside soils particle size 1400µm (Warm and Dry Season).

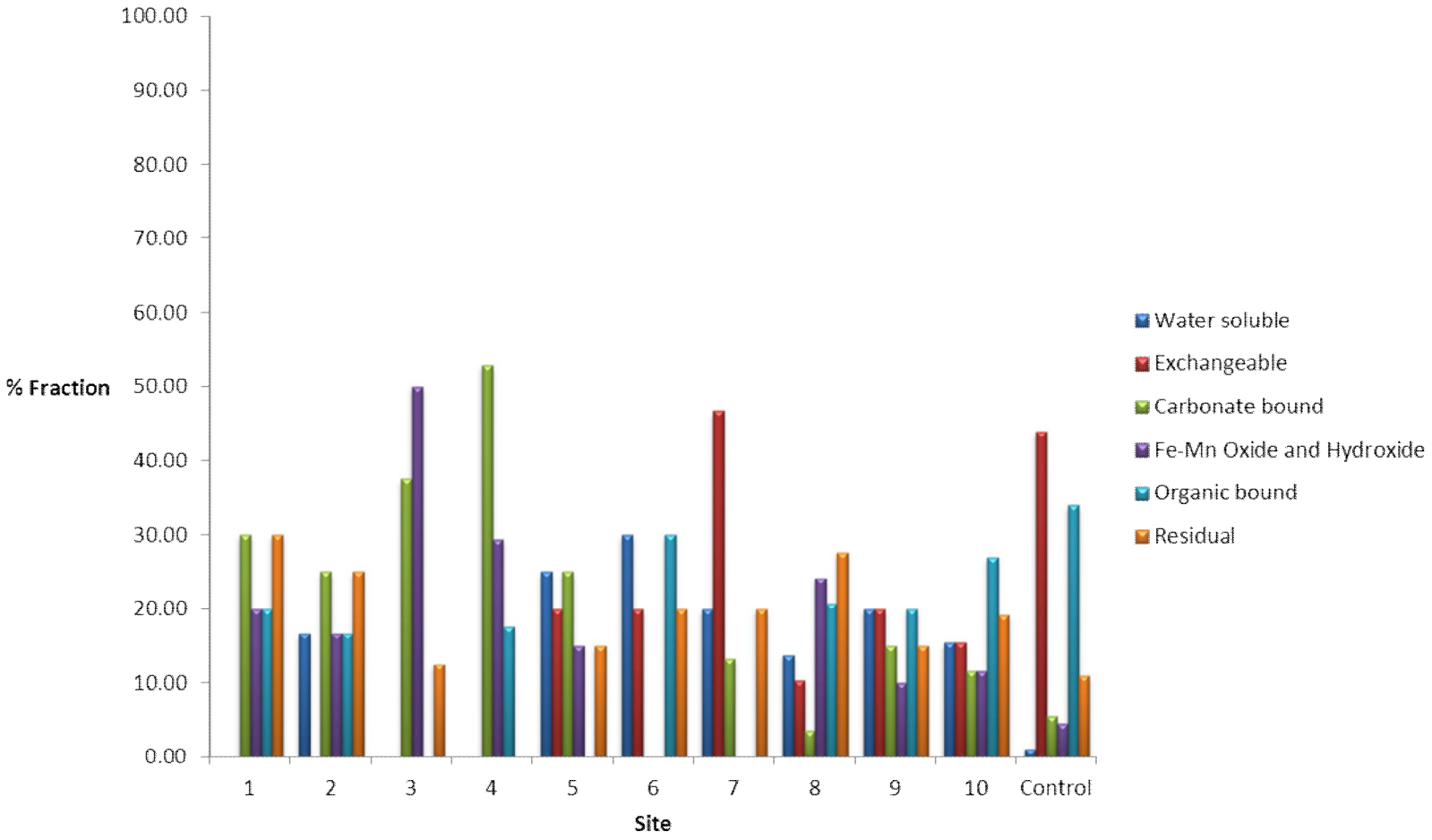


Fig. 4.4b. Percentage Cd in each operationally fraction of roadside soils particle size 355µm (Warm and Dry Season).

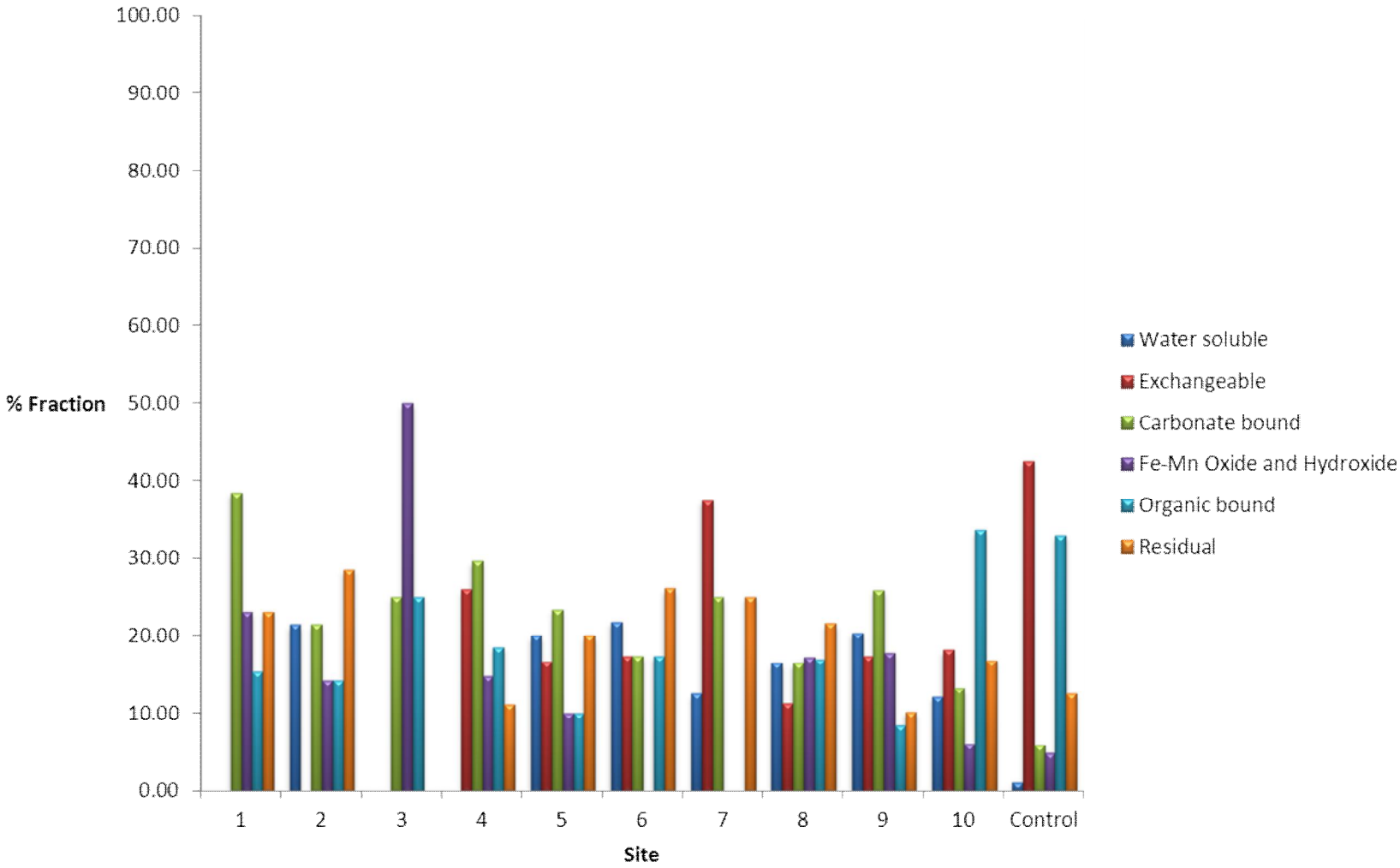


Fig. 4.4c. Percentage Cd in each operationally fraction of roadside soils particle size 150µm (Warm and Dry Season).

Similarly, for samples of grain size 150µm, dominant fractions were exchangeable (Site 6 and 7), Fe-Mn oxide bound (Site 3), carbonate bound (Site 1, 4 and 9), organic bound (Site 10), residual (Site 2, 8 and control), and water soluble (Site 5). Across the Seasons and Sites there were variations in percentages of the fractions. However, it was observed that Cd was generally localized in the non-residual fractions (sum of water soluble, exchangeable, carbonate bound, Fe-Mn oxide and hydroxide and organic bound) at all the sites and across the seasons.

Geochemical partitioning of Cr in the roadside soils across the seasons is shown in Figs. 4.5 – 4.8a-c. For grain size 1400µm, the percentage were ND (FI - FV) – 92.93% (FVI), ND (FI - FV) – 94.06% (FVI), ND (FI - FV) – 92.79% (FVI) and ND (FI - FV) – 100% (FV and FVI) for Cool and Dry Season, Hot and Dry Season, Warm and Wet Season and Warm and Dry Season, respectively. The ranges ND (FI - FV) – 88.80% (FIV), ND (FI - FV) – 87.76% (FIV), ND (FI - FV) – 87.72% (FIV) and ND (FI - FV) – 86.91% (FIV) were obtained for samples with 355µm grain size across the four seasons in the same sequence as for 1400µm, respectively. For samples with 150µm grain size, the range of ND (FI, FIV and FV) – 90.86% (FVI), ND (FI, FIV and FV) – 92.73% (FVI), ND (FI, FIV and FV) – 90.90% (FVI) and ND (FI - FV) – 93.93% (FVI) for Cool and Dry Season, Hot and Dry Season, Warm and Wet Season, and Warm and Dry Season were obtained, respectively.

As shown in the bar graphs, the dominant fractions for sample with 1400µm grain size were residual (Site 1, 3, 5, 7, 8, 9 and 10), Fe-Mn oxide (Site 2, 4 and 6). For samples with grain size 355µm the dominant fractions were Fe-Mn oxide (Site 2, 6 and 7), residual (Site 1, 3, 4, 5, 8 and 9) and carbonate bound (control). Similar to 1400µm, the highest fractions in samples with grain size 150µm were residual (1, 2, 3, 4, 5, 6, 8 and 9), organic

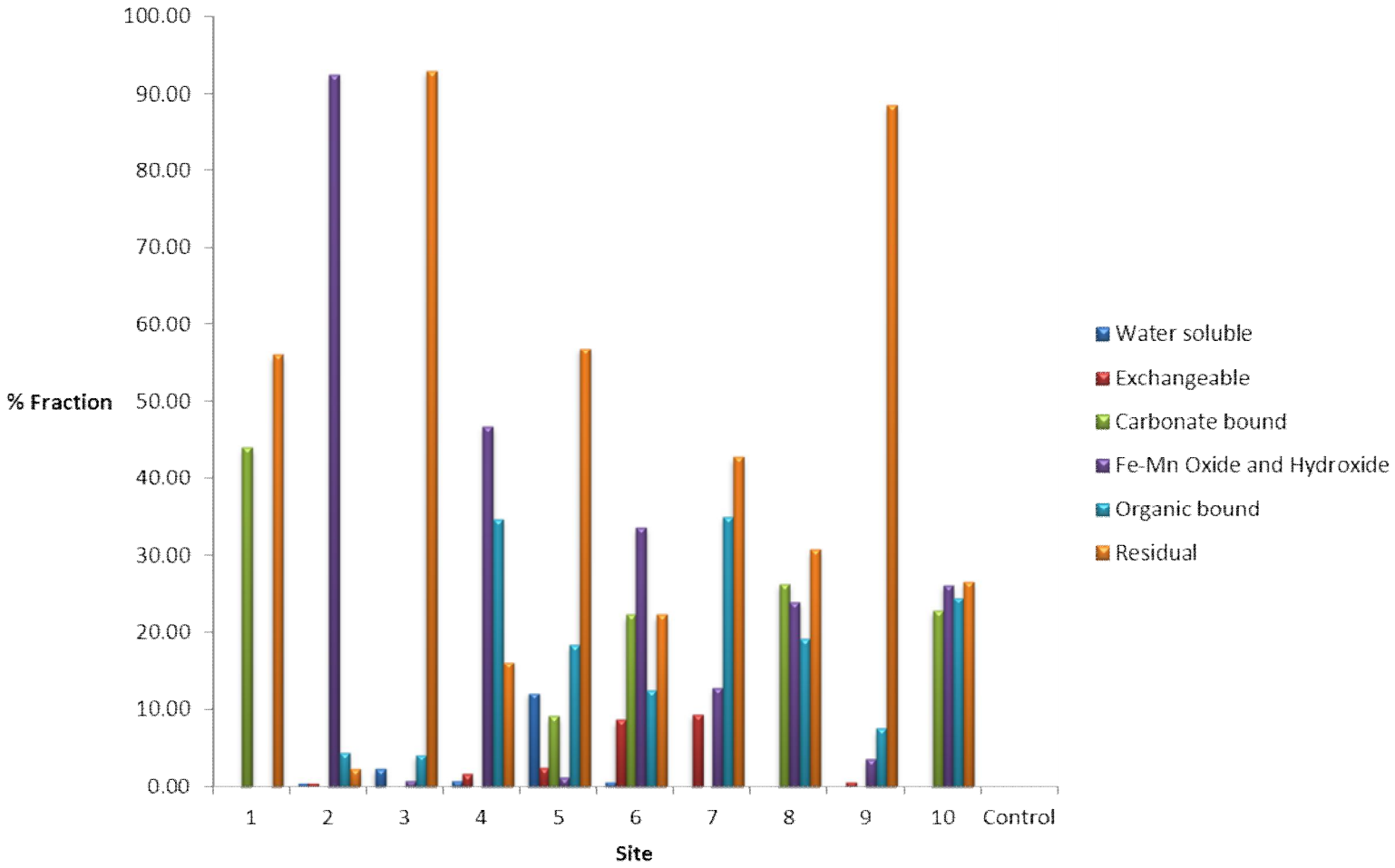


Fig. 4.5a. Percentage Cr in each operationally fraction of roadside soils particle size 1400µm (Cool and Dry Season).

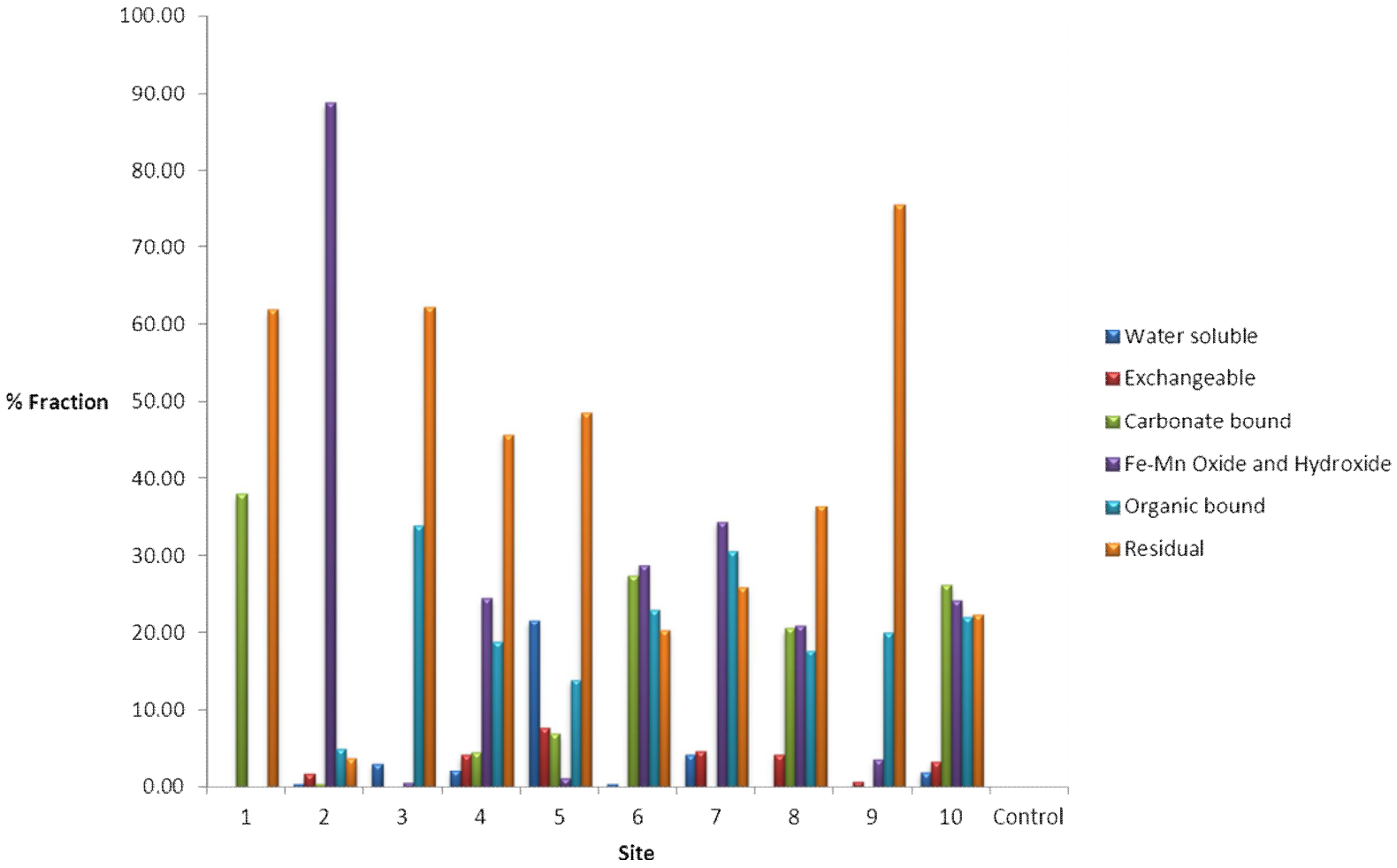


Fig. 4.5b. Percentage Cr in each operationally fraction of roadside soils particle size 355µm (Cool and Dry Season).

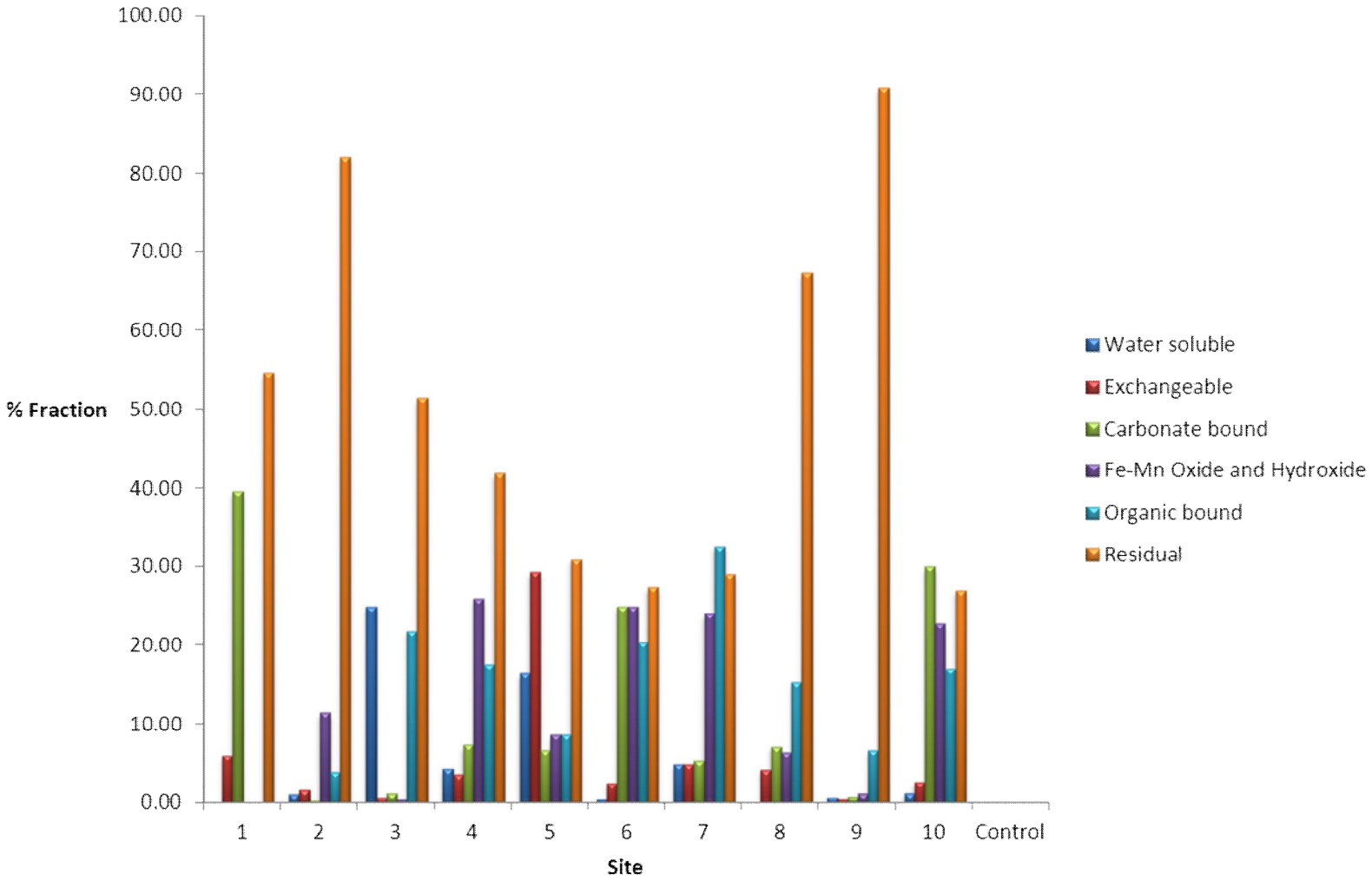


Fig. 4.5c Percentage Cr in each operationally fraction of roadside soils particle size 150µm (Cool and Dry Season).

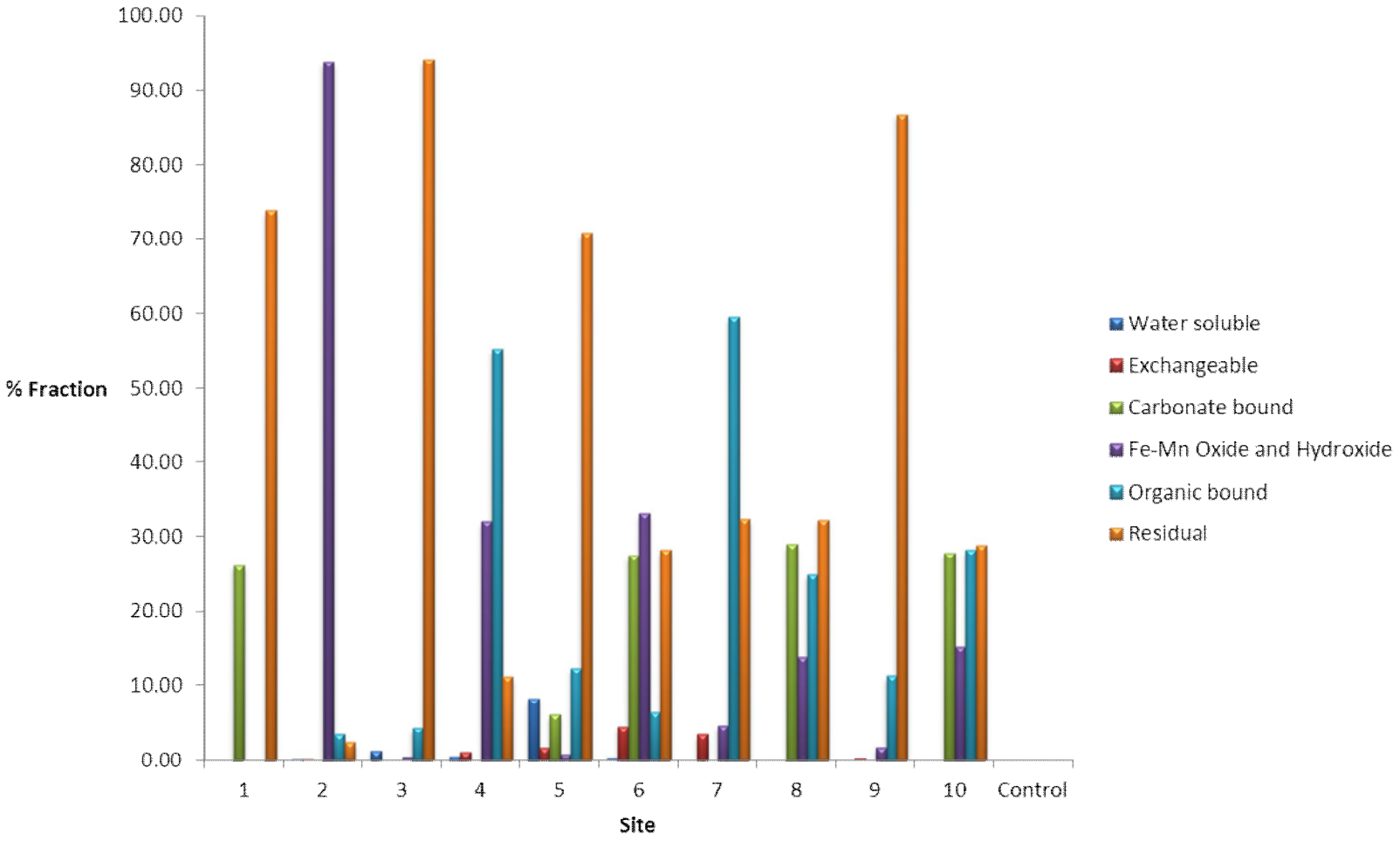


Fig. 4.6a Percentage Cr in each operationally fraction of roadside soils particle size 1400µm (Hot and Dry Season).

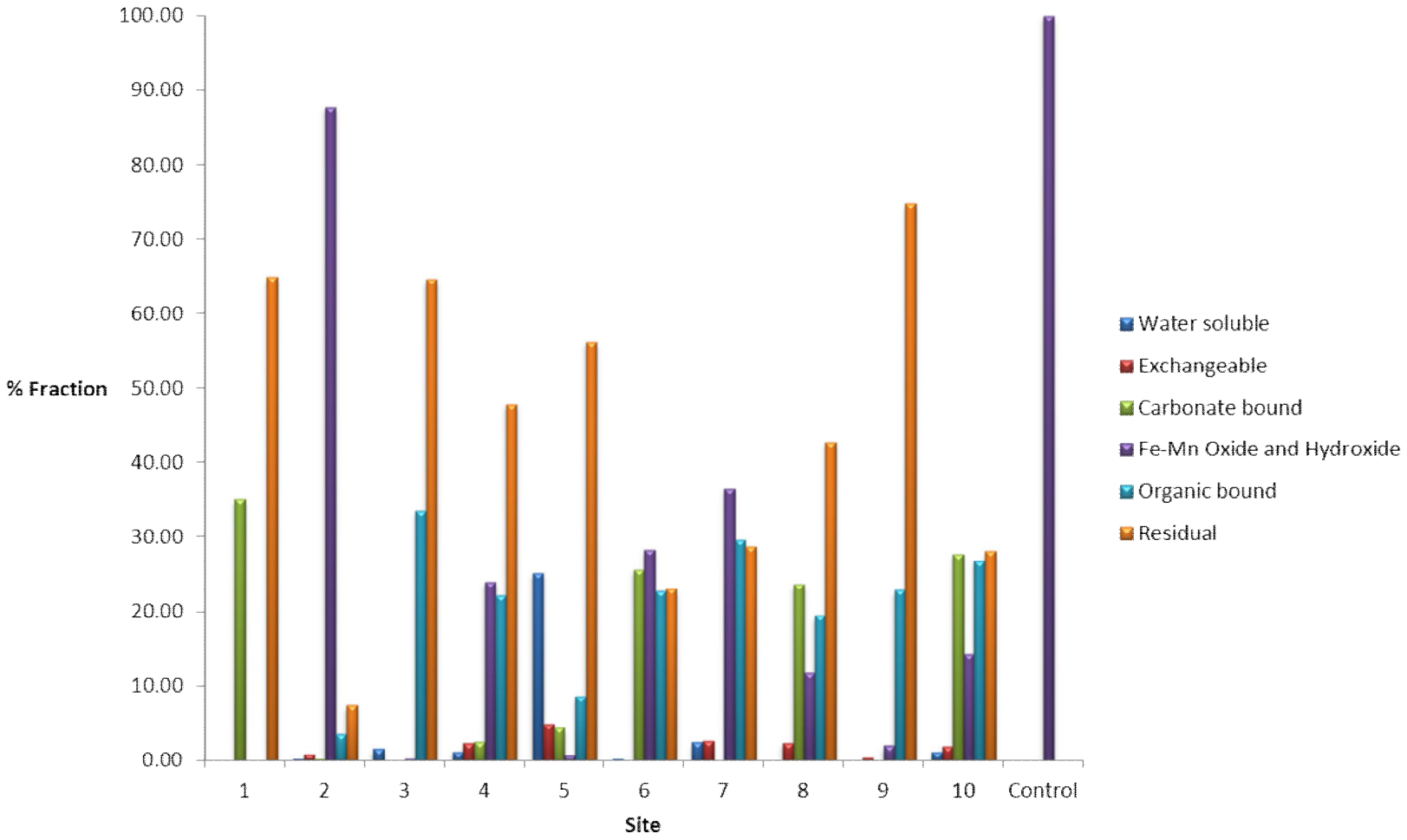


Fig. 4.6b Percentage Cr in each operationally fraction of roadside soils particle size 355µm (Hot and Dry Season).

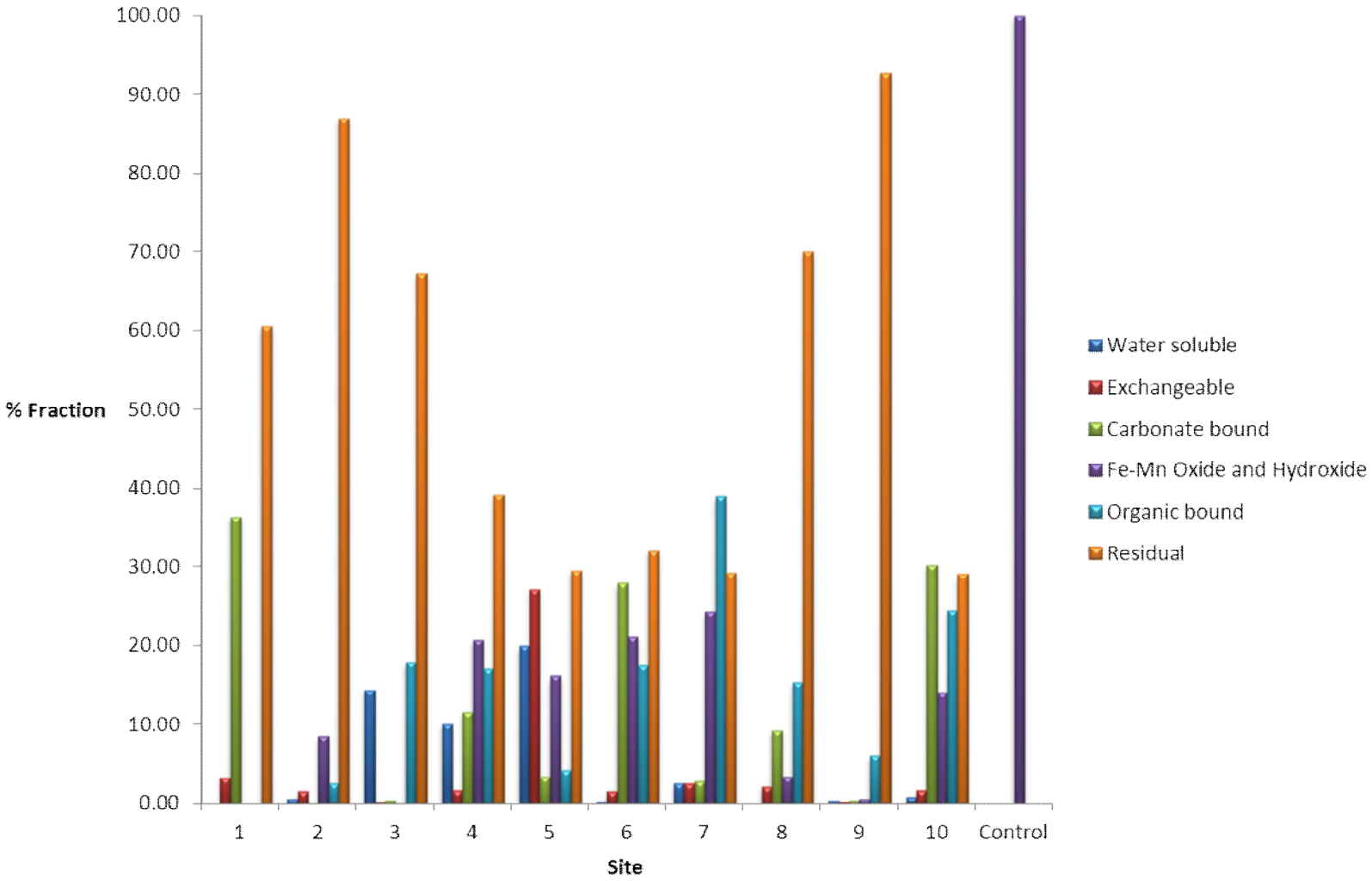


Fig. 4.6c. Percentage Cr in each operationally fraction of roadside soils particle size 150µm (Hot and Dry Season).

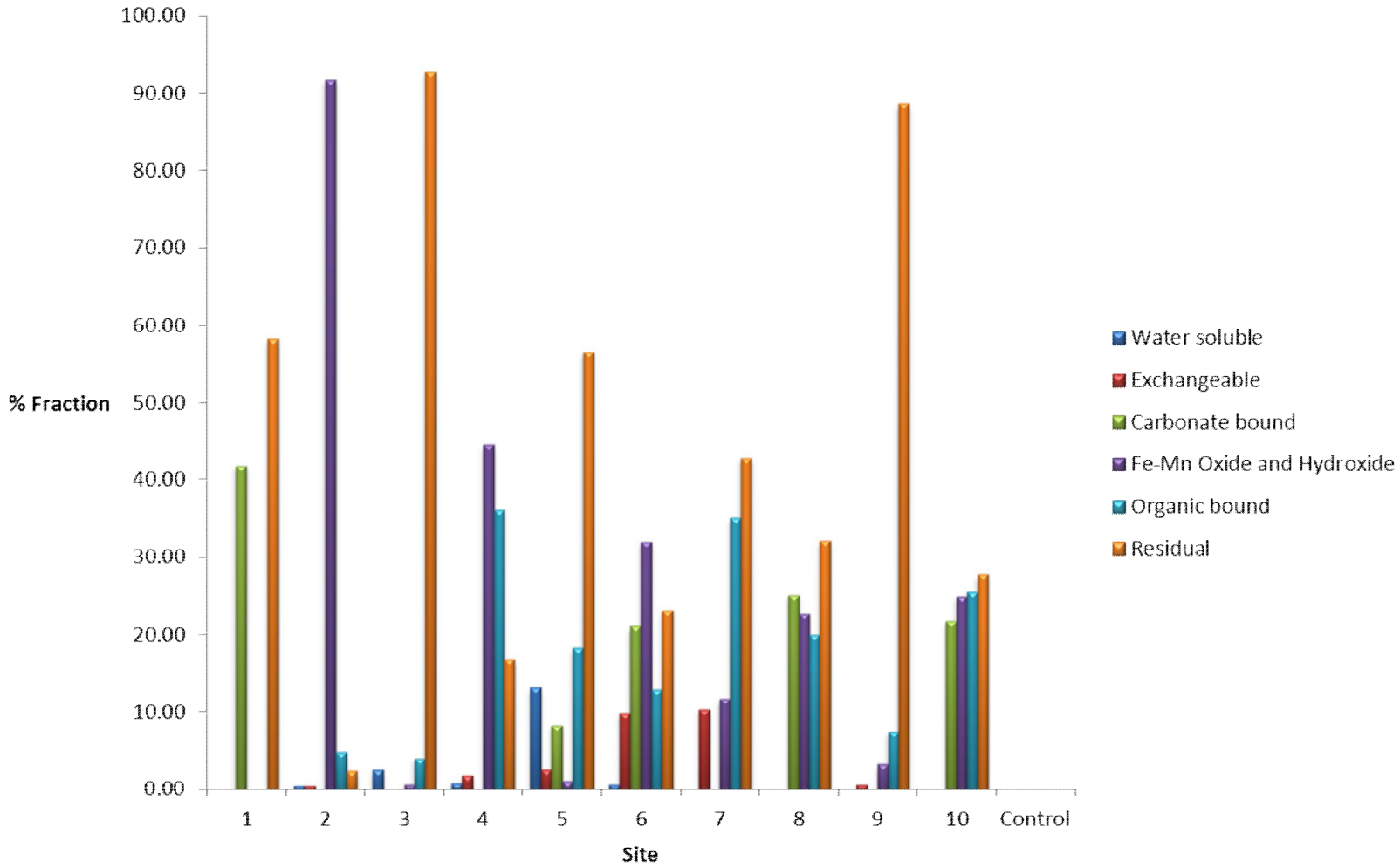


Fig. 4.7a. Percentage Cr in each operationally fraction of roadside soils particle size 1400µm (Warm and Wet Season).

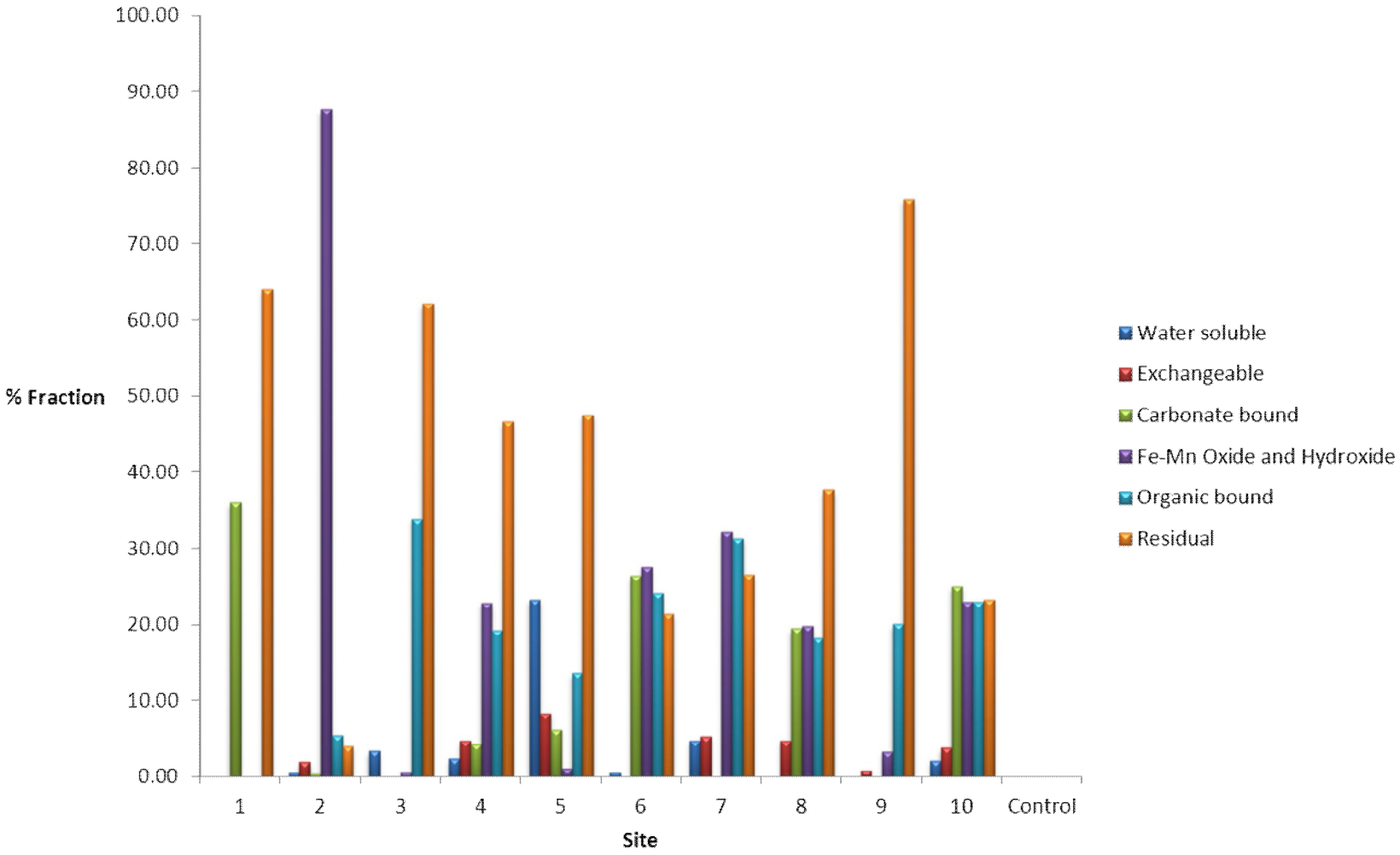


Fig. 4.7b. Percentage Cr in each operationally fraction of roadside soils particle size 355µm (Warm and Wet Season).

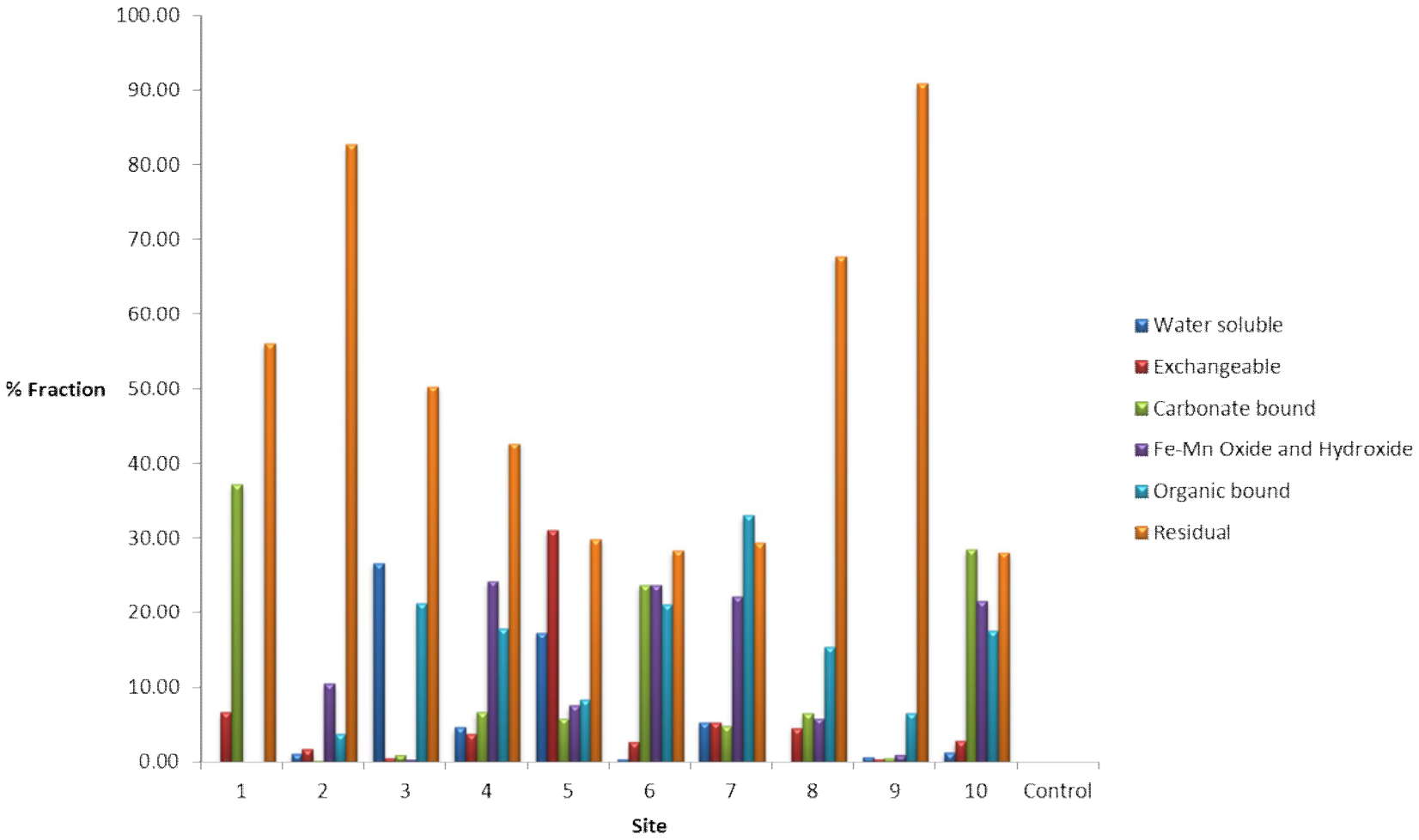


Fig. 4.7c. Percentage Cr in each operationally fraction of roadside soils particle size 150µm (Warm and Wet Season).

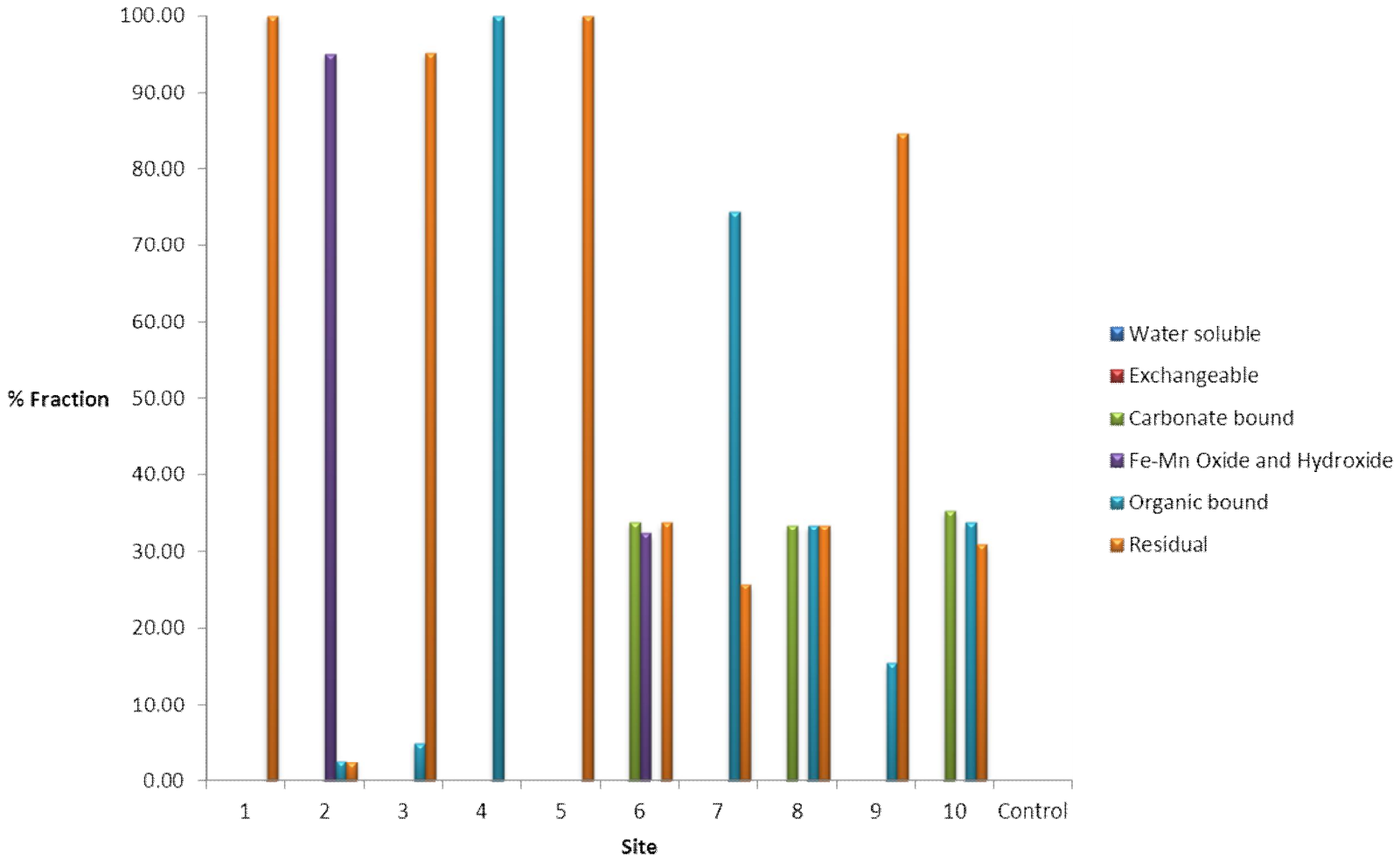


Fig. 4.8a. Percentage Cr in each operationally fraction of roadside soils particle size 1400µm (Warm and Dry Season).

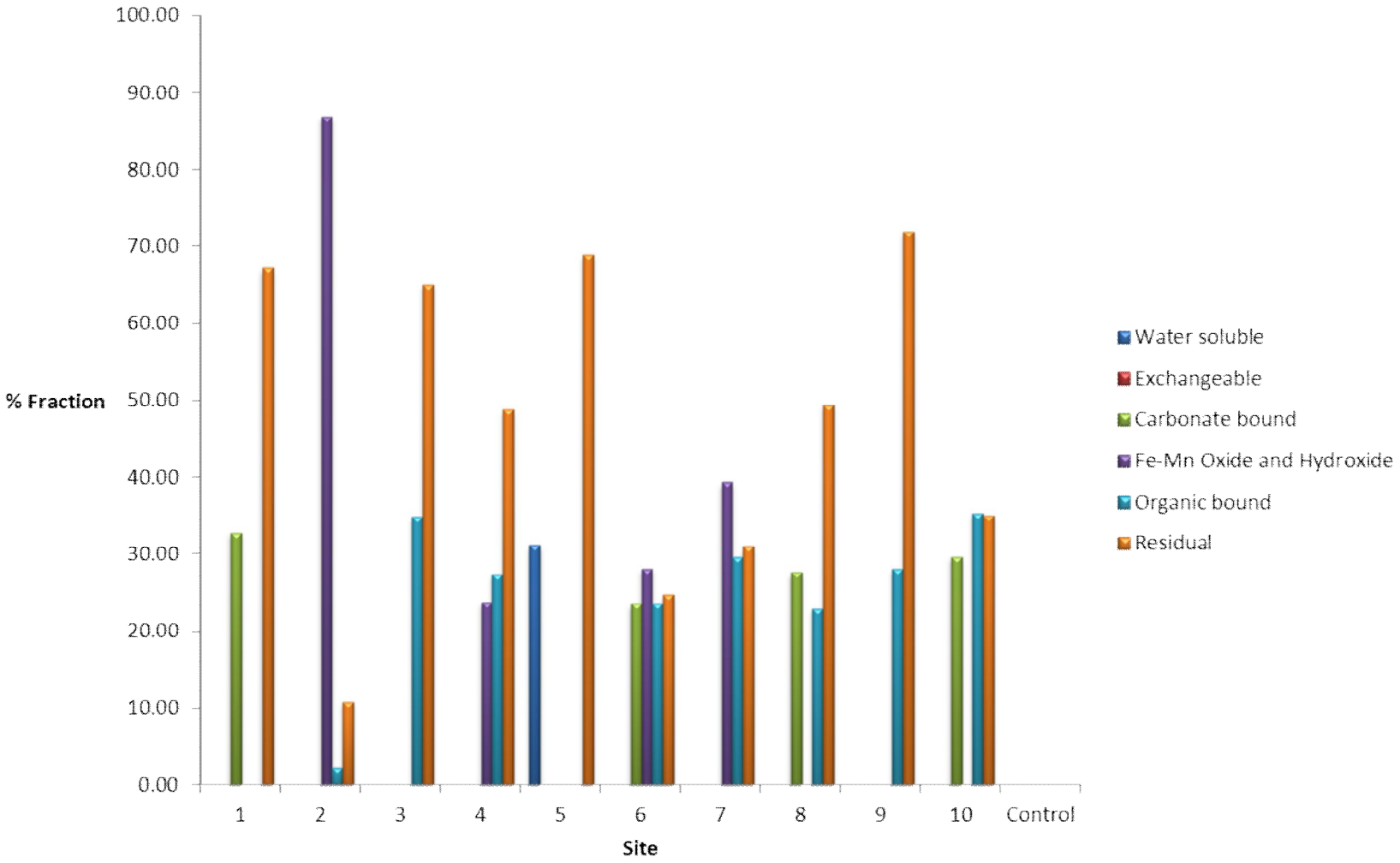


Fig. 4.8b. Percentage Cr in each operationally fraction of roadside soils particle size 355µm (Warm and Dry Season).

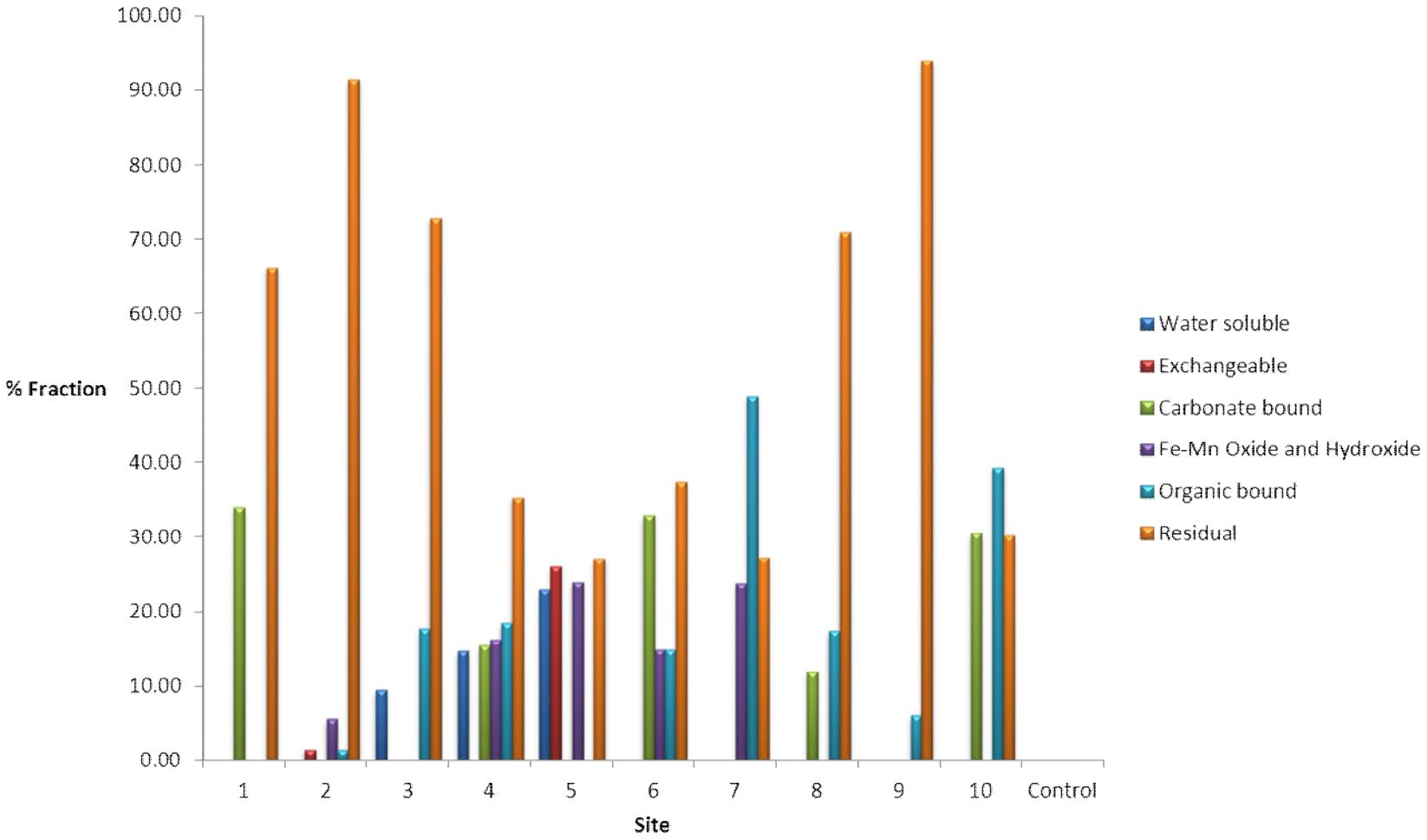


Fig. 4.8c. Percentage Cr in each operationally fraction of roadside soils particle size 150µm (Warm and Dry Season).

bound (Site 7) and carbonate bound (Site 10). Generally, the results revealed that more sites across the seasons had Cr concentrated in the residual fraction followed by Fe-Mn oxide and hydroxide fractions then organic fraction. This indicated that Cr may not be readily available at some sites compared to others.

The percentage fractions of Ni in the roadside soils across the seasons are shown in Figs. 4.9 – 4.12a-c. For samples with 1400µm grain size, the range of ND (FV) – 56.54% (FI), ND (FV) – 58.43% (FI), ND (FV) – 59.29% (FI) and ND (FI - FV) – 71.68% (FVI) for Cool and Dry, Hot and Dry, Warm and Wet and Warm and Dry Season, respectively, were observed. The range of ND (FV) – 45.55% (FIV), ND (FV) – 46.87% (FIV), ND (FV) – 43.42% (FIV) and ND (FI – FIII and FV) – 48.82% (FIV) were also observed for samples with 355µm grain size during Cool and Dry, Hot and Dry, Warm and Wet and Warm and Dry Seasons, respectively. For samples with 150µm grain size, the ranges were 0.89 (FV) – 48.49% (FV), 0.43 (FV) – 48.77% (FV), 0.94 (FV) – 48.79% (FV) and ND (FII and FV) – 52.16% (FV) for Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry season respectively. As shown in the bar graphs, dominance of Ni was found in Fe-Mn oxide (Site 2) and organic bound (Site 10) for samples with 355µm and 150µm grain size, respectively, across the seasons. it could be noticed that samples with 1400µm grain size had the highest fractions in water soluble phase (Site 1) except for Warm and Dry season with highest fraction in residual phase (Site 6).

As shown in Figs. 4.13 – 4.16a-c, Pb fractions in the soil were in the range ND (FI) – 71.99% (FVI), ND (FII) – 79.47% (FVI), ND (FI) – 71.96% (FVI) and ND (FI - FVI) – 90.91% (FV) for samples with 1400µm grain size during Cool and Dry, Hot and Dry, Warm and Wet and Warm and Dry Season, respectively.

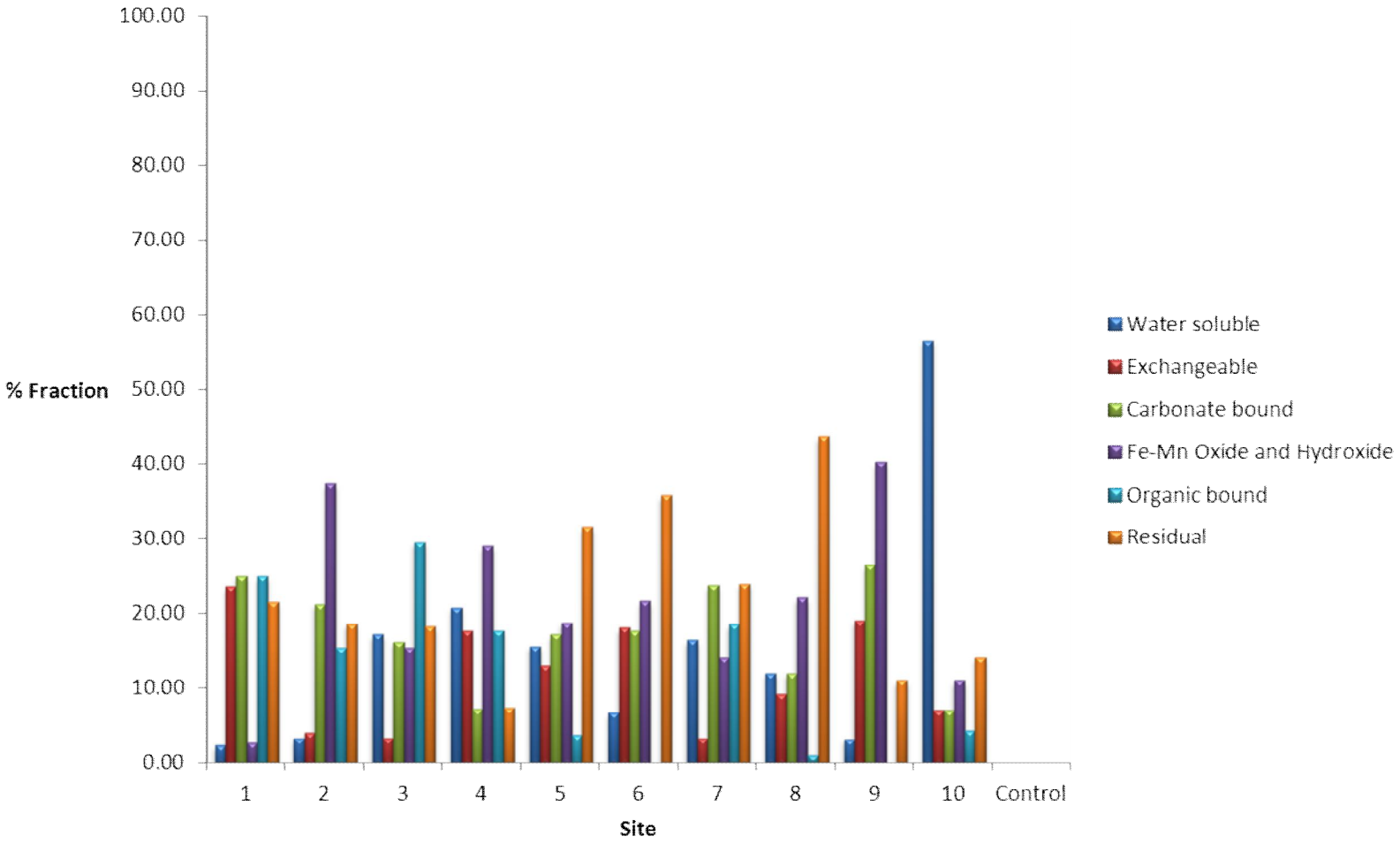


Fig. 4.9a. Percentage Ni in each operationally fraction of roadside soils particle size 1400µm (Cool and Dry Season).

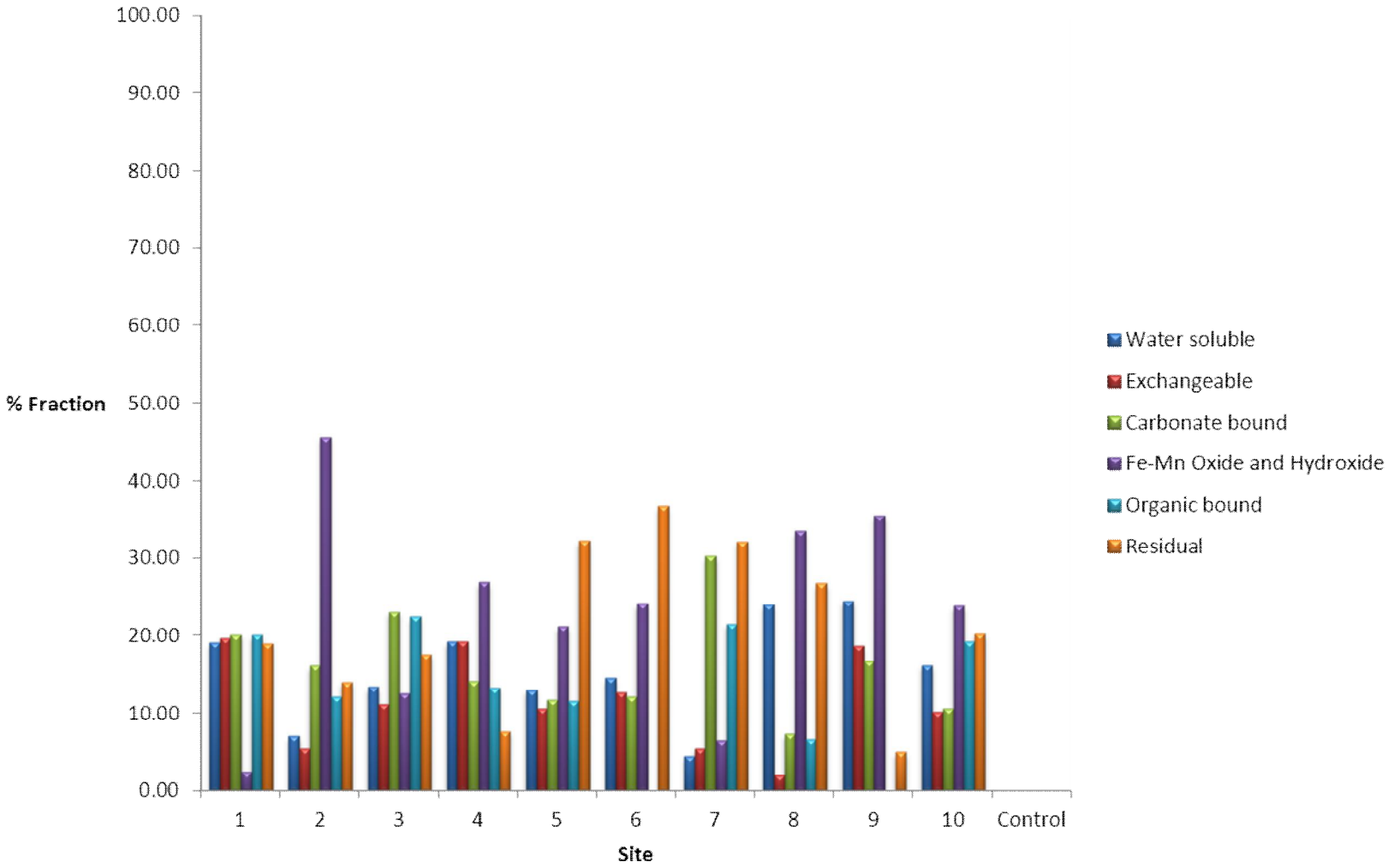


Fig. 4.9b. Percentage Ni in each operationally fraction of roadside soils particle size 355µm (Cool and Dry Season).

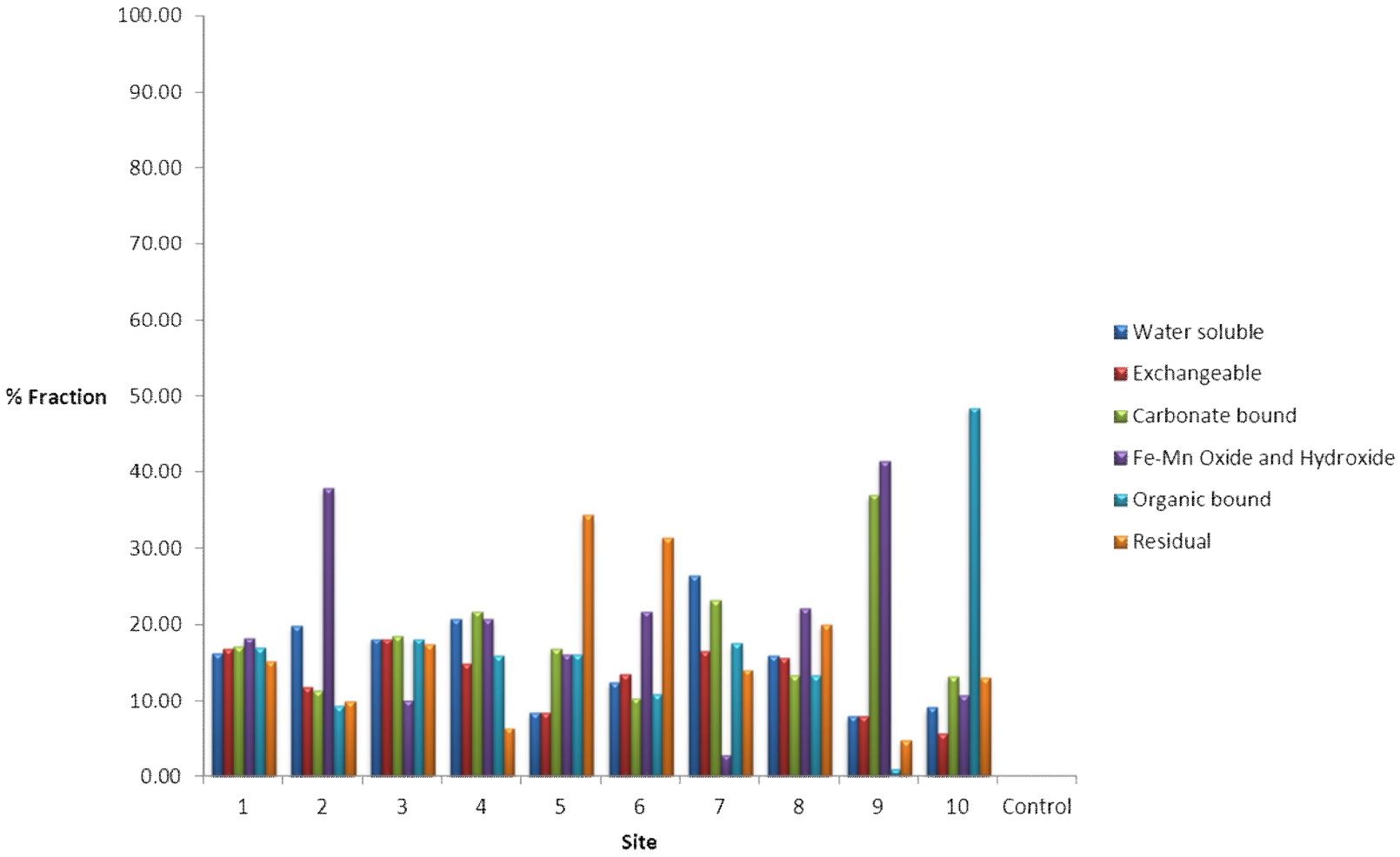


Fig. 4.9c. Percentage Ni in each operationally fraction of roadside soils particle size 150µm (Cool and Dry Season).

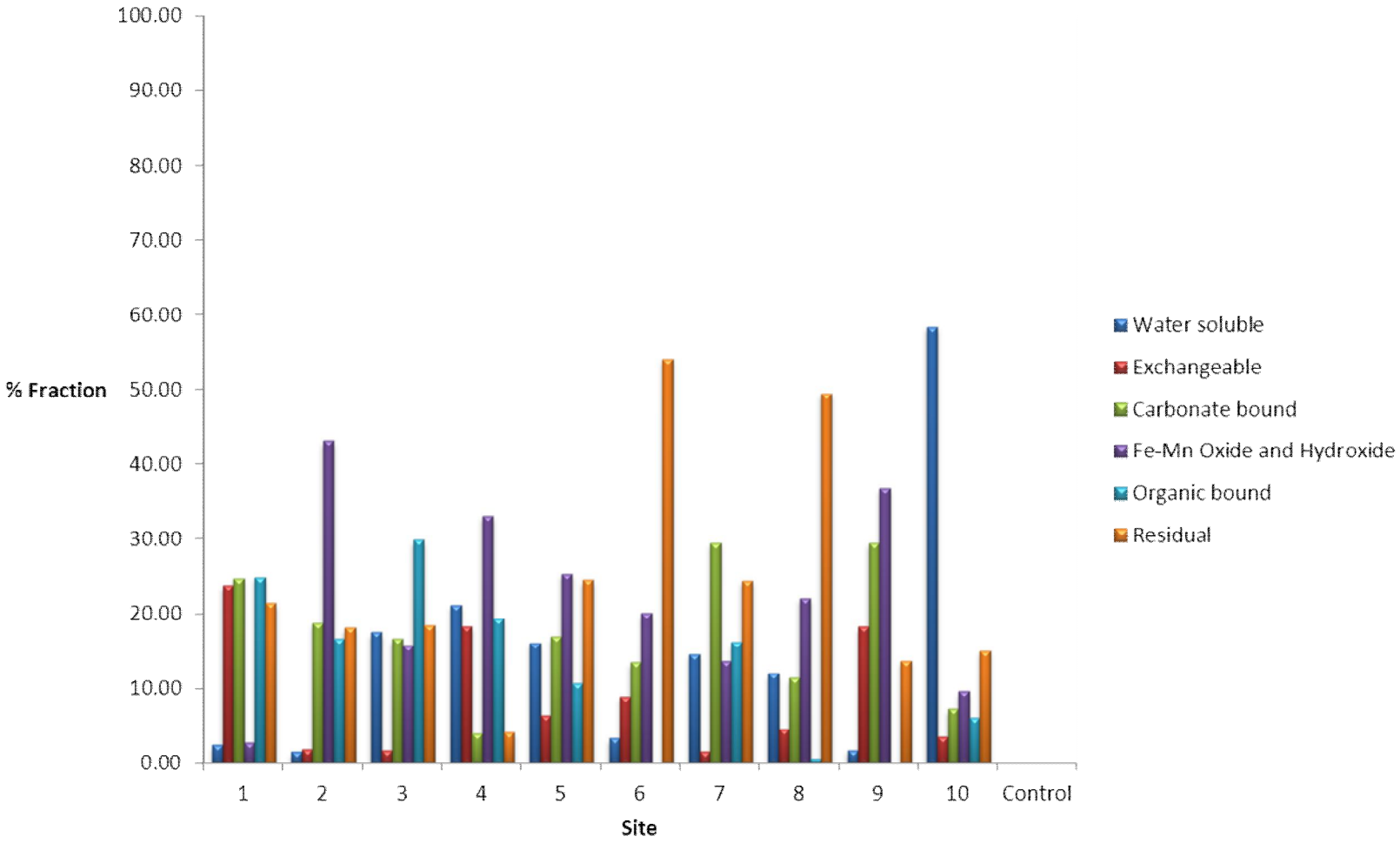


Fig. 4.10a. Percentage Ni in each operationally fraction of roadside soils particle size 1400µm (Hot and Dry Season).

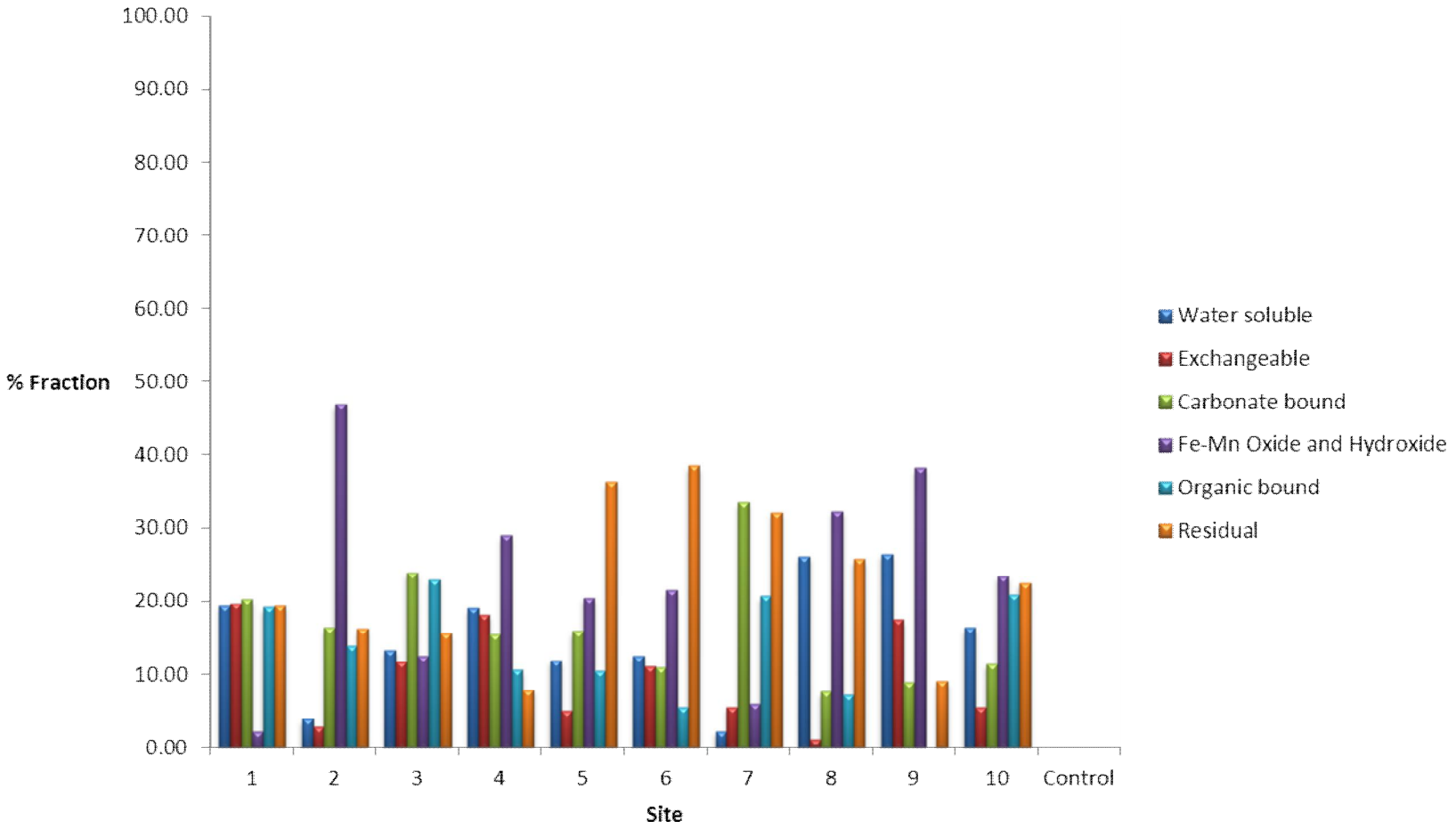


Fig. 4.10b. Percentage Ni in each operationally fraction of roadside soils particle size 355µm (Hot and Dry Season).

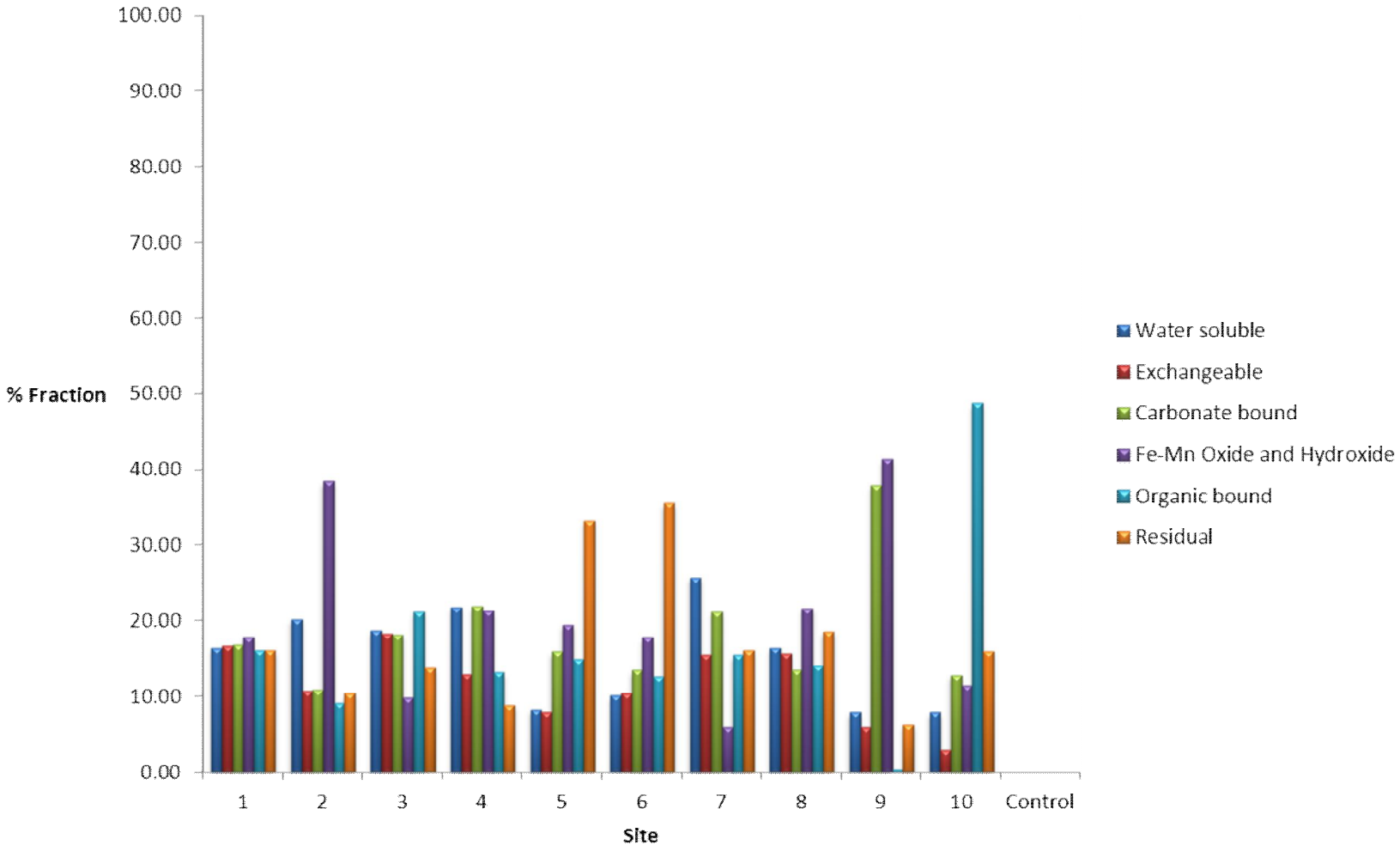


Fig. 4.10c. Percentage Ni in each operationally fraction of roadside soils particle size 150µm (Hot and Dry Season).

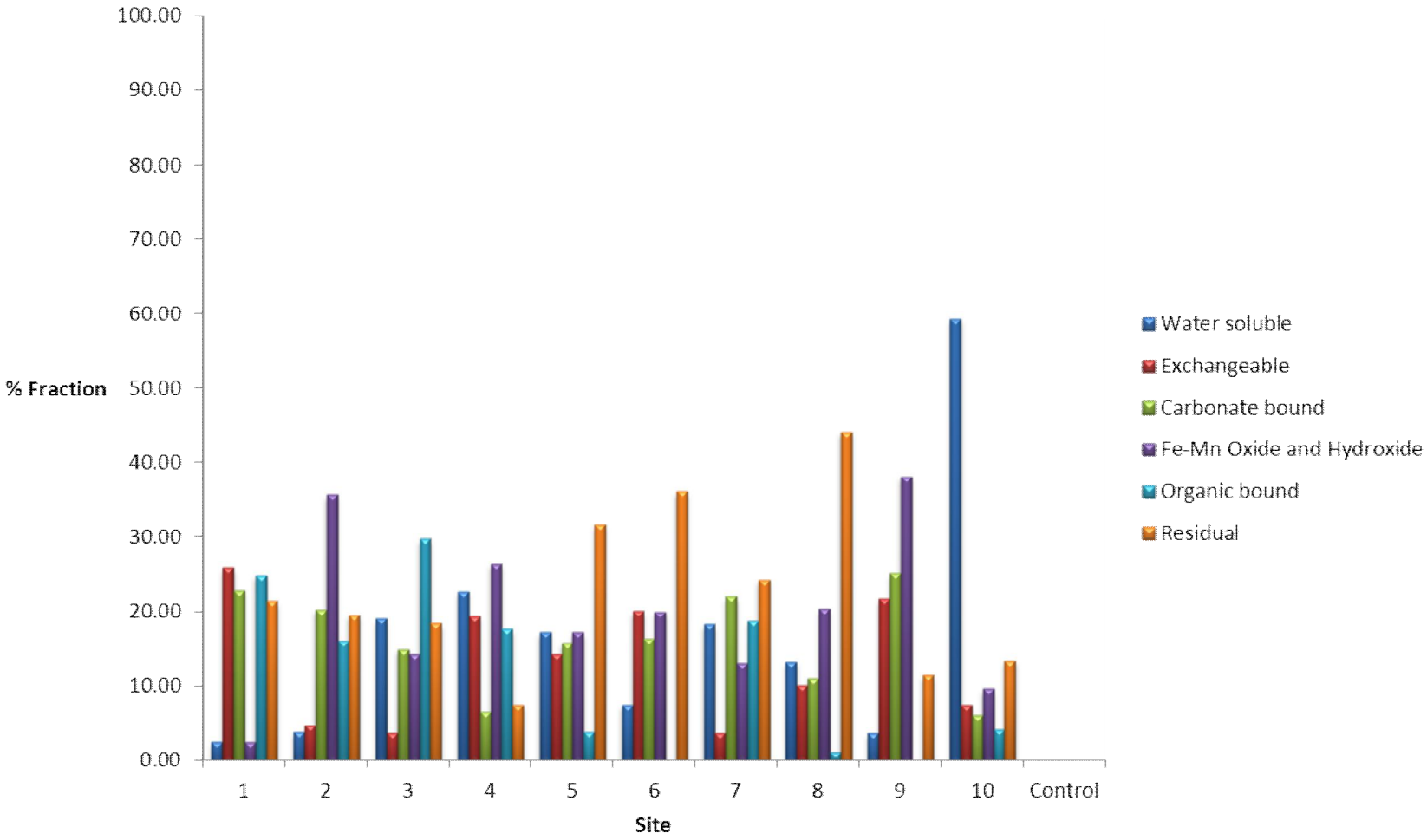


Fig. 4.11a. Percentage Ni in each operationally fraction of roadside soils particle size 1400µm (Warm and Wet Season).

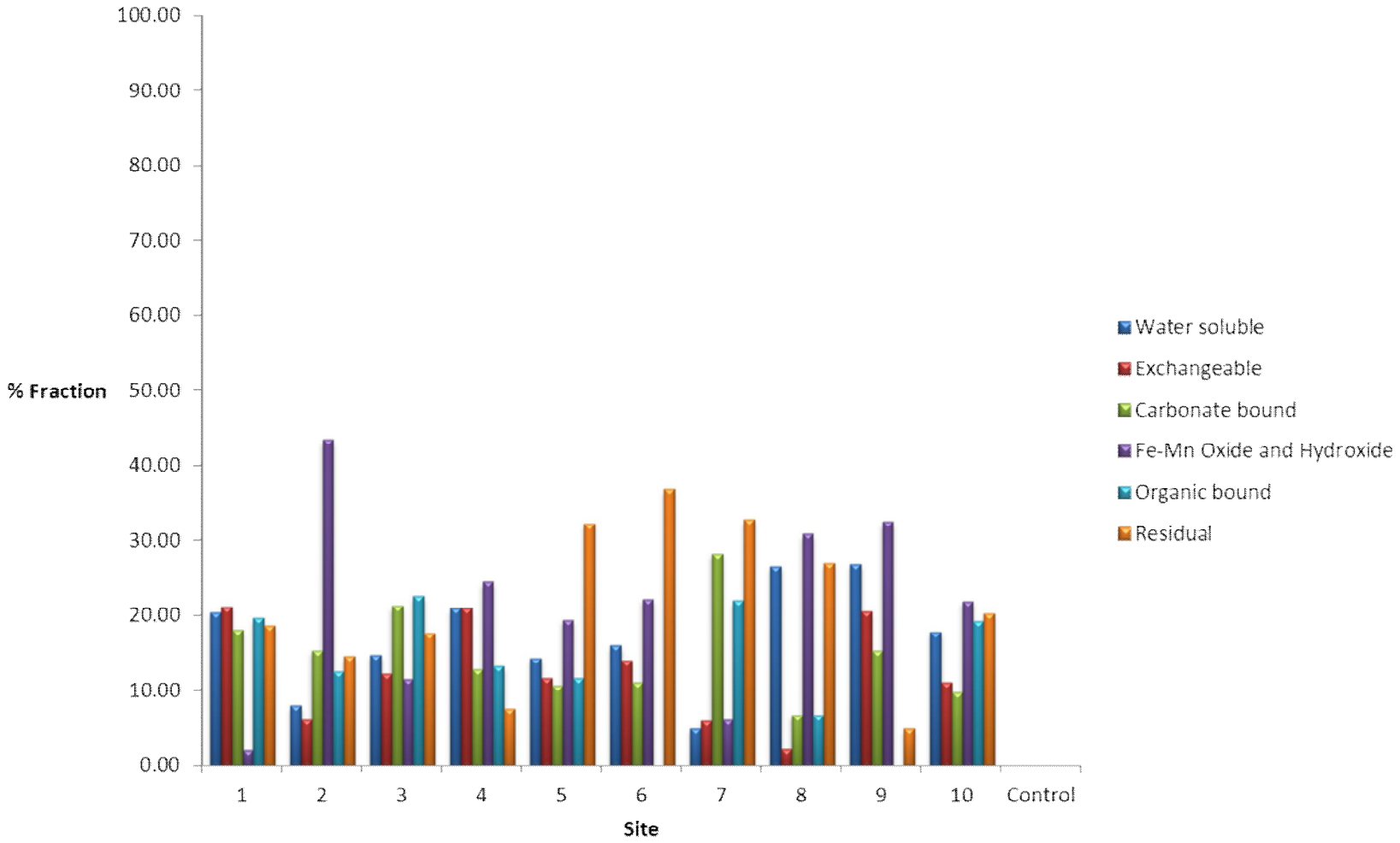


Fig. 4.11b. Percentage Ni in each operationally fraction of roadside soils particle size 355µm (Warm and Wet Season).

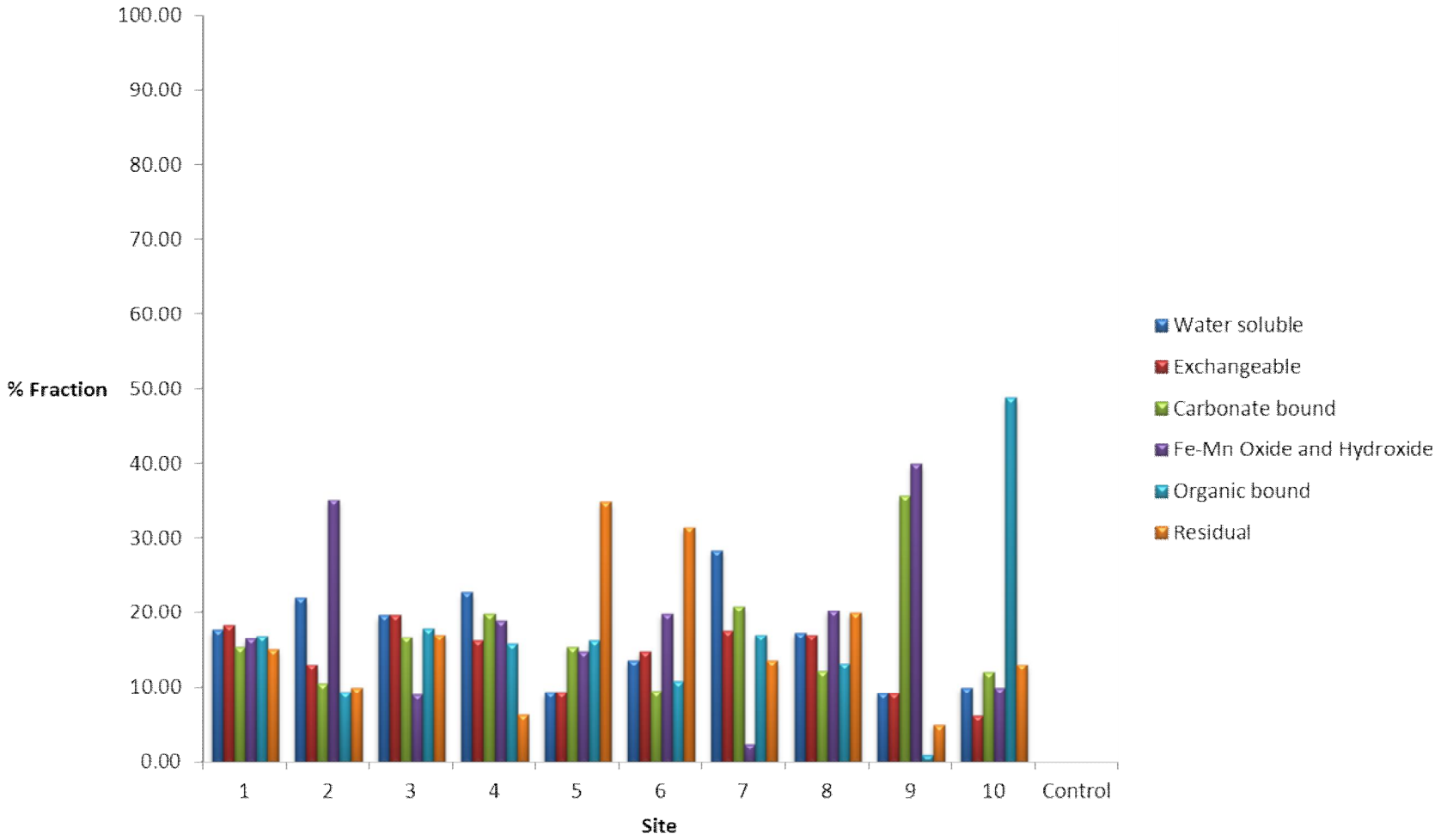


Fig. 4.11c. Percentage Ni in each operationally fraction of roadside soils particle size 150µm (Warm and Wet Season).

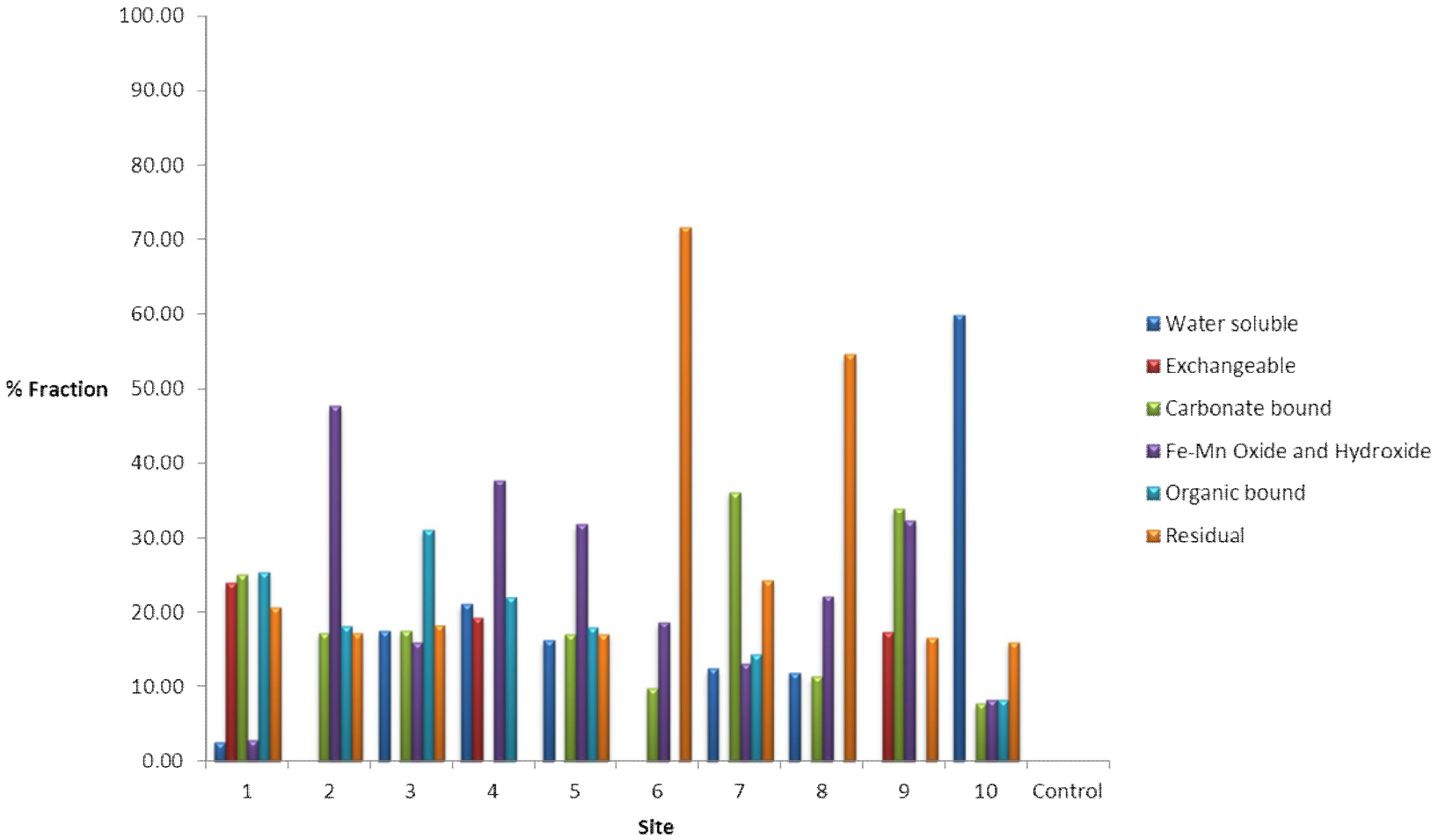


Fig. 4.12a. Percentage Ni in each operationally fraction of roadside soils particle size 1400µm (Warm and Dry Season).

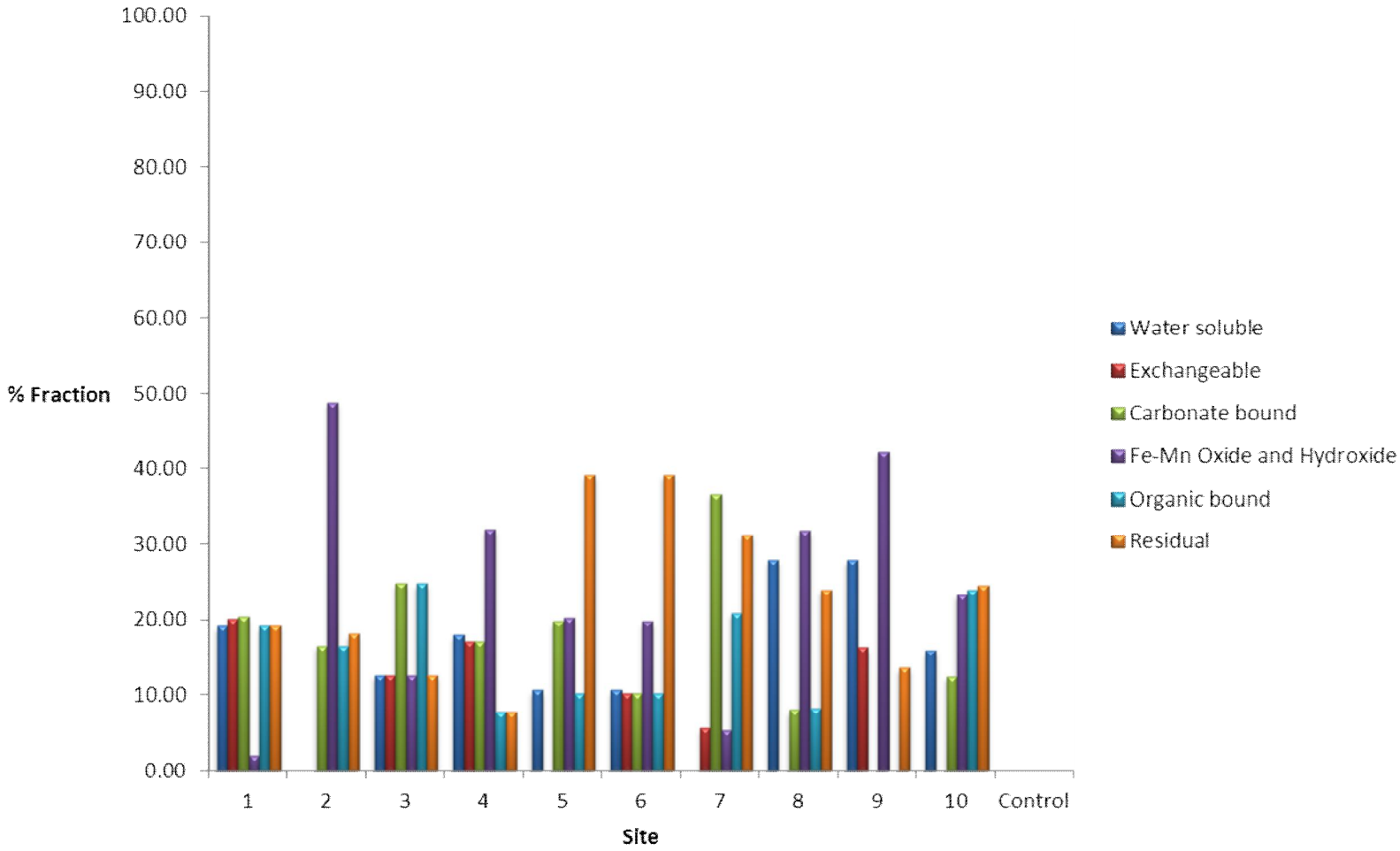


Fig. 4.12b. Percentage Ni in each operationally fraction of roadside soils particle size 355µm (Warm and Dry Season).

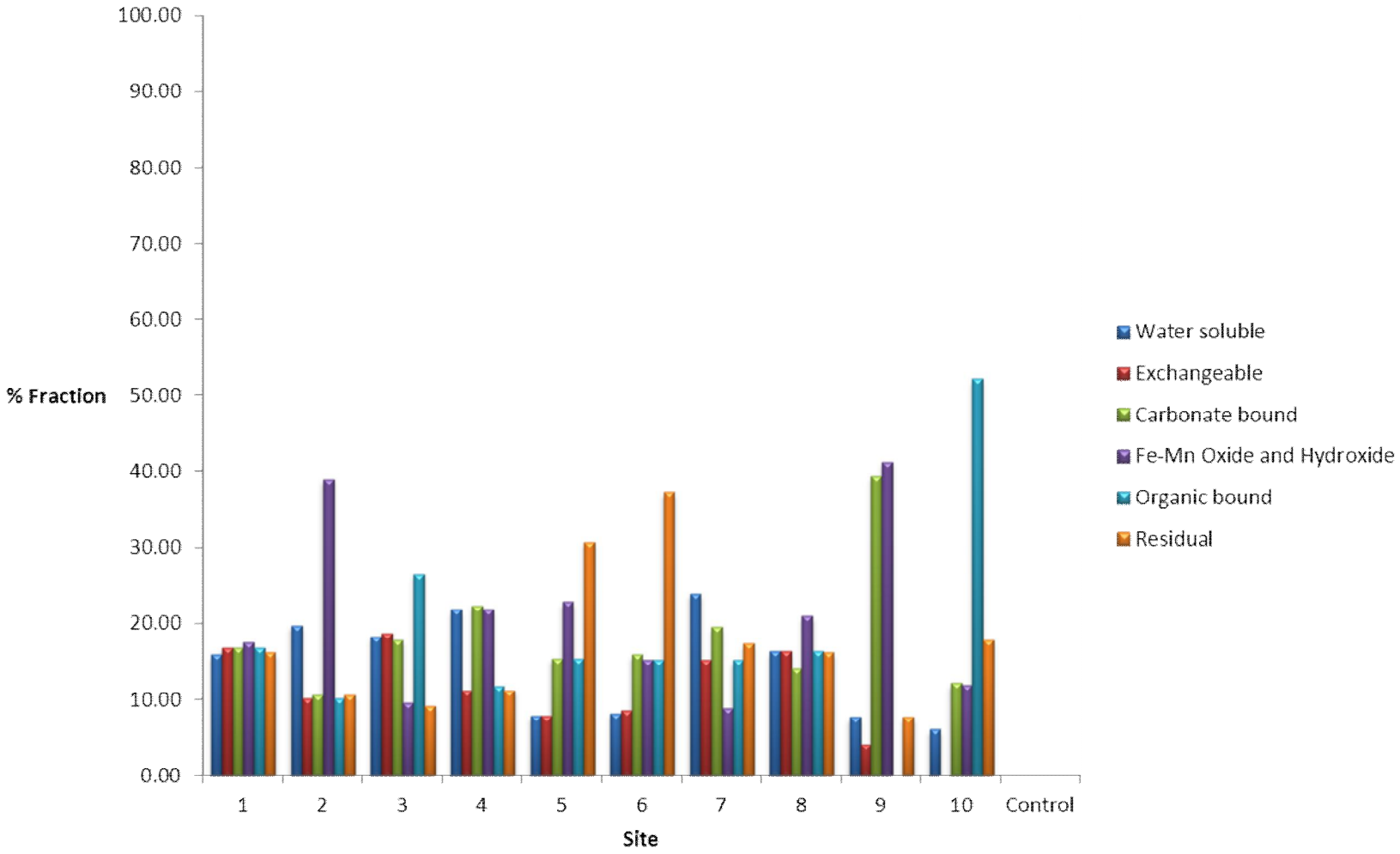


Fig. 4.12c. Percentage Ni in each operationally fraction of roadside soils particle size 150µm (Warm and Dry Season).

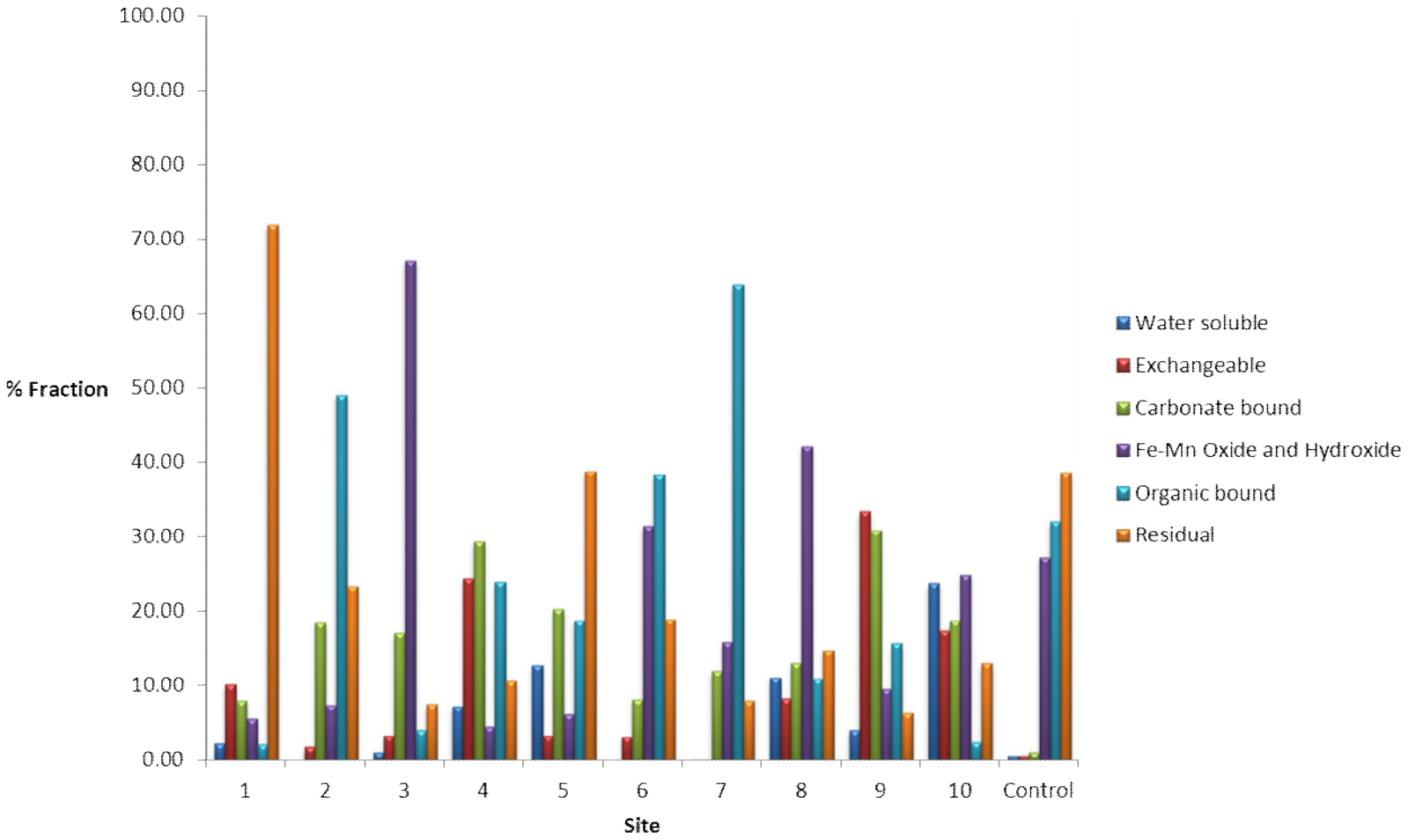


Fig. 4.13a. Percentage Pb in each operationally fraction of roadside soils particle size 1400µm (Cool and Dry Season).

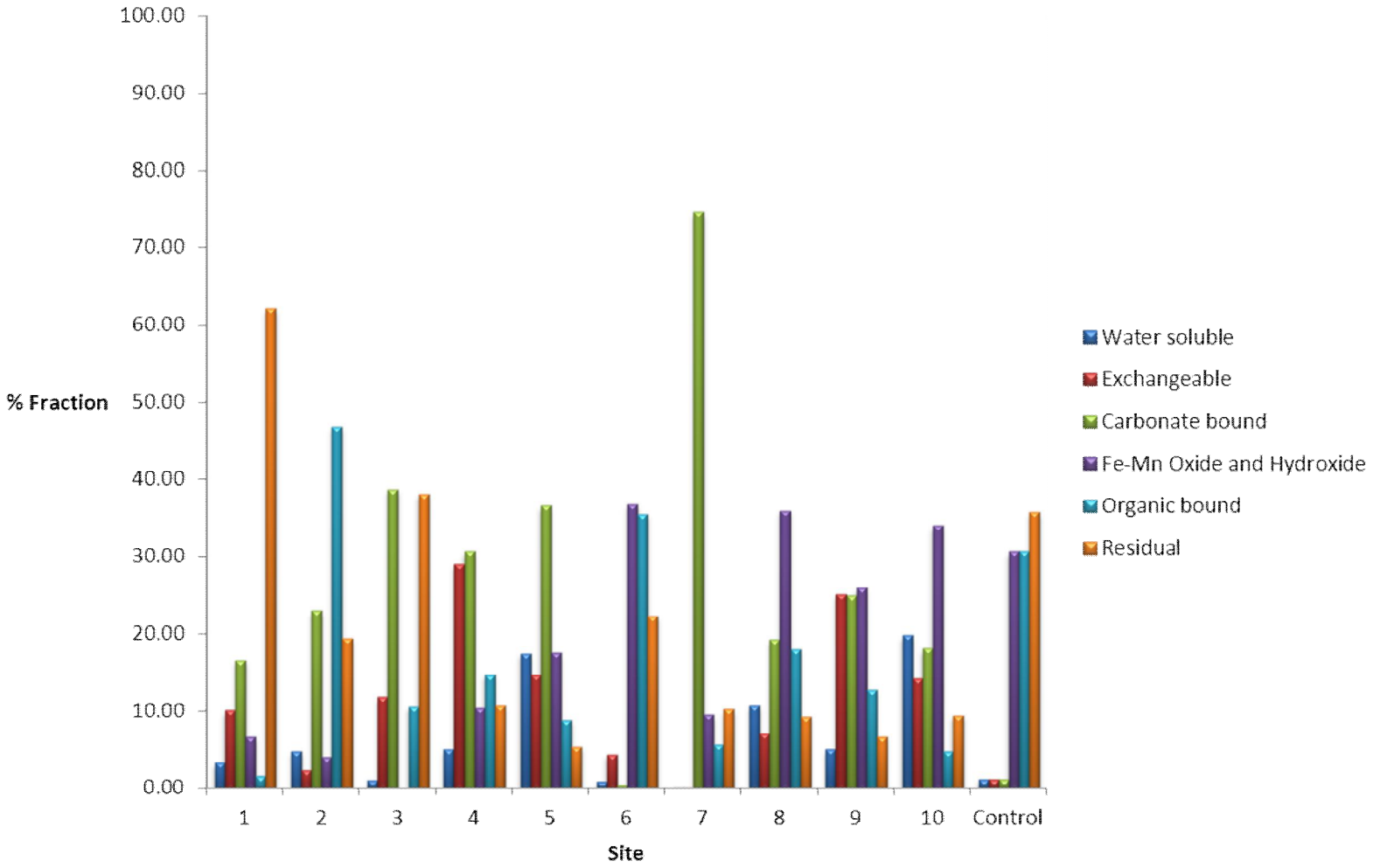


Fig. 4.13b. Percentage Pb in each operationally fraction of roadside soils particle size 355µm (Cool and Dry Season).

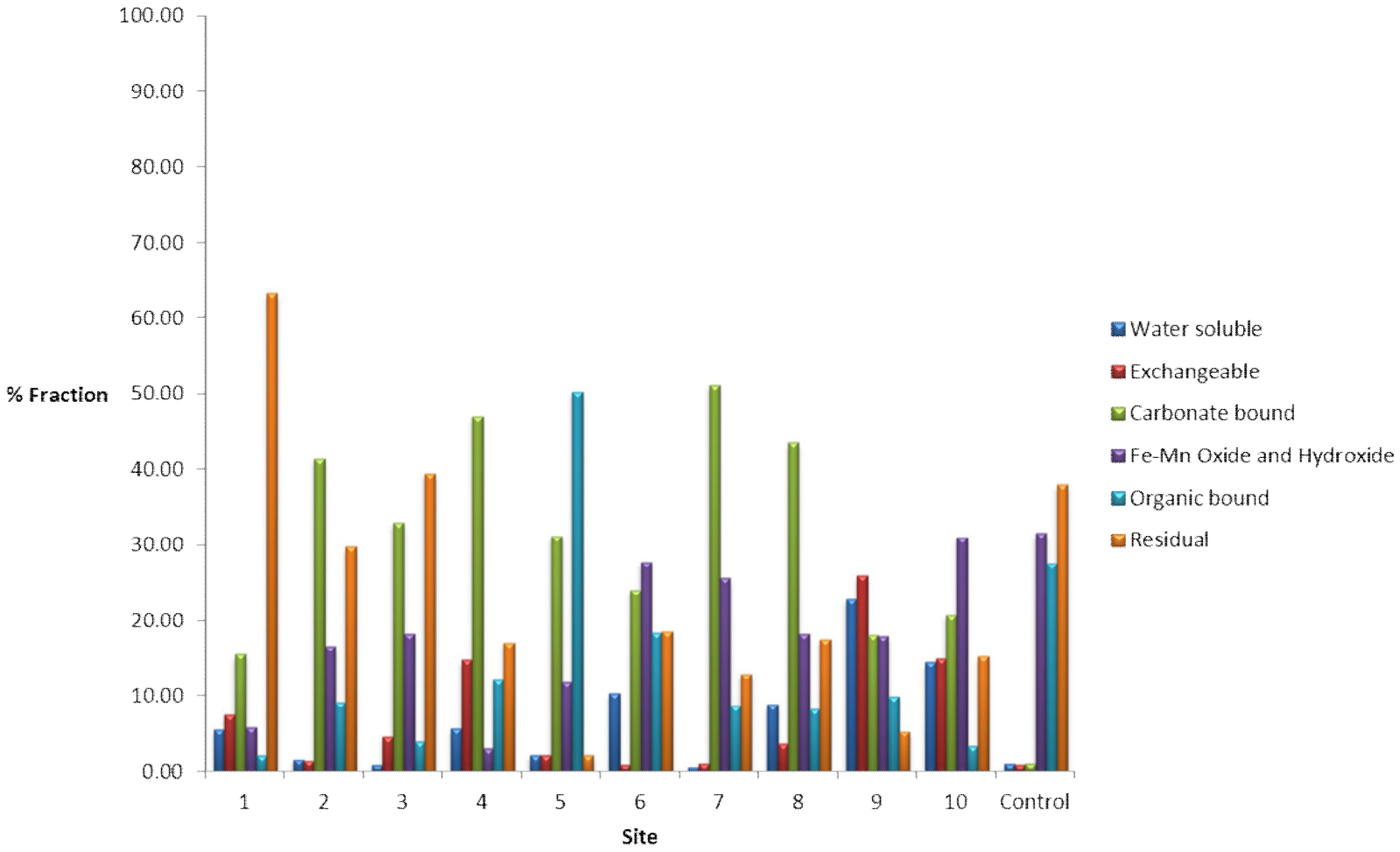


Fig. 4.13c. Percentage Pb in each operationally fraction of roadside soils particle size 150µm (Cool and Dry Season).

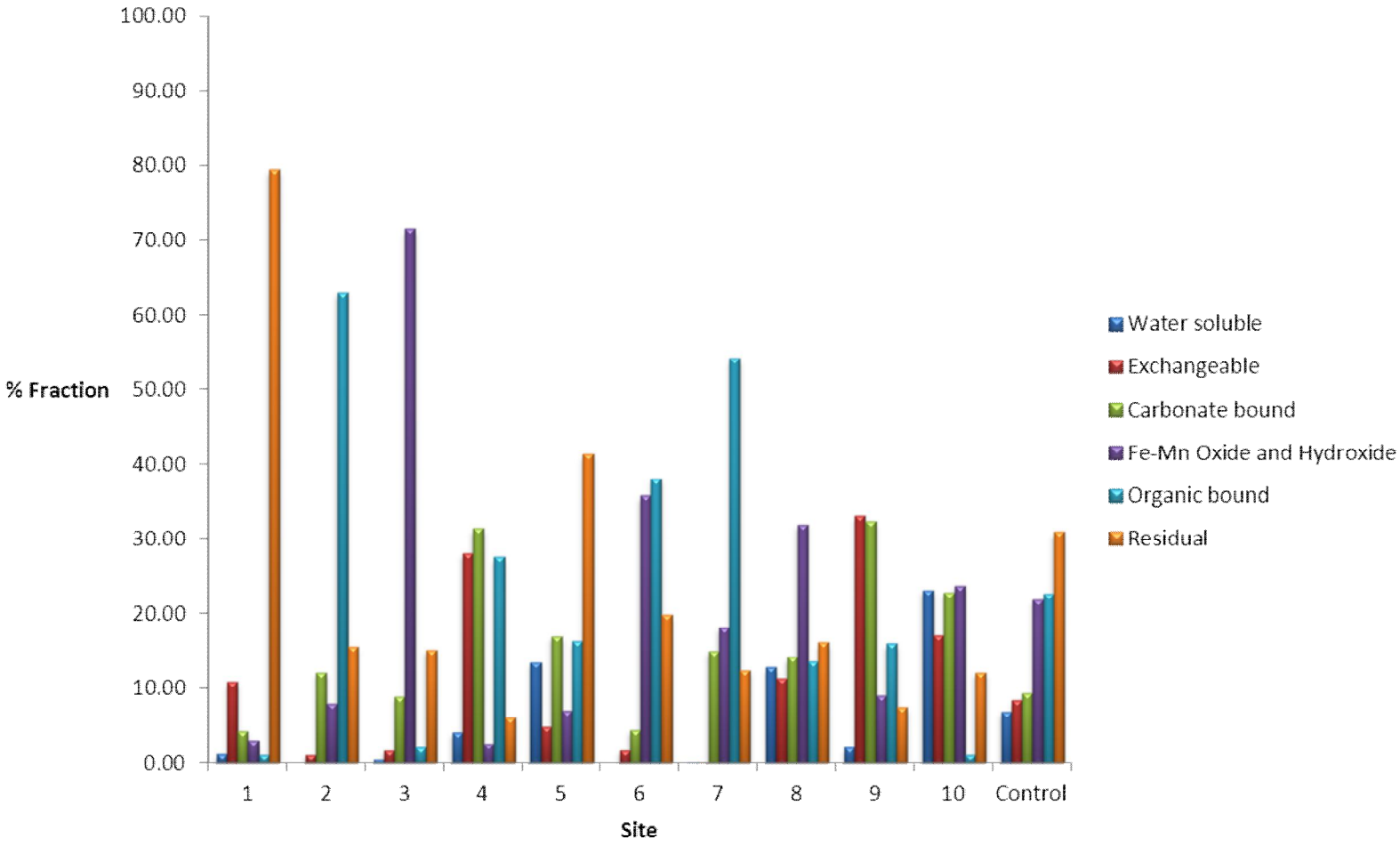


Fig. 4.14a. Percentage Pb in each operationally fraction of roadside soils particle size 1400µm (Hot and Dry Season).

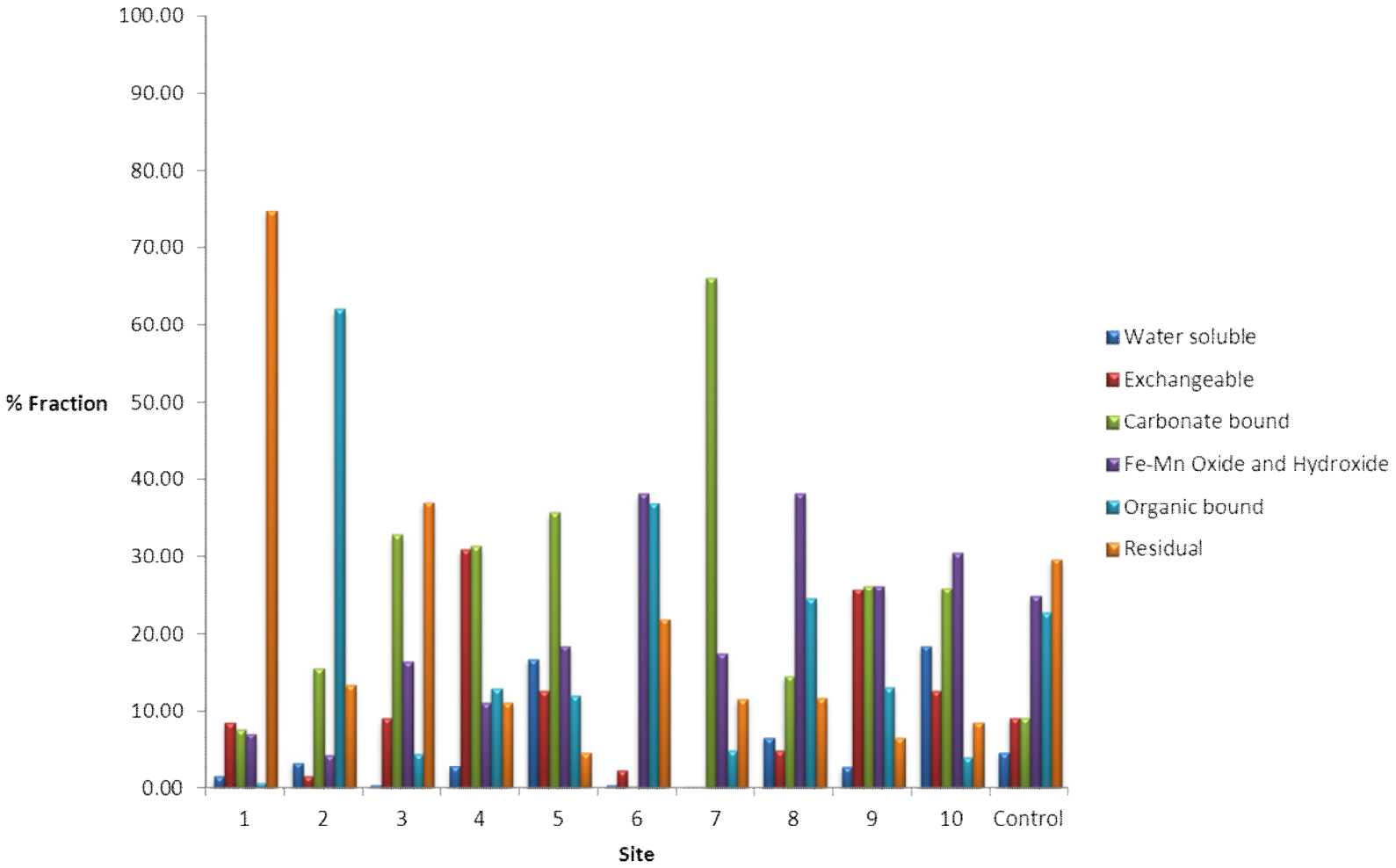


Fig. 4.14b. Percentage Pb in each operationally fraction of roadside soils particle size 355µm (Hot and Dry Season).

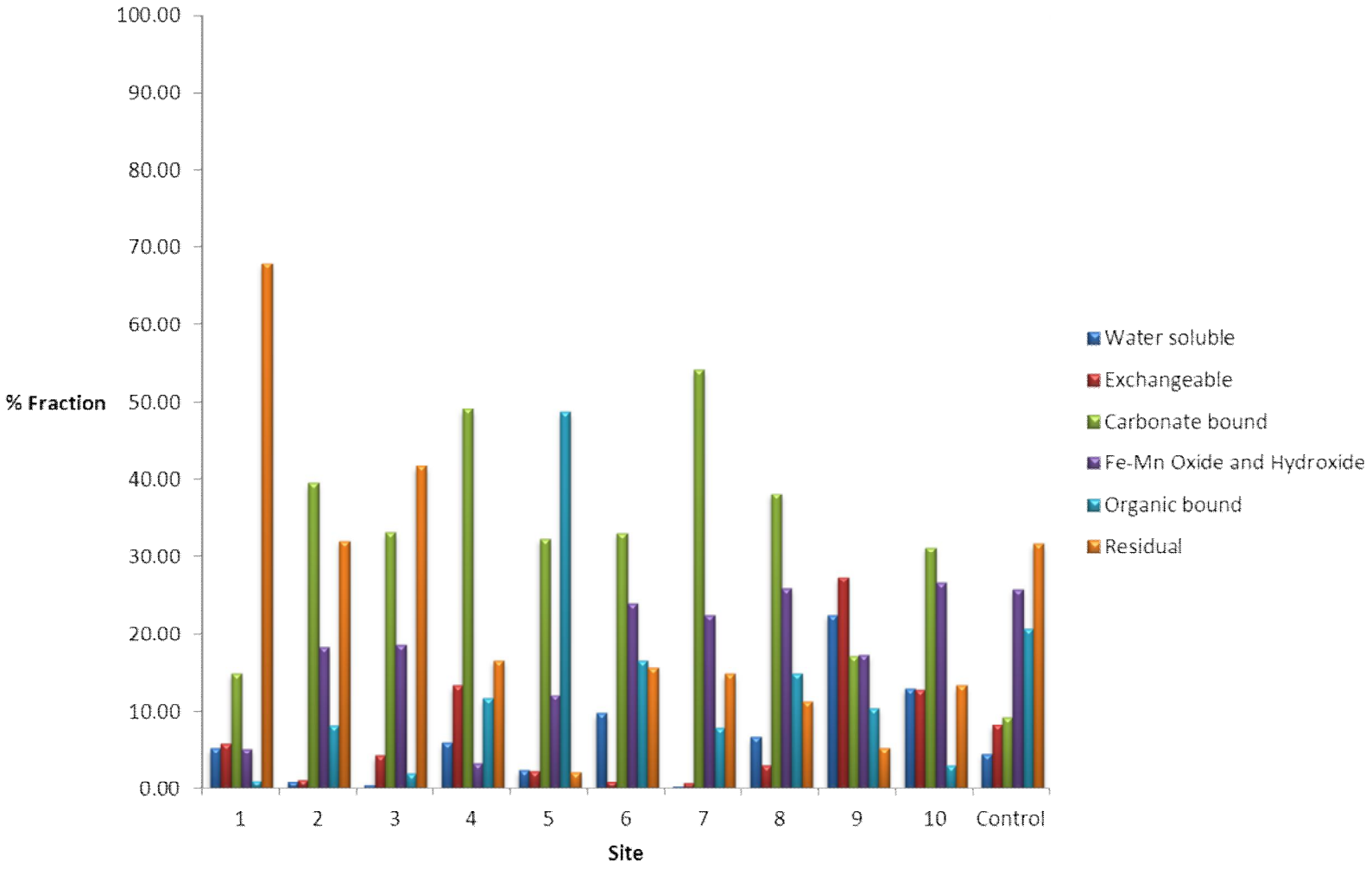


Fig. 4.14c. Percentage Pb in each operationally fraction of roadside soils particle size 150µm (Hot and Dry Season).

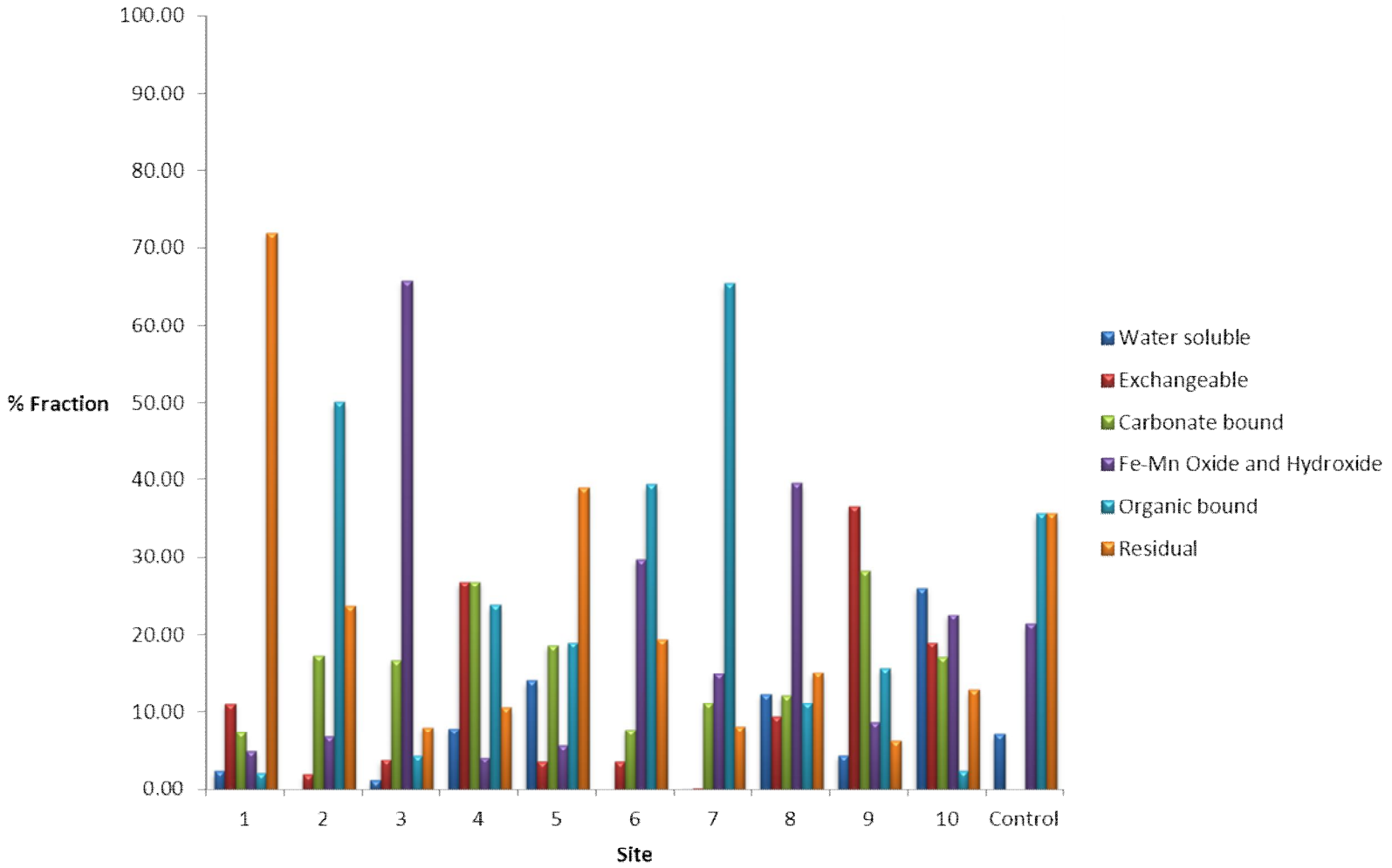


Fig. 4.15a. Percentage Pb in each operationally fraction of roadside soils particle size 1400µm (Warm and Wet Season).

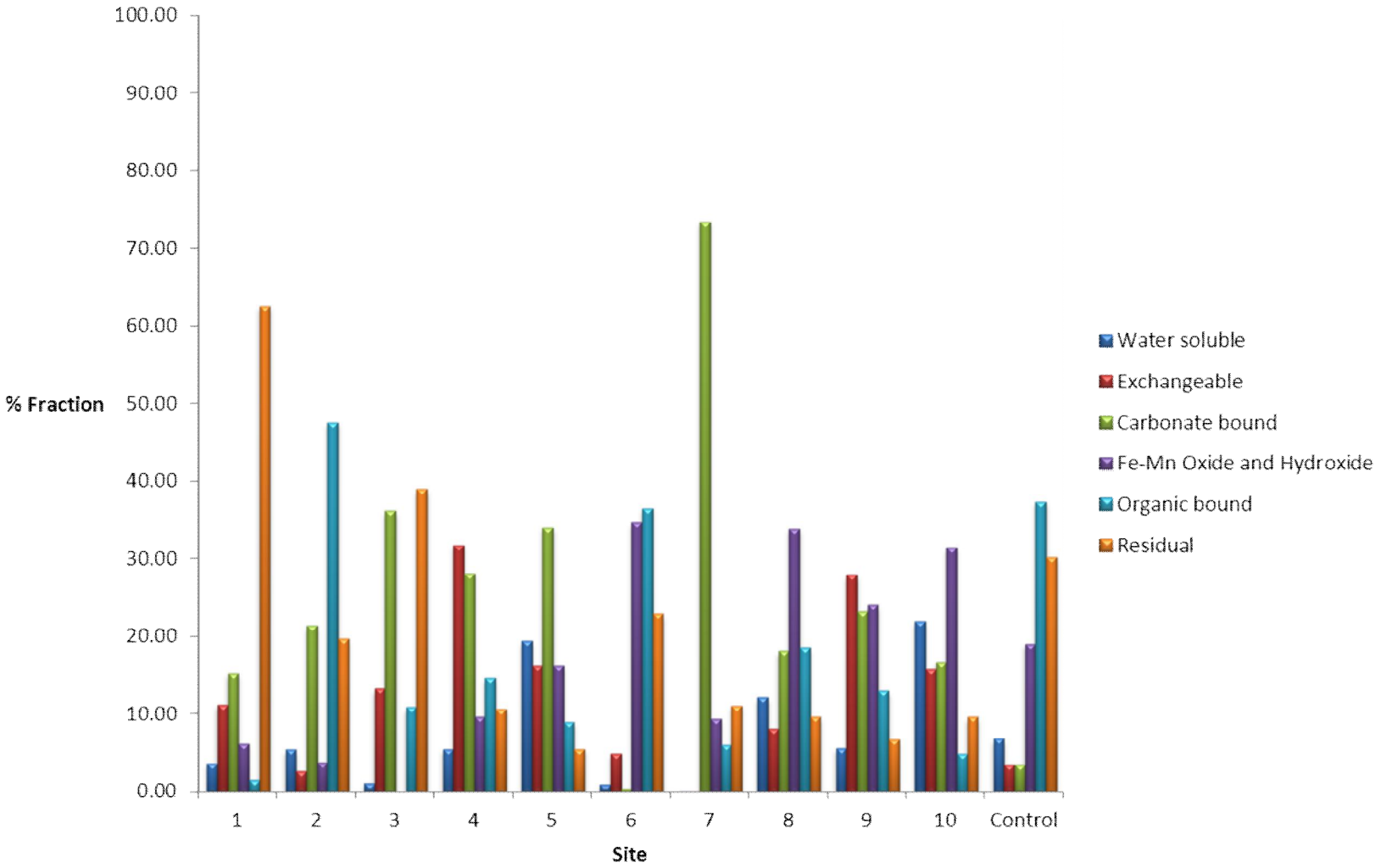


Fig. 4.15b. Percentage Pb in each operationally fraction of roadside soils particle size 355µm (Warm and Wet Season).

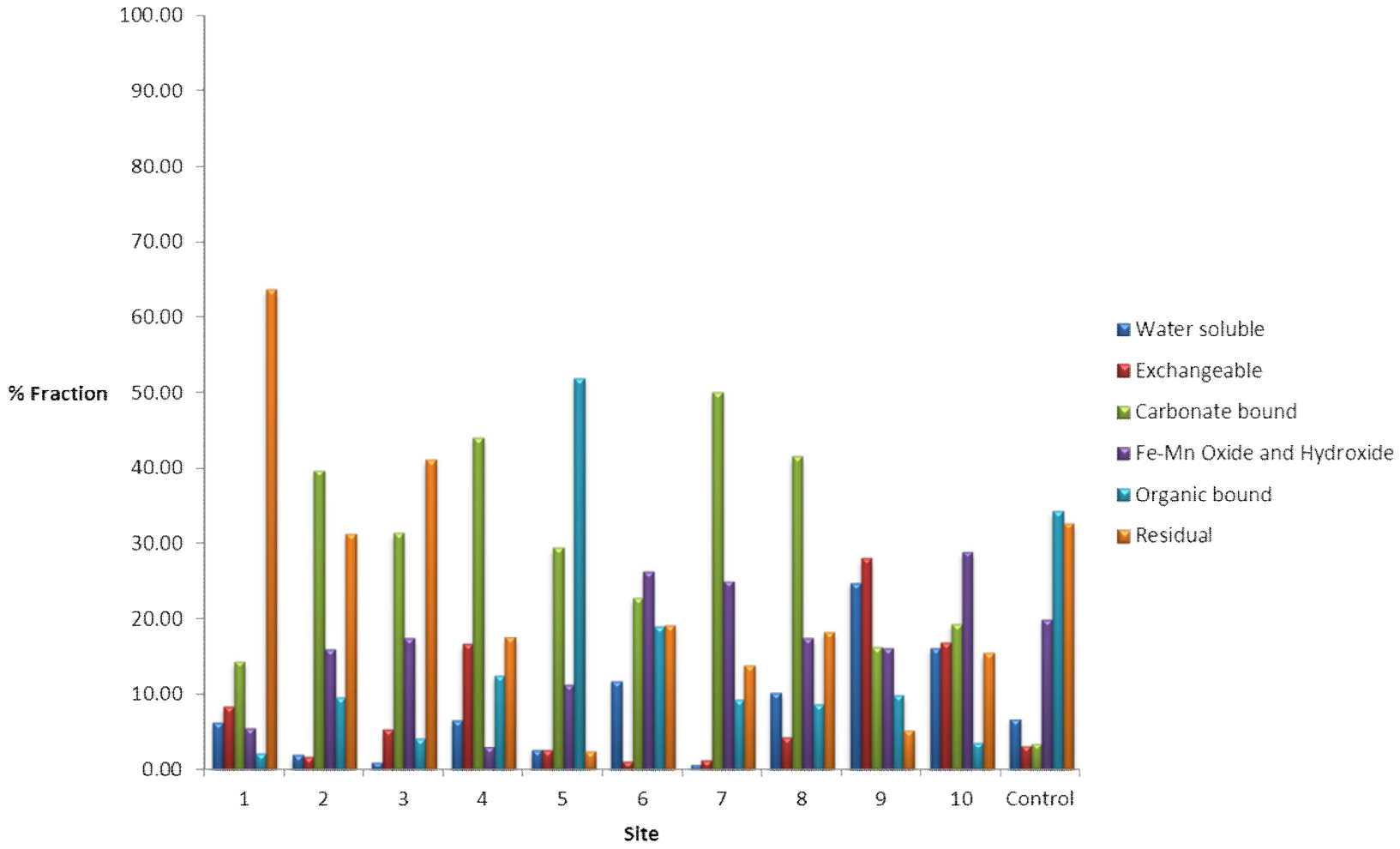


Fig. 4.15c. Percentage Pb in each operationally fraction of roadside soils particle size 150µm (Warm and Wet Season).

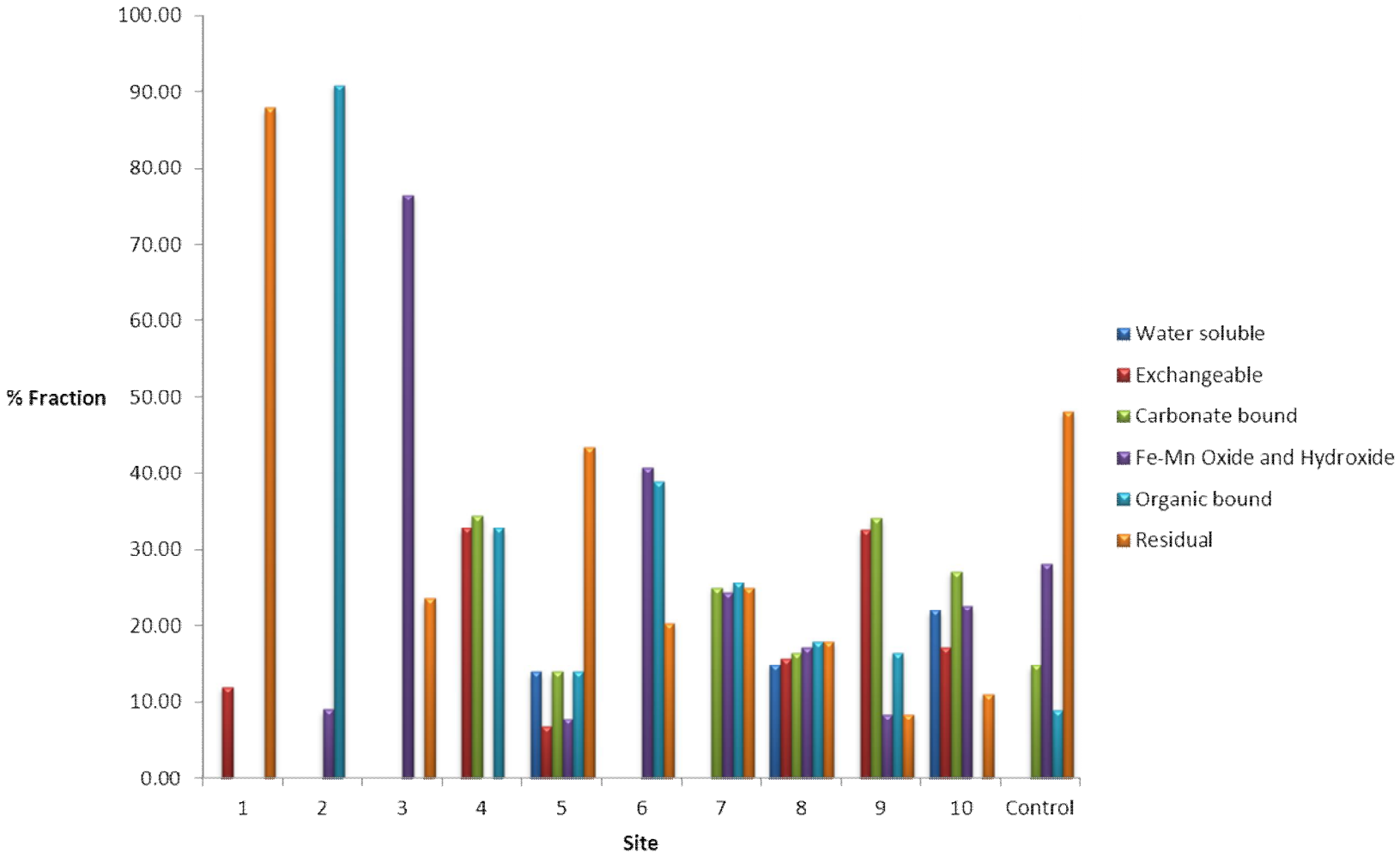


Fig. 4.16a. Percentage Pb in each operationally fraction of roadside soils particle size 1400µm (Warm and Dry Season).

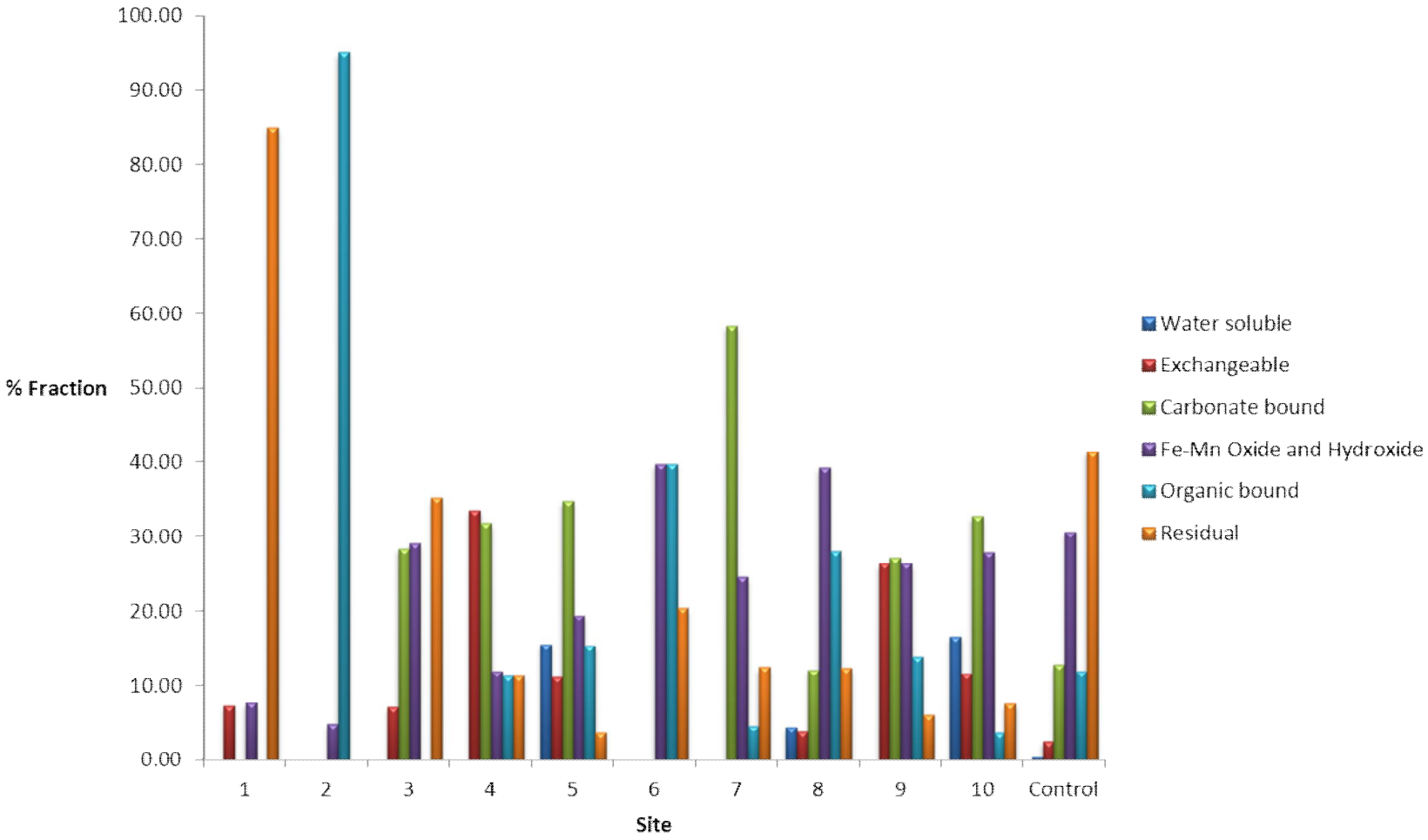


Fig. 4.16b. Percentage Pb in each operationally fraction of roadside soils particle size 355µm (Warm and Dry Season).

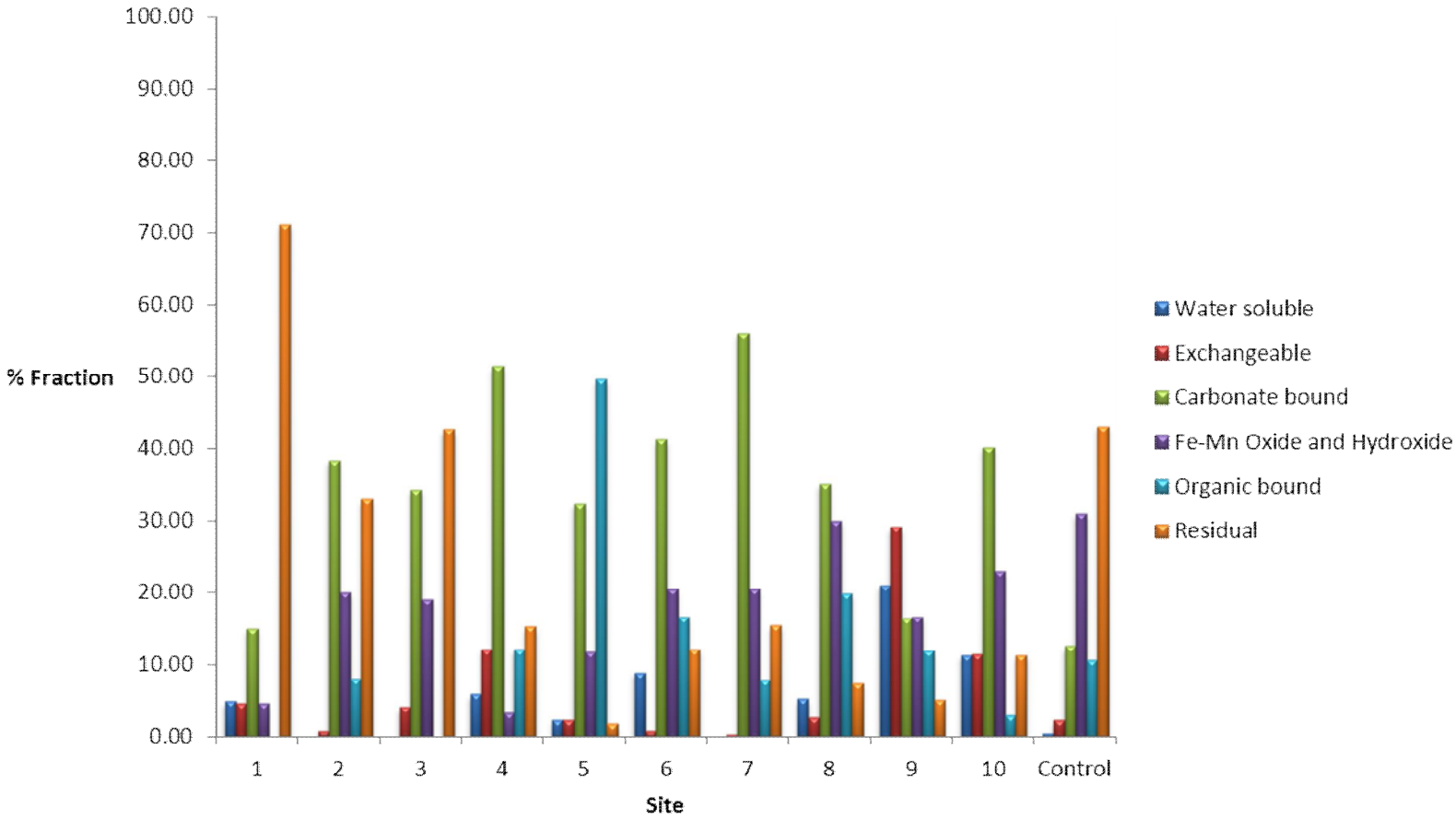


Fig. 4.16c. Percentage Pb in each operationally fraction of roadside soils particle size 150µm (Warm and Dry Season).

The range of ND (FIV) – 74.52% (FIII), 0.04 (FI) – 74.74% (FVI), ND (FIV) – 62.50% (FVI) and ND (FI – FIII, FV and FVI) – 95.13% (FV) were found for samples with 355µm grain size across the four seasons, respectively. For samples with 150µm grain size, the range of 0.92 (FII) – 63.29% (FVI), 0.20 (FI) – 67.89% (FVI), 0.62 (FI) – 63.63% (FVI) and ND (FI and FV) – 71.14% (FVI) were recorded during Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Season, respectively.

Also from the bar graphs, Pb was mainly found in residual (Site 1, 5 and control), Fe-Mn oxide (Site 3, 8 and 10), organic bound (Site 2, 6 and 7), exchangeable (Site 9), and carbonate bound (Site 4) fractions for samples with 1400µm grain size. For samples with 355µm grain size, dominant fractions were carbonate bound (Site 3, 4, 5 and 7), residual (Site 1 and control), organic bound (Site 2), Fe-Mn oxide (Site 6, 8, 9 and 10). Furthermore, samples with 150µm grain size had Pb mainly localized in residual (Site 1, 3 and control), carbonate bound (Site 2, 4, 7 and 8), organic bound (Site 5), Fe-Mn oxide (Site 6 and 10) fractions. With few exceptions in Cool and Dry and Warm and Dry Seasons, highest percentage fraction of Pb (95.13) was found in residual phase (Site 1).

Similar to other metals, fractions of Cu in soils across the seasons are shown in Fig. 4.17 – 4.20a-c. For samples with 1400µm grain size, the ranges were ND (FI - FVI and FVI) – 100% (FIII), ND (FI) – 95.56% (FV), ND (FI - FVI) – 100% (FIII) and ND (FI - FVI) – 100% (FV and FVI) during Cool and Dry, Hot and Dry, Warm and Wet and Warm and Dry Seasons, respectively. The ranges ND (FI - FV) – 78.24% (FV), ND (FI - FV) – 82.09% (FVI), ND (FI - FV) – 77.94% (FV) and ND (FI - FVI) – 100% (FVI) were also recorded for samples with 355µm grain size across the four seasons in the same order, respectively.

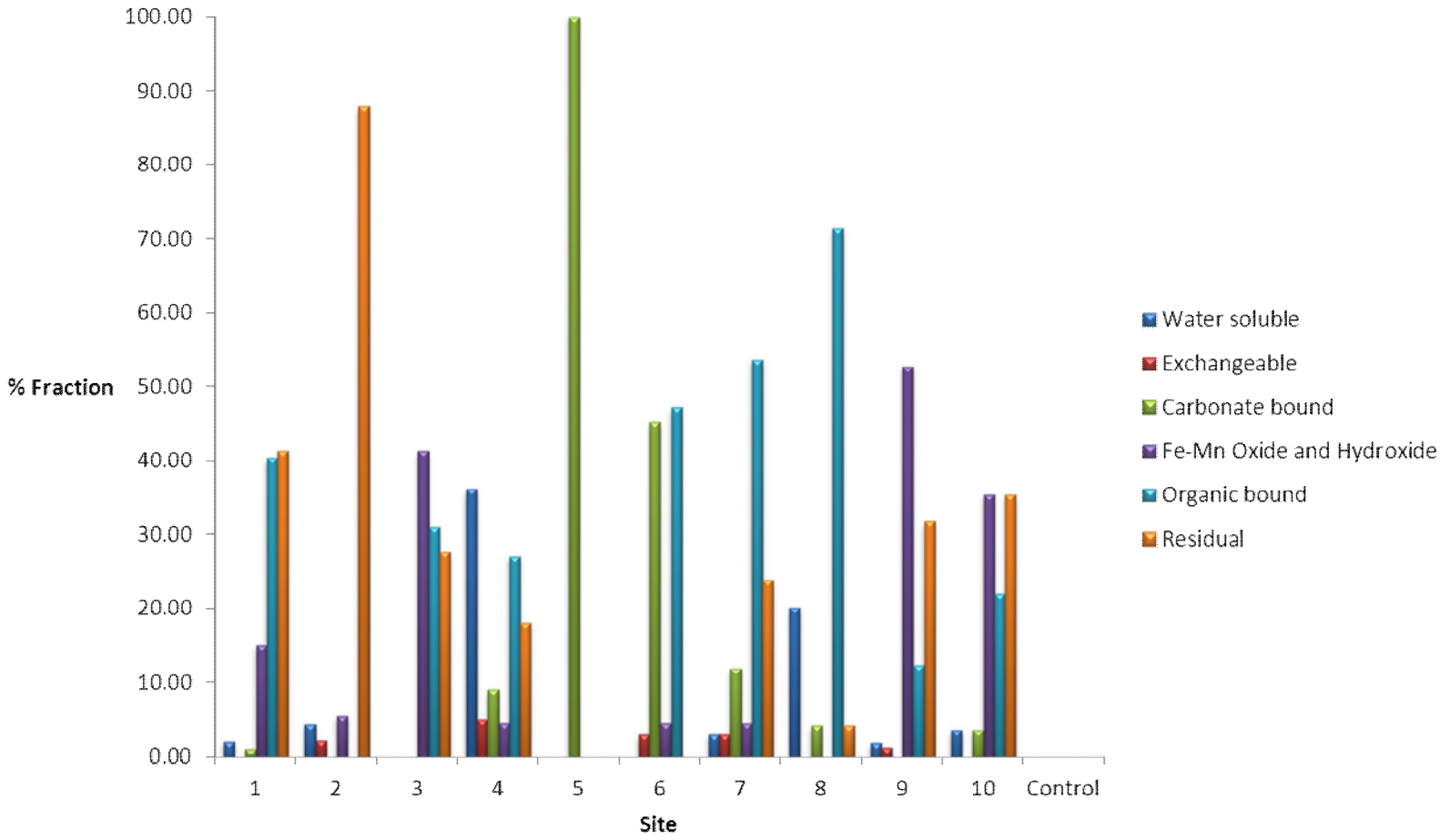


Fig. 4.17a. Percentage Cu in each operationally fraction of roadside soils particle size 1400µm (Cool and Dry Season).

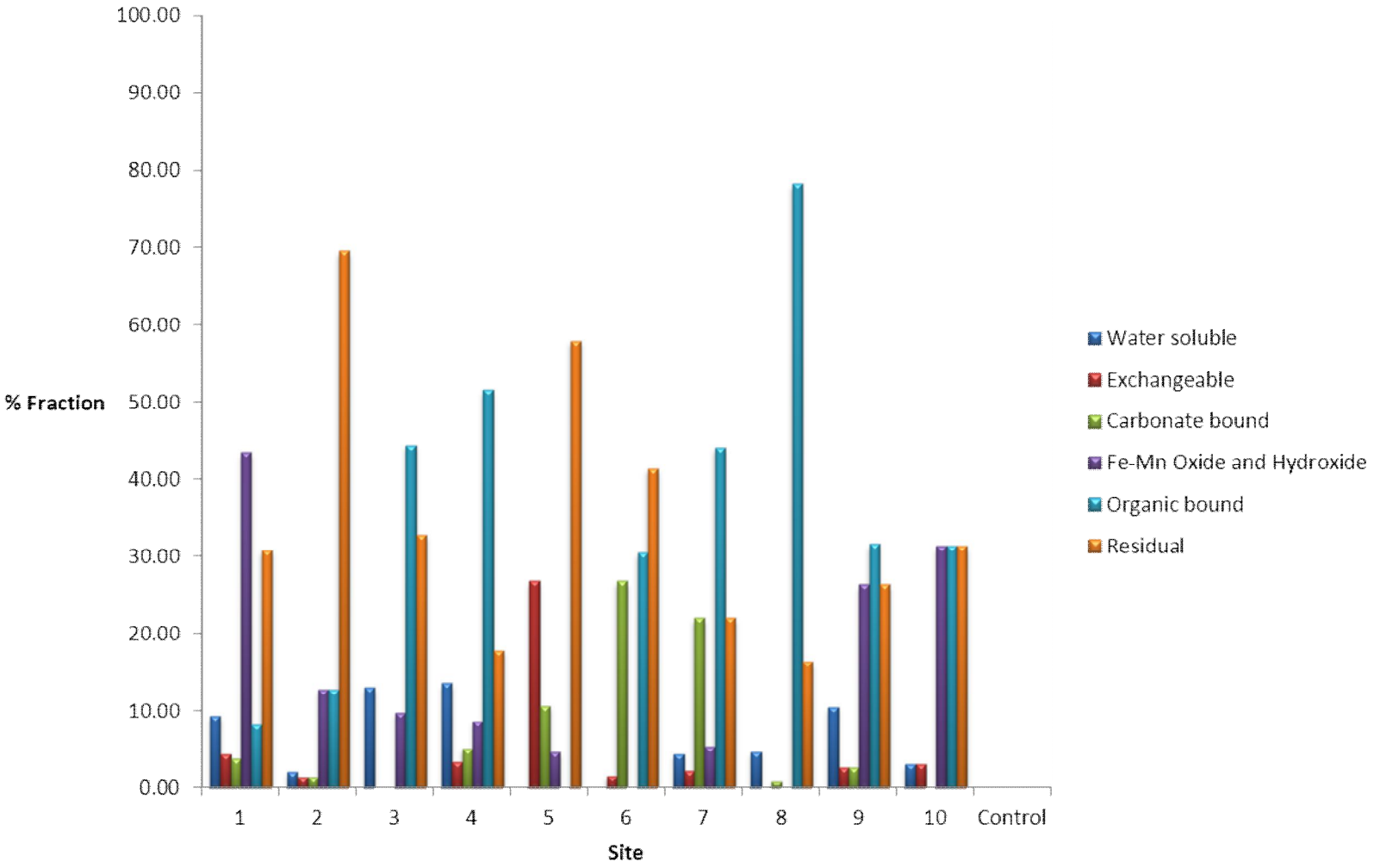


Fig. 4.17b. Percentage Cu in each operationally fraction of roadside soils particle size 355µm (Cool and Dry Season).

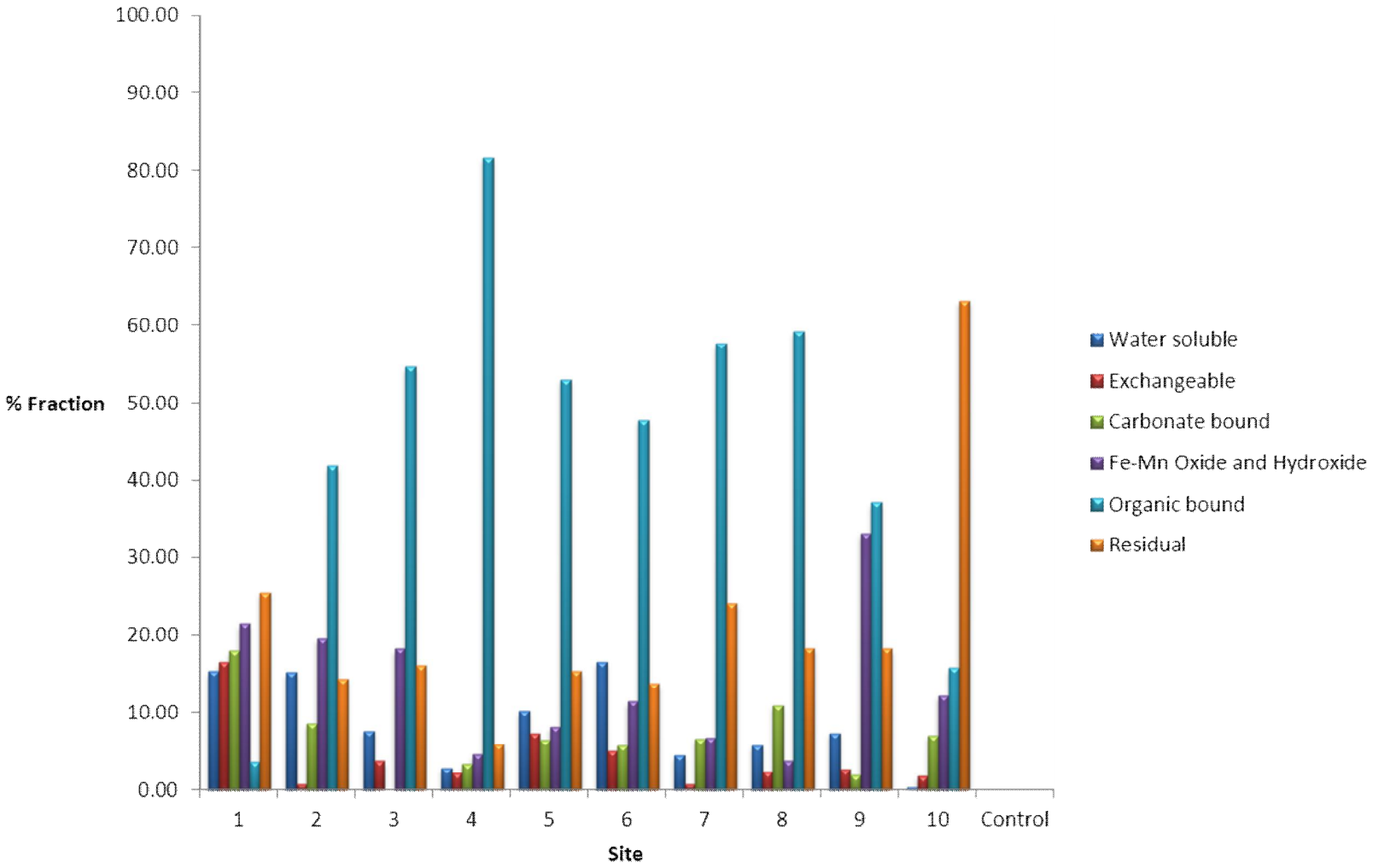


Fig. 4.17c. Percentage Cu in each operationally fraction of roadside soils particle size 150µm (Cool and Dry Season).

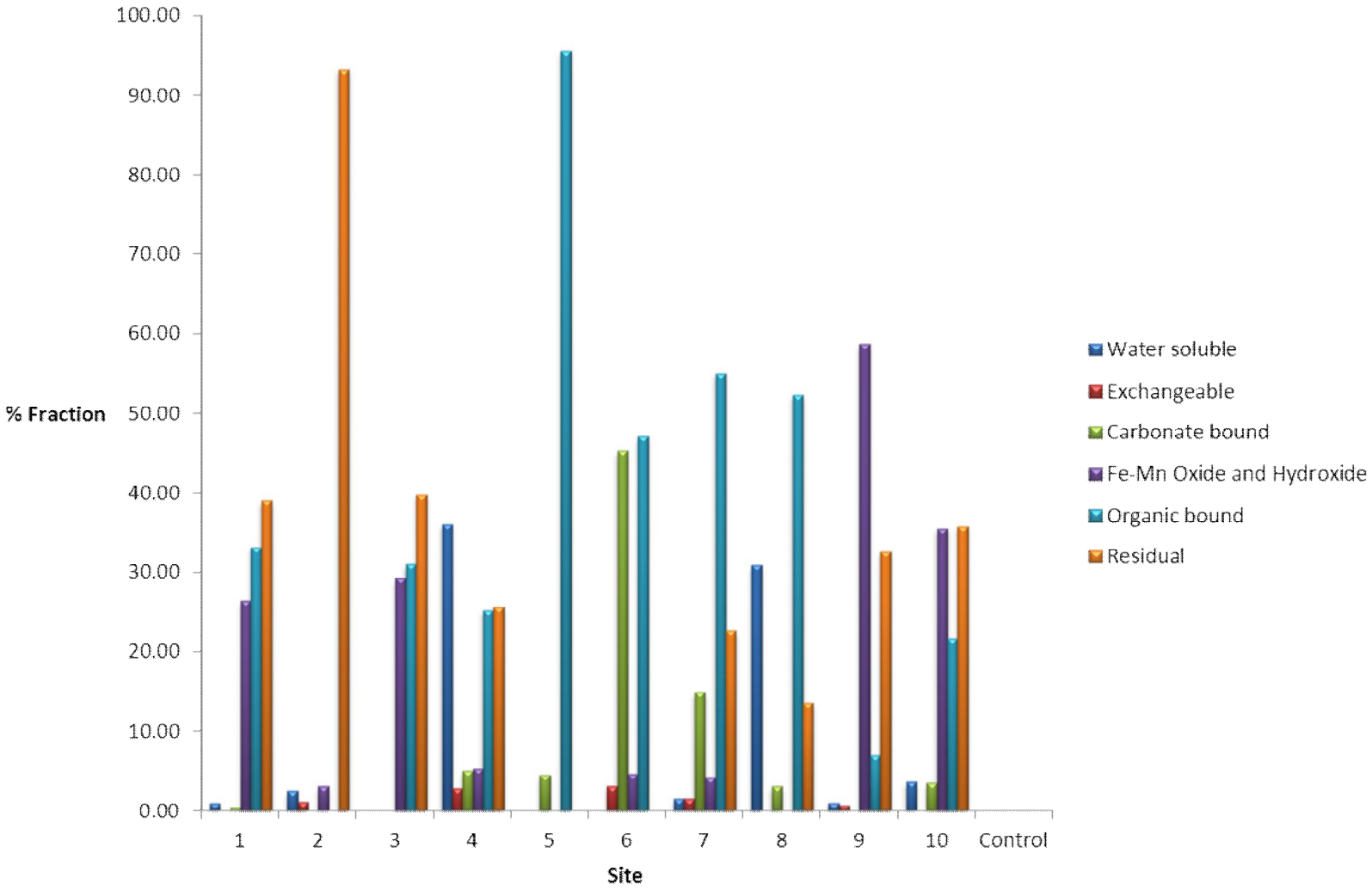


Fig. 4.18a. Percentage Cu in each operationally fraction of roadside soils particle size 1400µm (Hot and Dry Season).

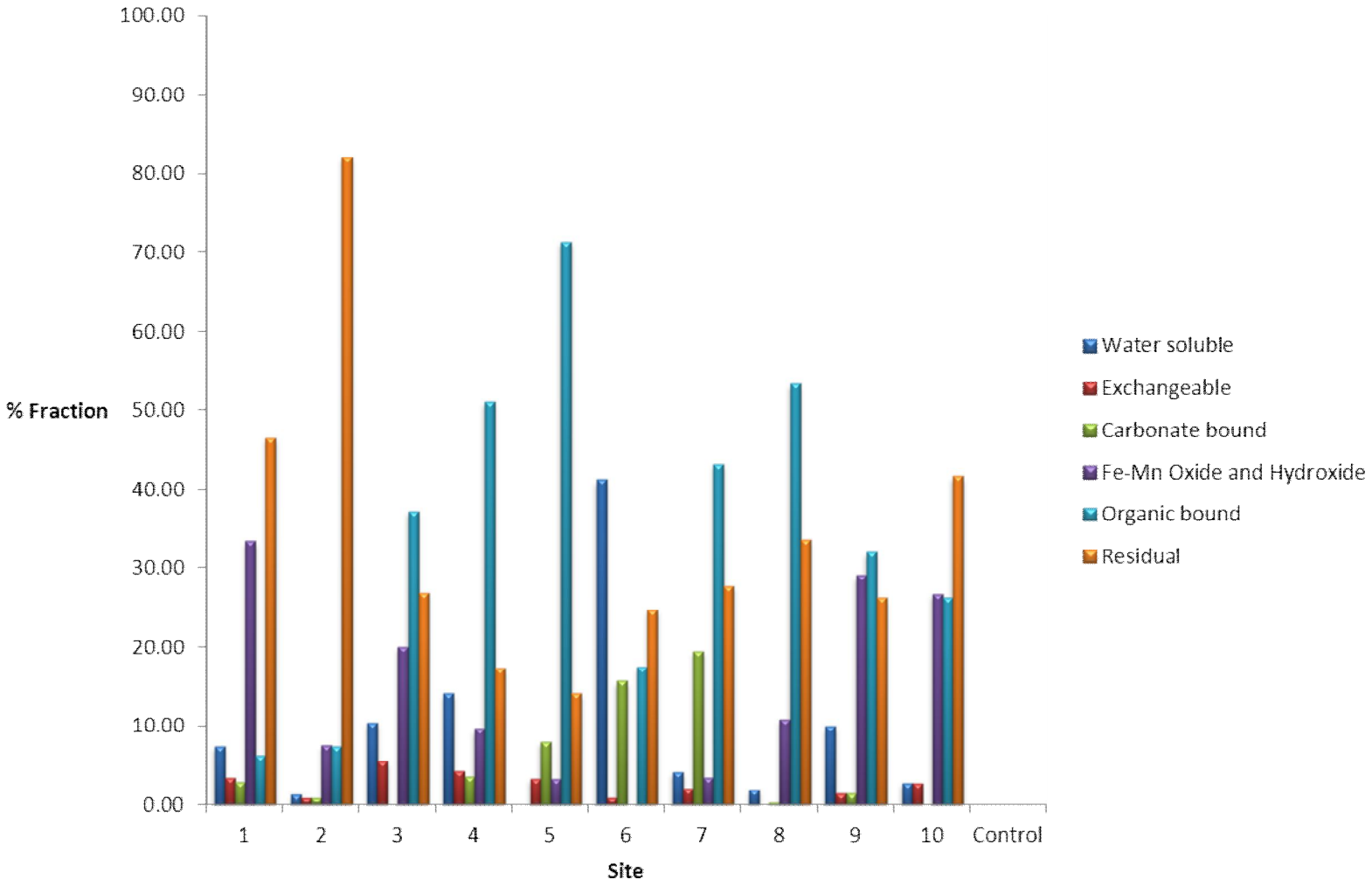


Fig. 4.18b. Percentage Cu in each operationally fraction of roadside soils particle size 355µm (Hot and Dry Season).

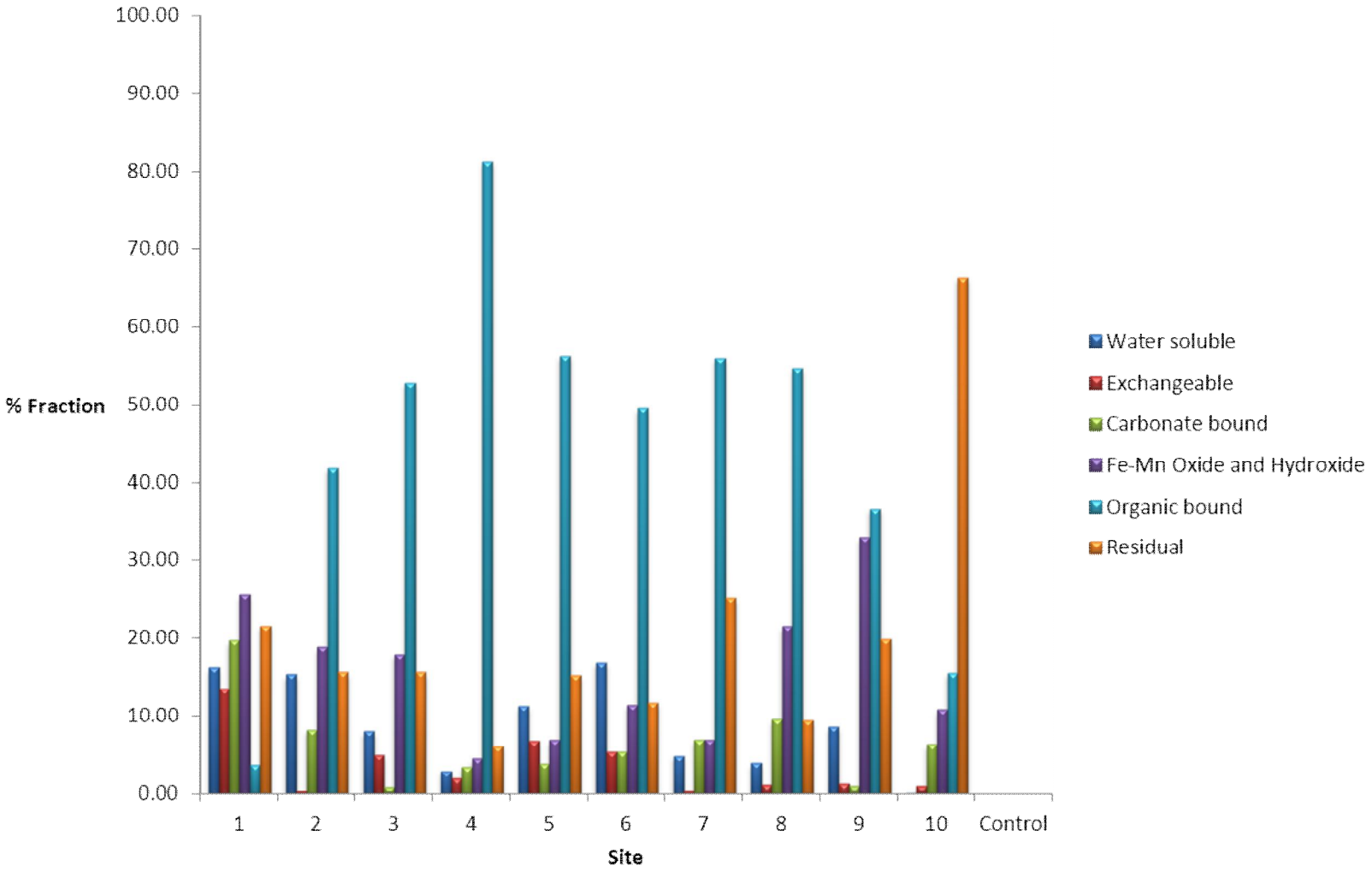


Fig. 4.18c. Percentage Cu in each operationally fraction of roadside soils particle size 150µm (Hot and Dry Season).

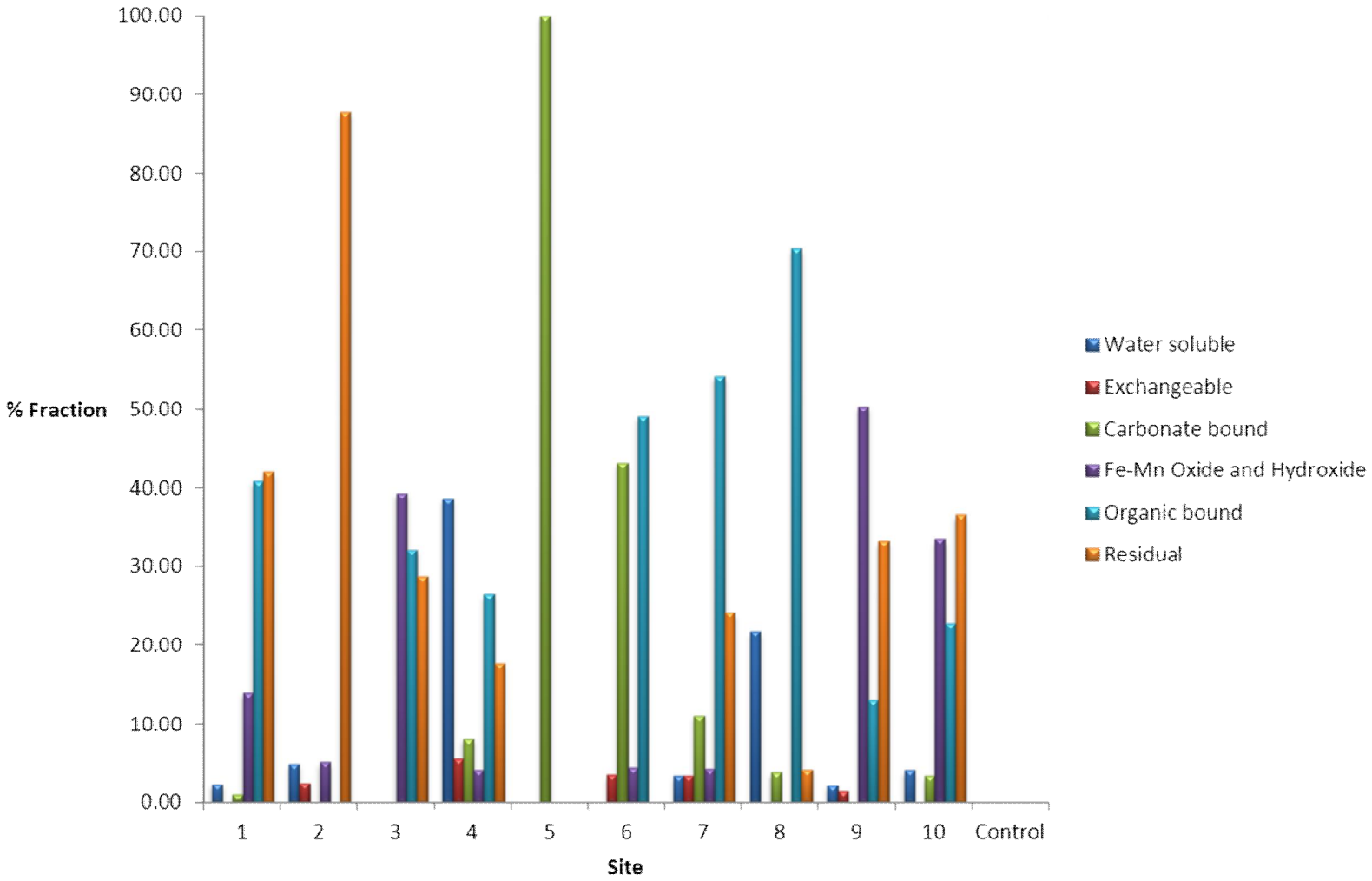


Fig. 4.19a. Percentage Cu in each operationally fraction of roadside soils particle size 1400µm (Warm and Wet Season).

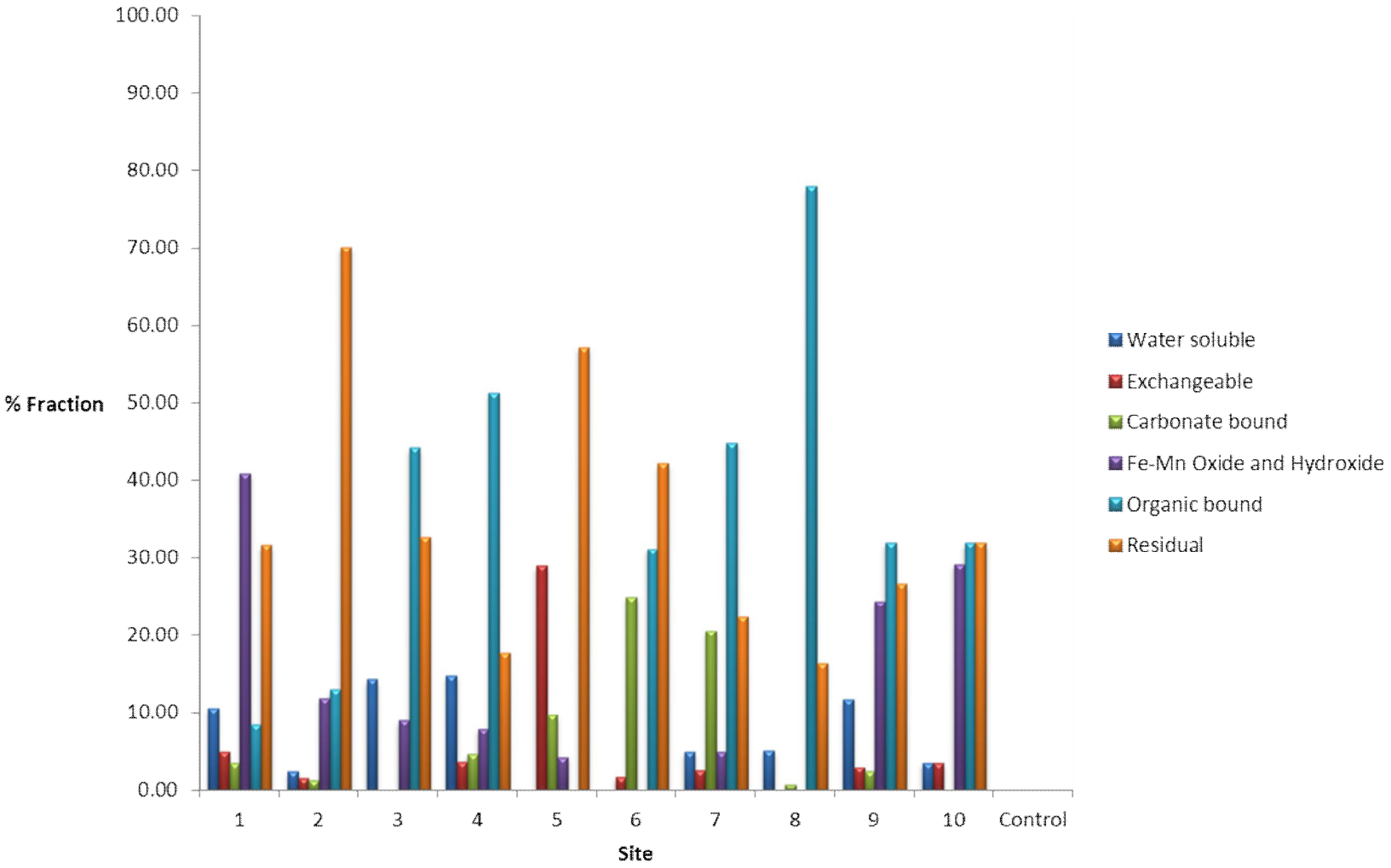


Fig. 4.19b. Percentage Cu in each operationally fraction of roadside soils particle size 355µm (Warm and Wet Season).

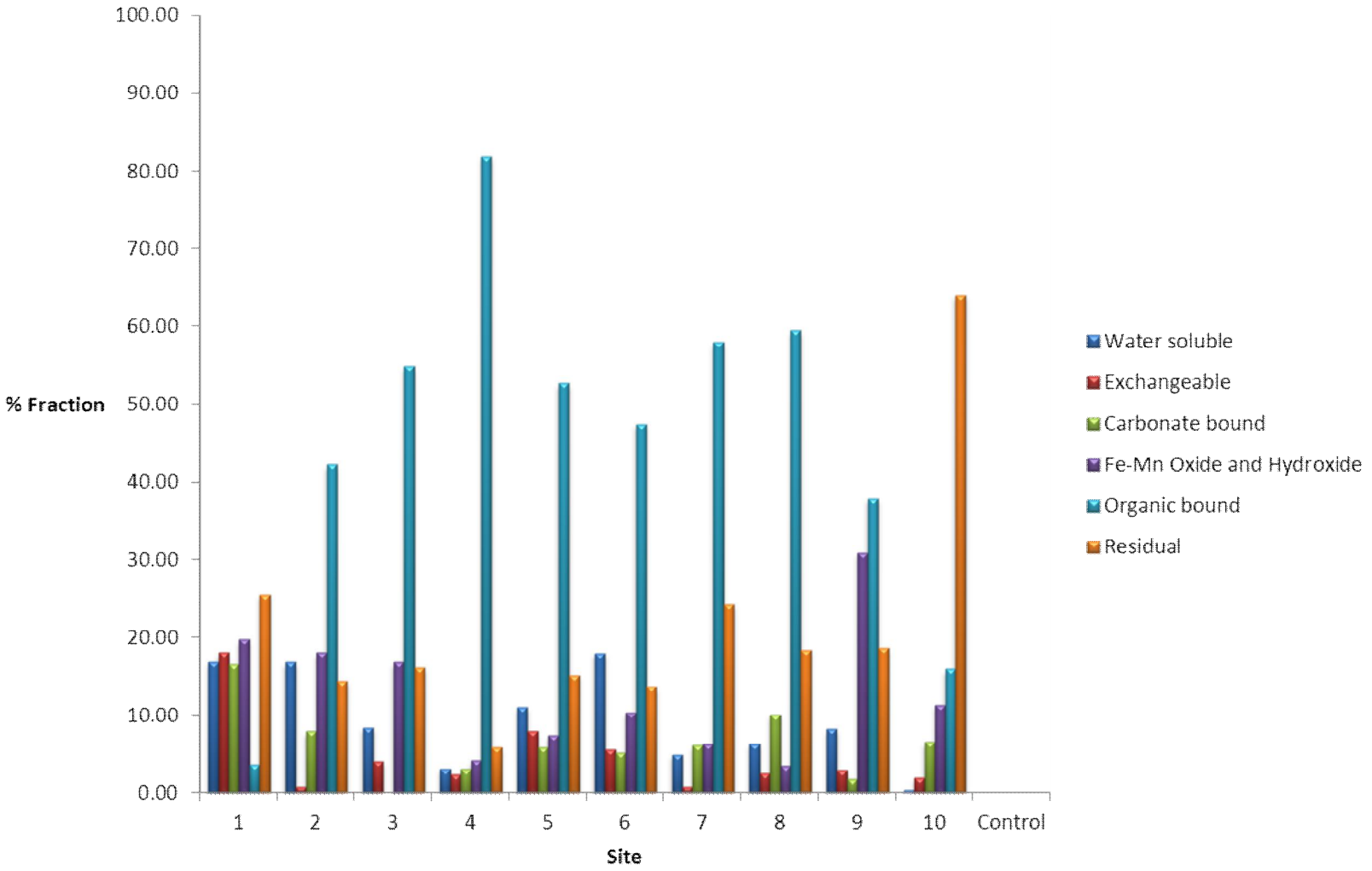


Fig. 4.19c. Percentage Cu in each operationally fraction of roadside soils particle size 150µm (Warm and Wet Season).

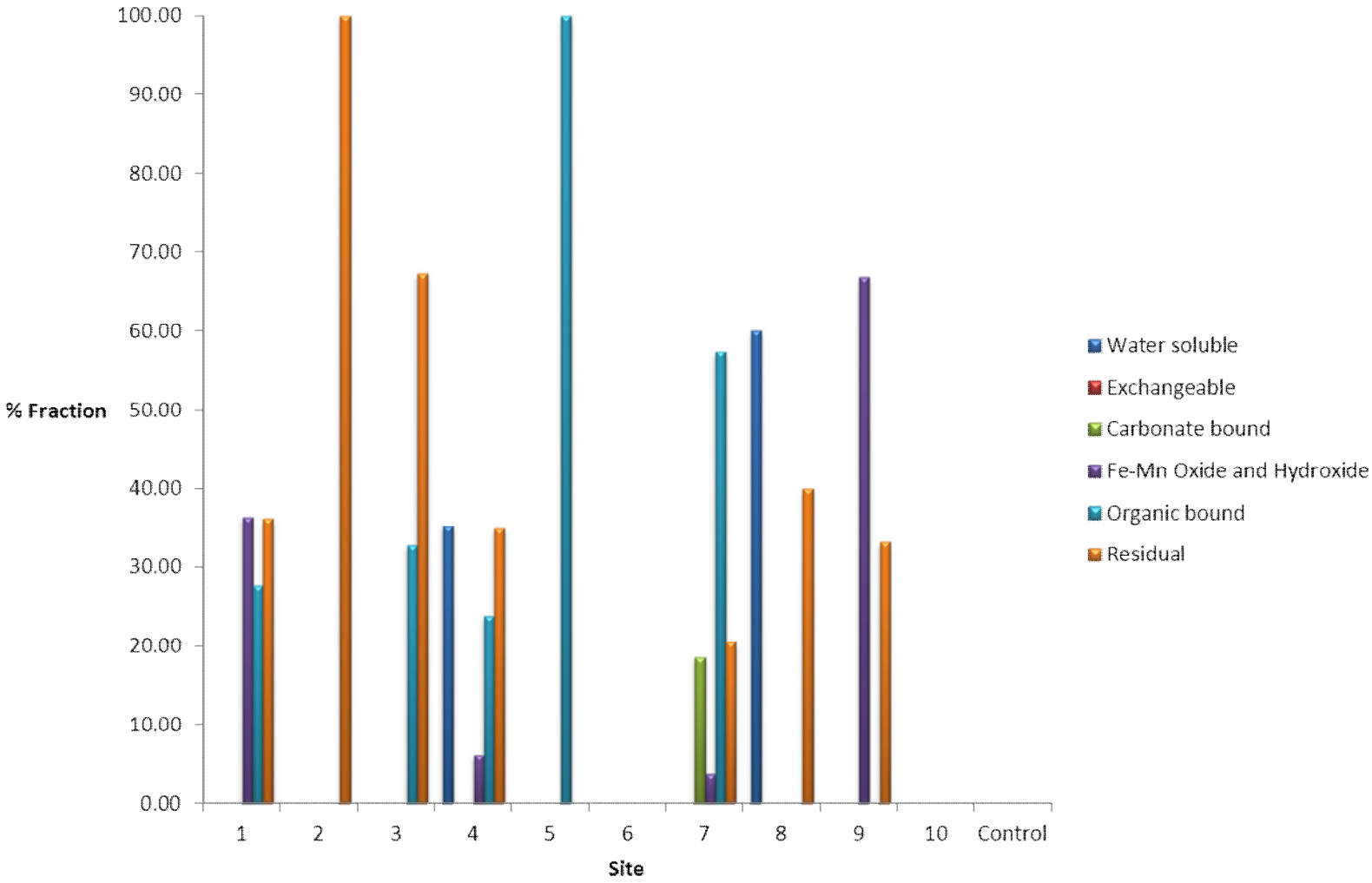


Fig. 4.20a. Percentage Cu in each operationally fraction of roadside soils particle size 1400µm (Warm and Dry Season).

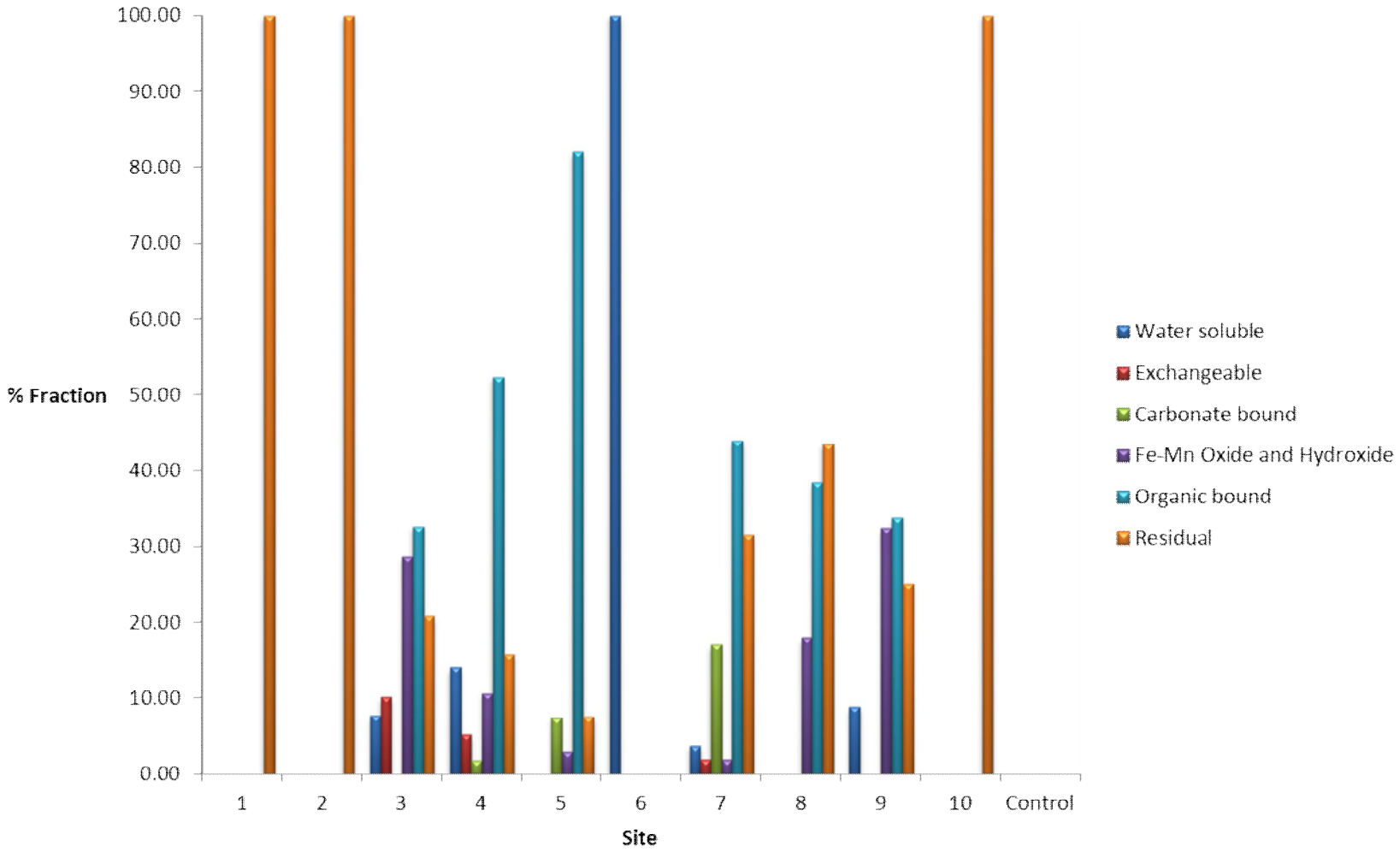


Fig. 4.20b. Percentage Cu in each operationally fraction of roadside soils particle size 355µm (Warm and Dry Season).

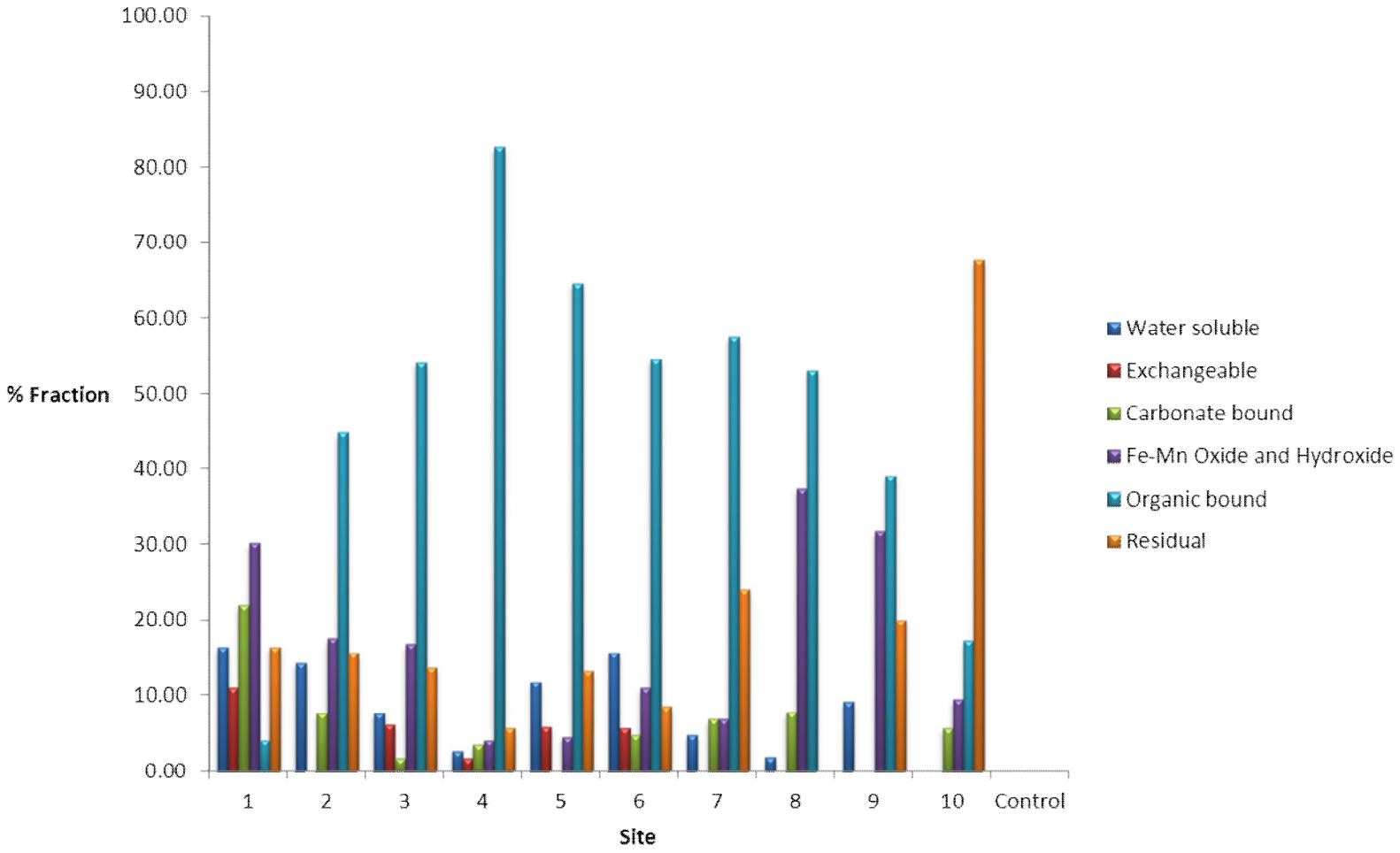


Fig. 4.20c. Percentage Cu in each operationally fraction of roadside soils particle size 150µm (Warm and Dry Season).

Also, for samples with 150µm grain size, the ranges ND (FIII) – 81.67% (FV), 0.81 (FI and FIII) – 81.28% (FV), ND (FIII) – 81.83% (FV) and ND (FI – FIII and FVI) – 82.67% (FV) were recorded during Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons, respectively. As could be seen, the dominant fractions for Cu concentration were carbonate bound, organic bound and residual phases in all samples.

Zn exhibits a partitioning pattern that varied from site to site across the seasons but was mainly found in the residual fraction for all samples as shown in Figs. 4.21 – 4.24a-c. For samples with 1400µm grain size, the range for this metal were ND (FI, FII and FV) – 93.68% (FVI), 0.01 (FI and FII) – 90.41% (FVI), ND (FI, FII and FV) – 94.69% (FVI) and 0.08 (FI) – 62.28% (FVI) during Cool and Dry, Hot and Dry, Warm and Wet and Warm and Dry Seasons, respectively. The following ranges ND (FI and FII) – 92.18% (FVI), 0.01 (FII) – 89.51% (FVI), ND (FI and FII) – 92.79% (FVI) and 0.16 (FI) – 61.78% (FVI) were for samples with 355µm grain size across the four seasons for the same metal, respectively. Lastly, for samples with 150µm grain size had of ND (FI and FII) – 90.72% (FVI), 0.05 (FI) – 88.94% (FVI), ND (FI and FII) – 91.40% (FVI) and 0.11 (FI) – 67.28% (FVI) ranges, respectively, recorded during Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons. The profile of Zn in different fractions across the seasons was residual > Fe-Mn oxide > carbonate bound > organic bound > water soluble = exchangeable with few exceptions.

4.7.2 Discussion

From the results shown in Figs. 4.1 – 4.4a-c, Cd seemed to be mainly distributed in the non-residual soil fractions FI – FV in all the soil samples.

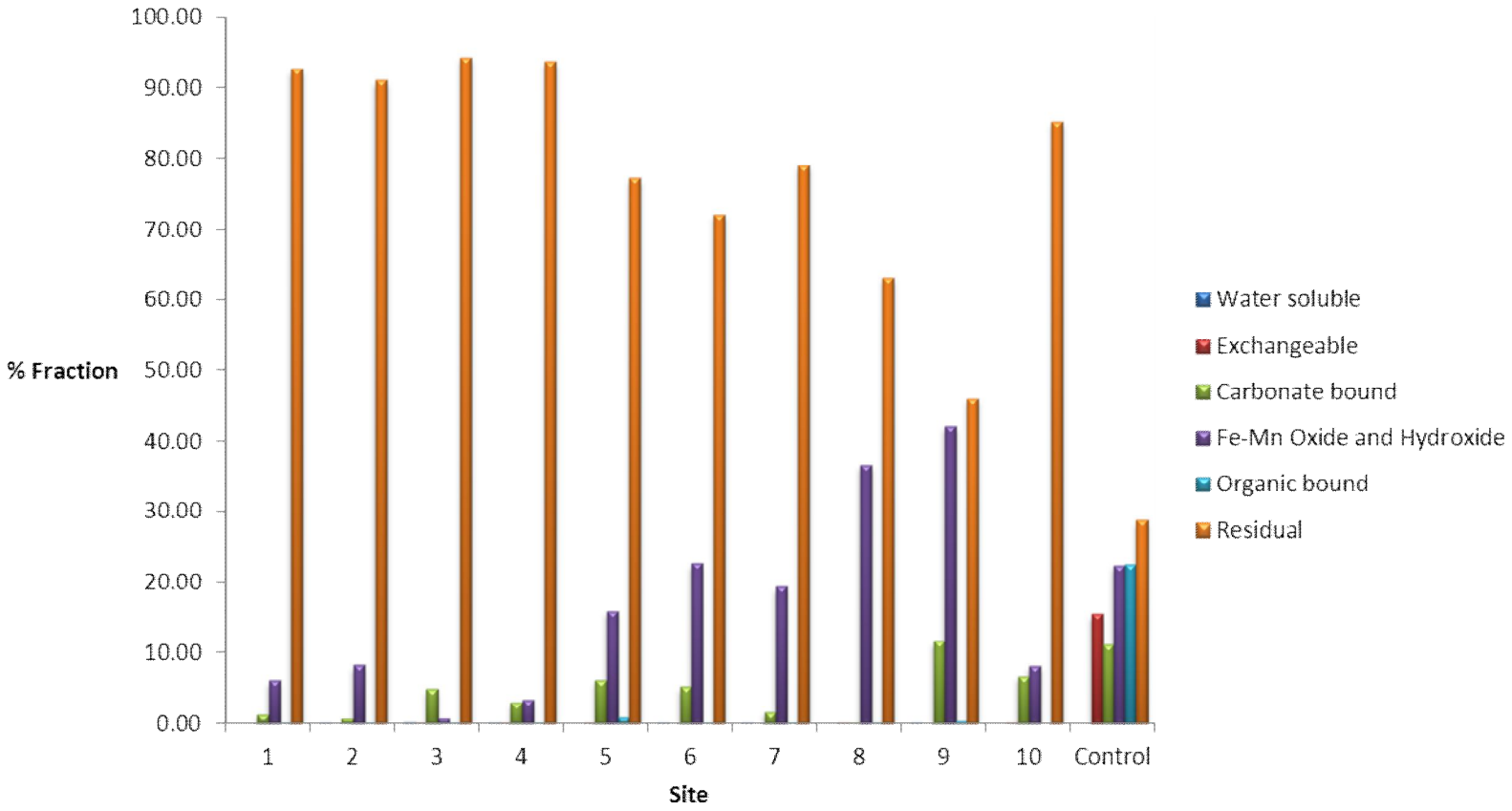


Fig. 4.21a. Percentage Zn in each operationally fraction of roadside soils particle size 1400µm (Cool and Dry Season).

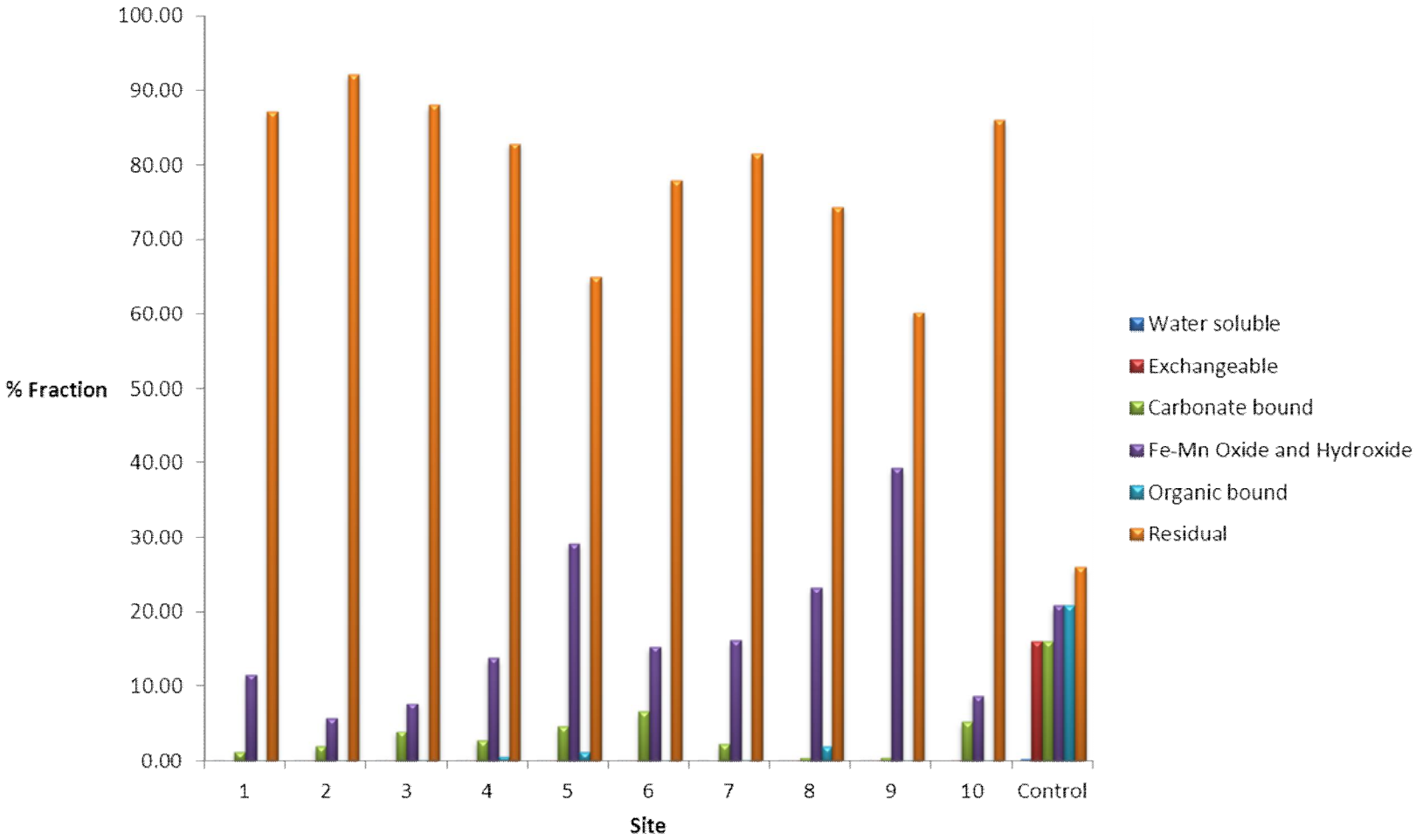


Fig. 4.21b. Percentage Zn in each operationally fraction of roadside soils particle size 355µm (Cool and Dry Season).

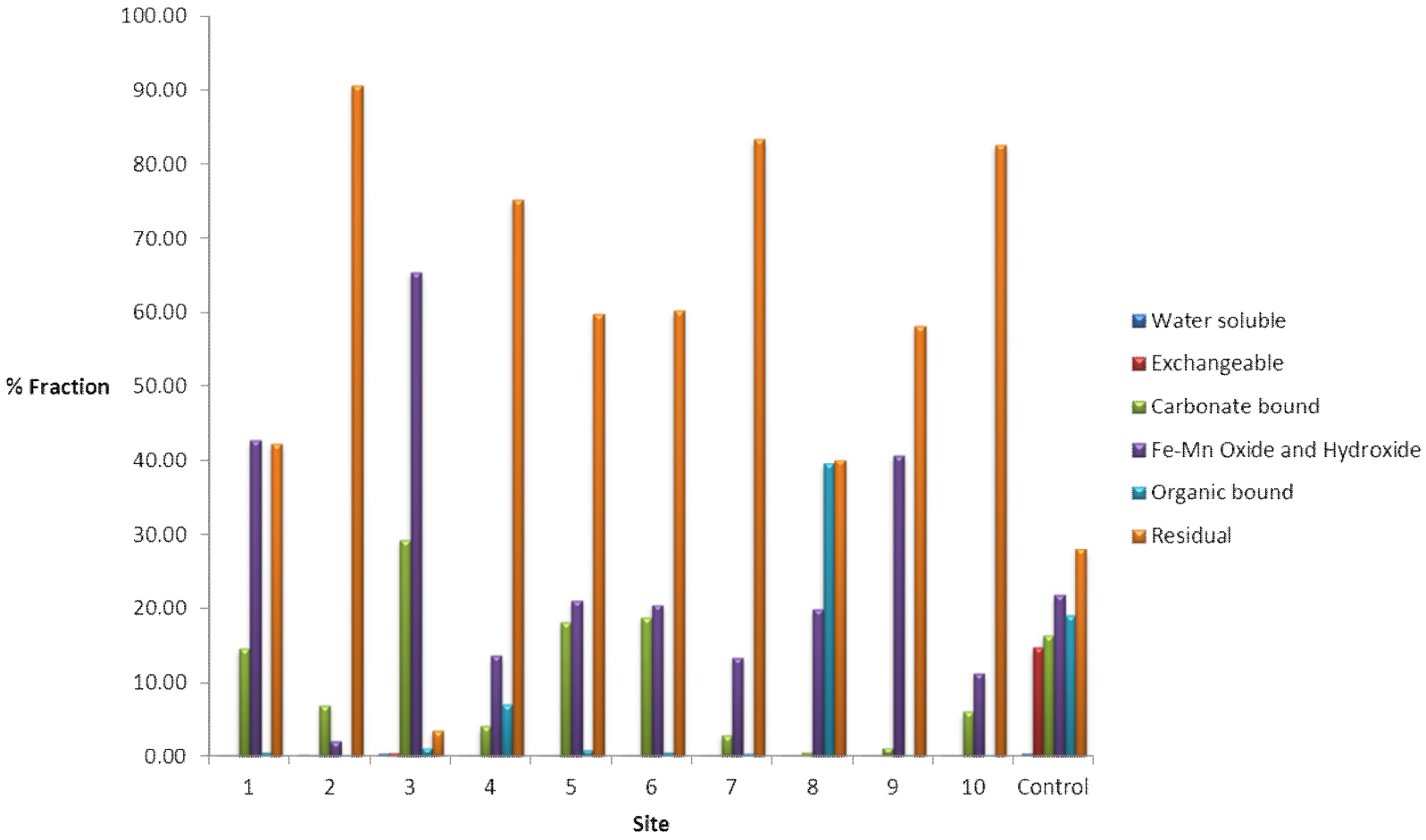


Fig. 4.21c. Percentage Zn in each operationally fraction of roadside soils particle size 150µm (Cool and Dry Season).

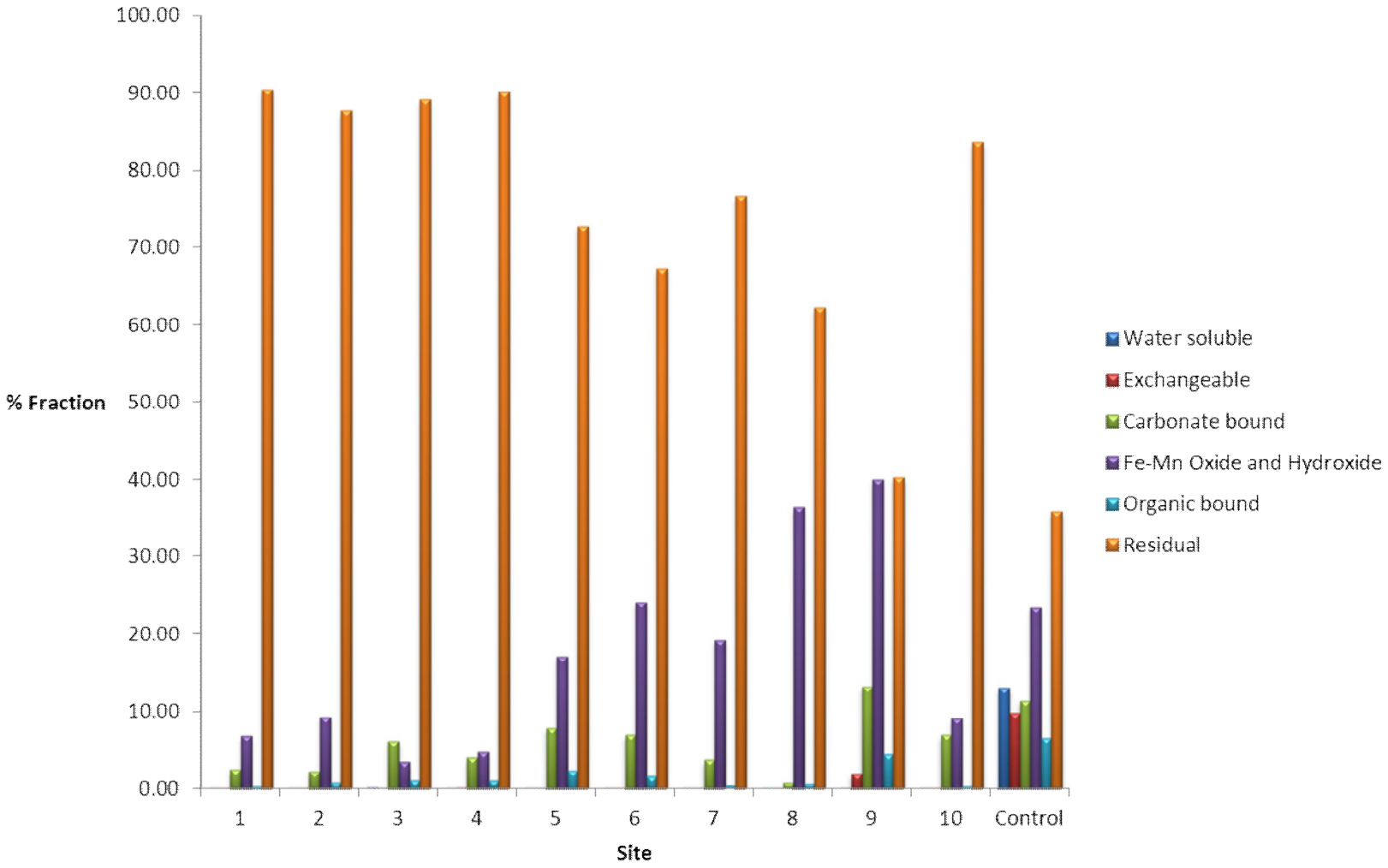


Fig. 4.22a. Percentage Zn in each operationally fraction of roadside soils particle size 1400µm (Hot and Dry Season).

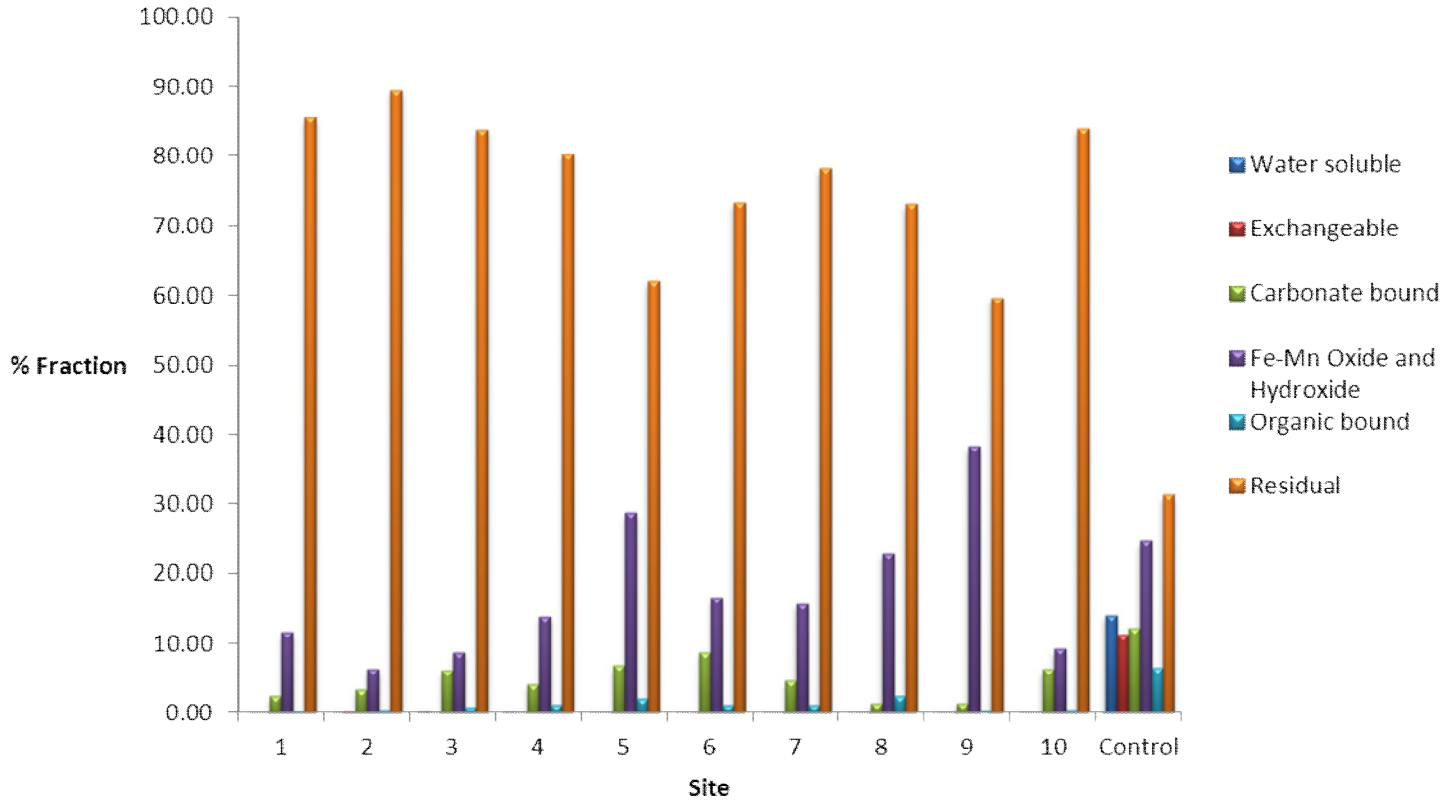


Fig. 4.22b. Percentage Zn in each operationally fraction of roadside soils particle size 355µm (Hot and Dry Season).

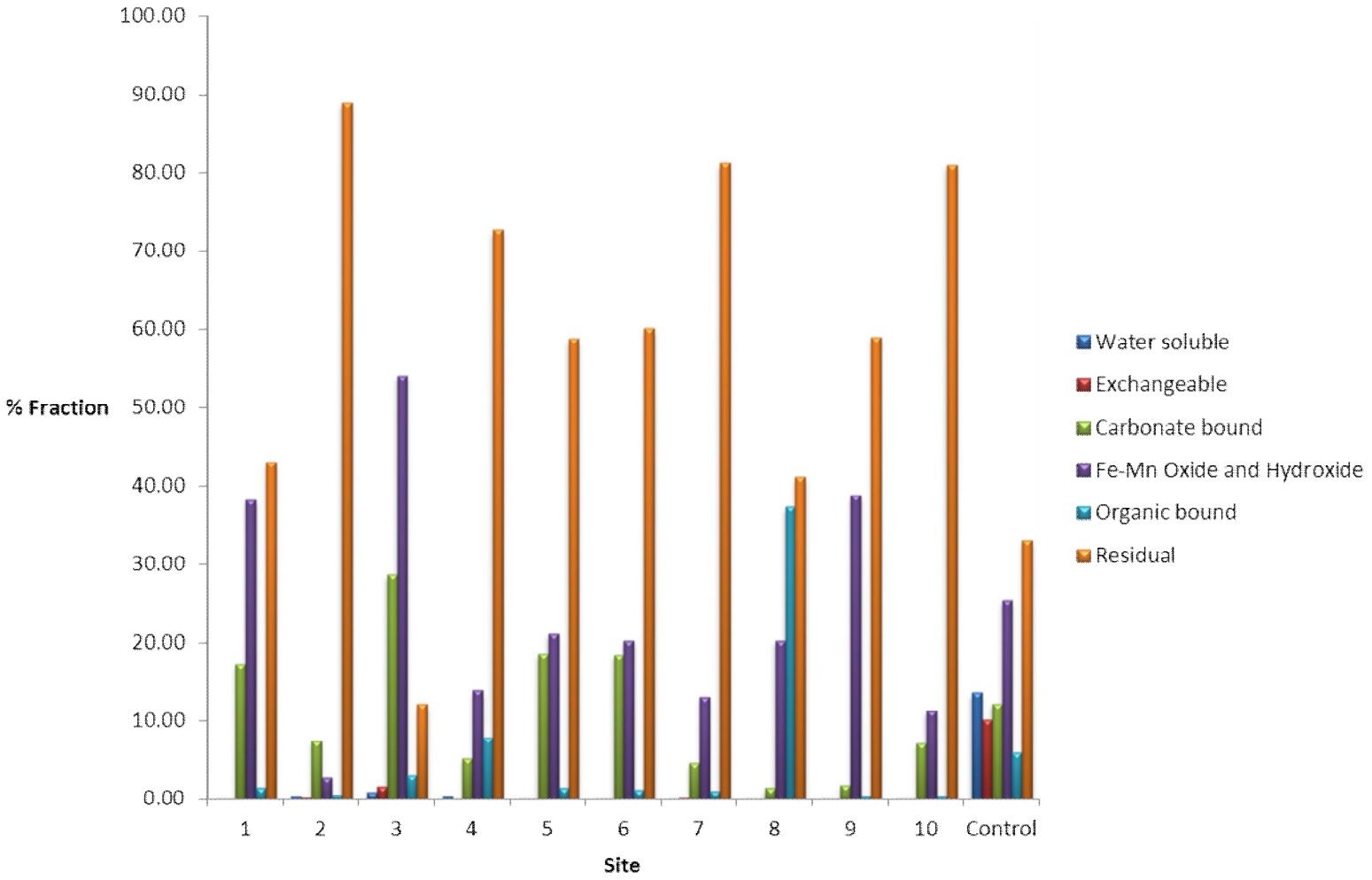


Fig. 4.22c. Percentage Zn in each operationally fraction of roadside soils particle size 150µm (Hot and Dry Season).

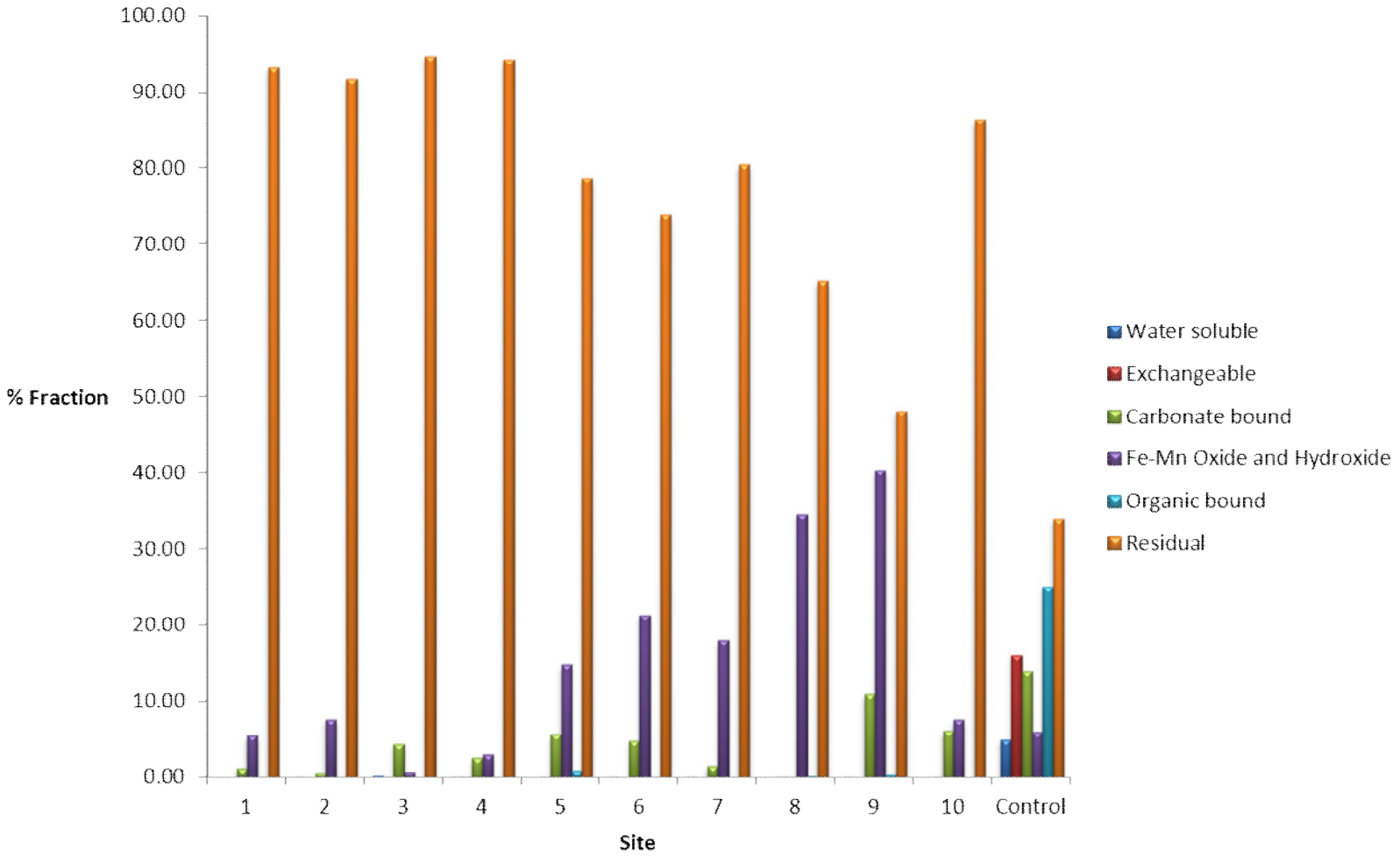


Fig. 4.23a. Percentage Zn in each operationally fraction of roadside soils particle size 1400µm (Warm and Wet Season).

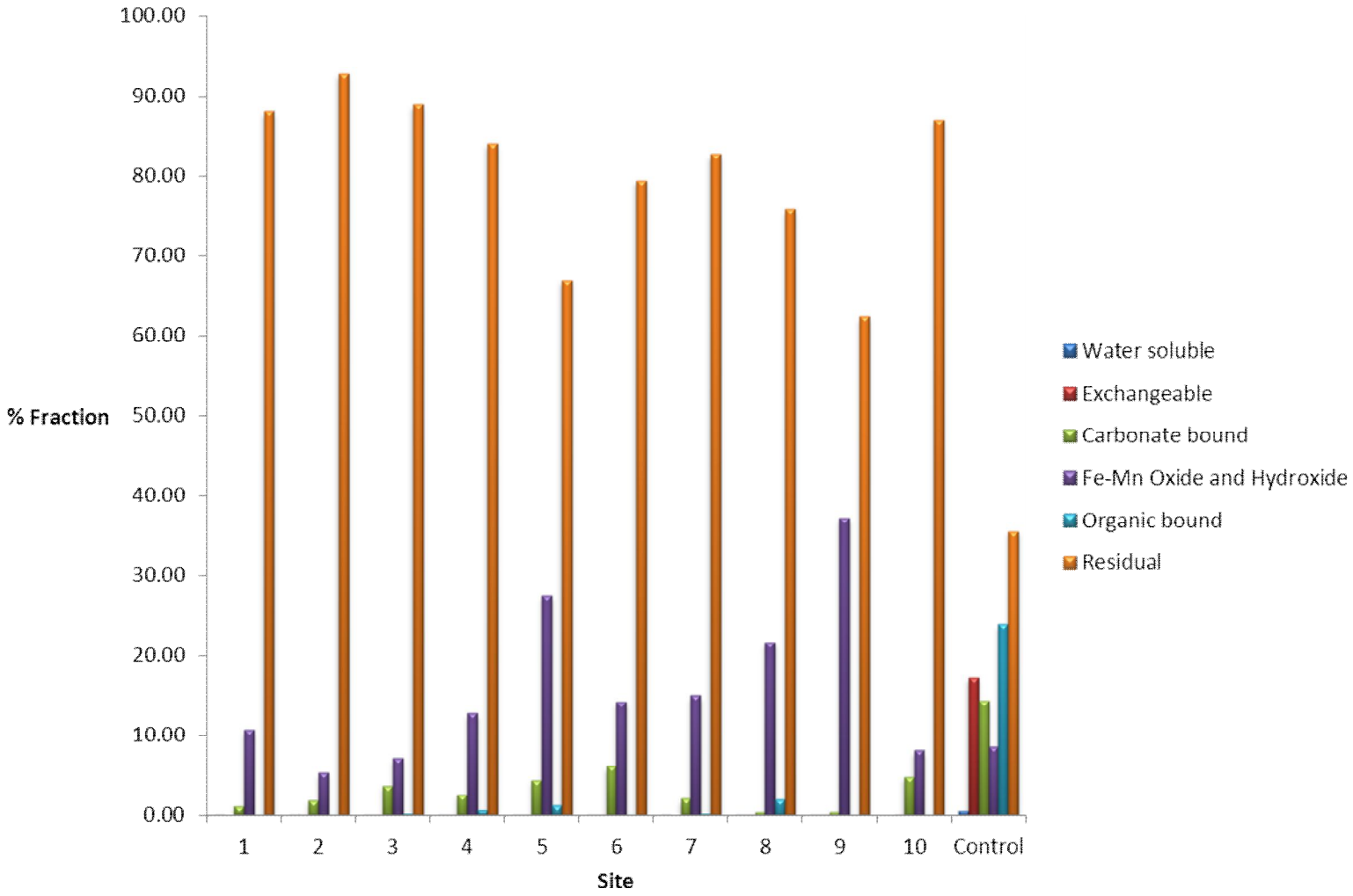


Fig. 4.23b. Percentage Zn in each operationally fraction of roadside soils particle size 355µm (Warm and Wet Season).

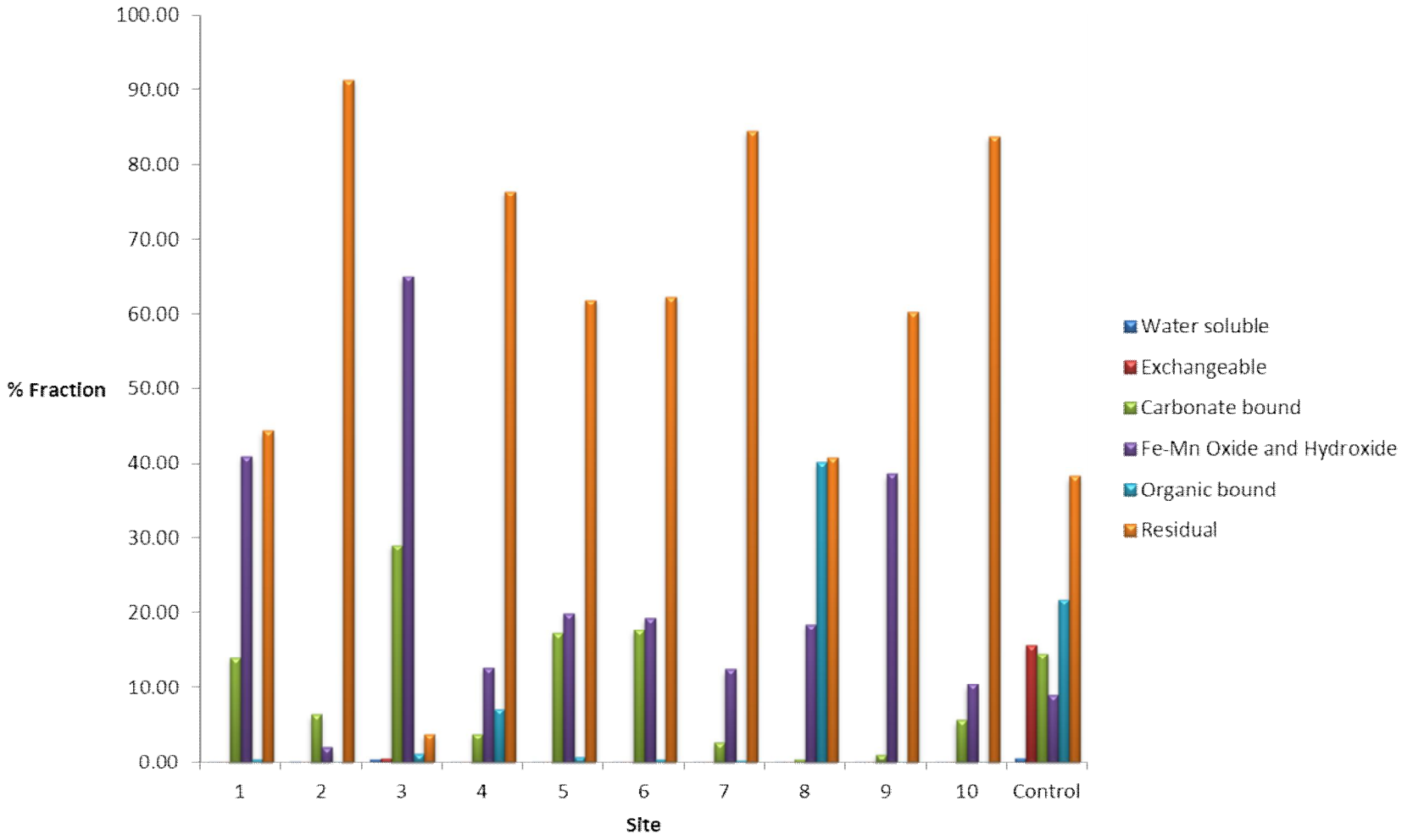


Fig. 4.23c. Percentage Zn in each operationally fraction of roadside soils particle size 150µm (Warm and Wet Season).

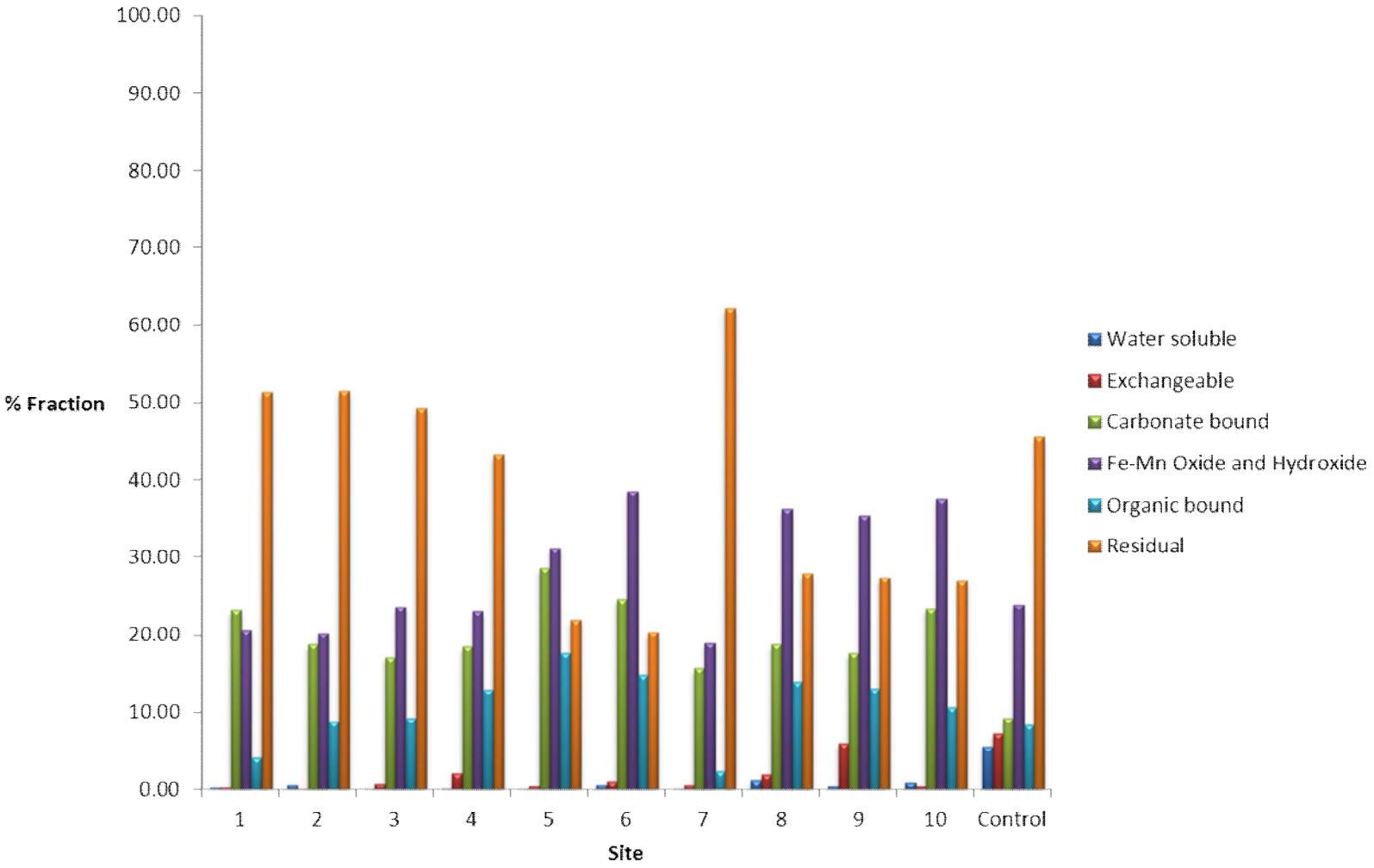


Fig. 4.24a. Percentage Zn in each operationally fraction of roadside soils particle size 1400µm (Warm and Dry Season).

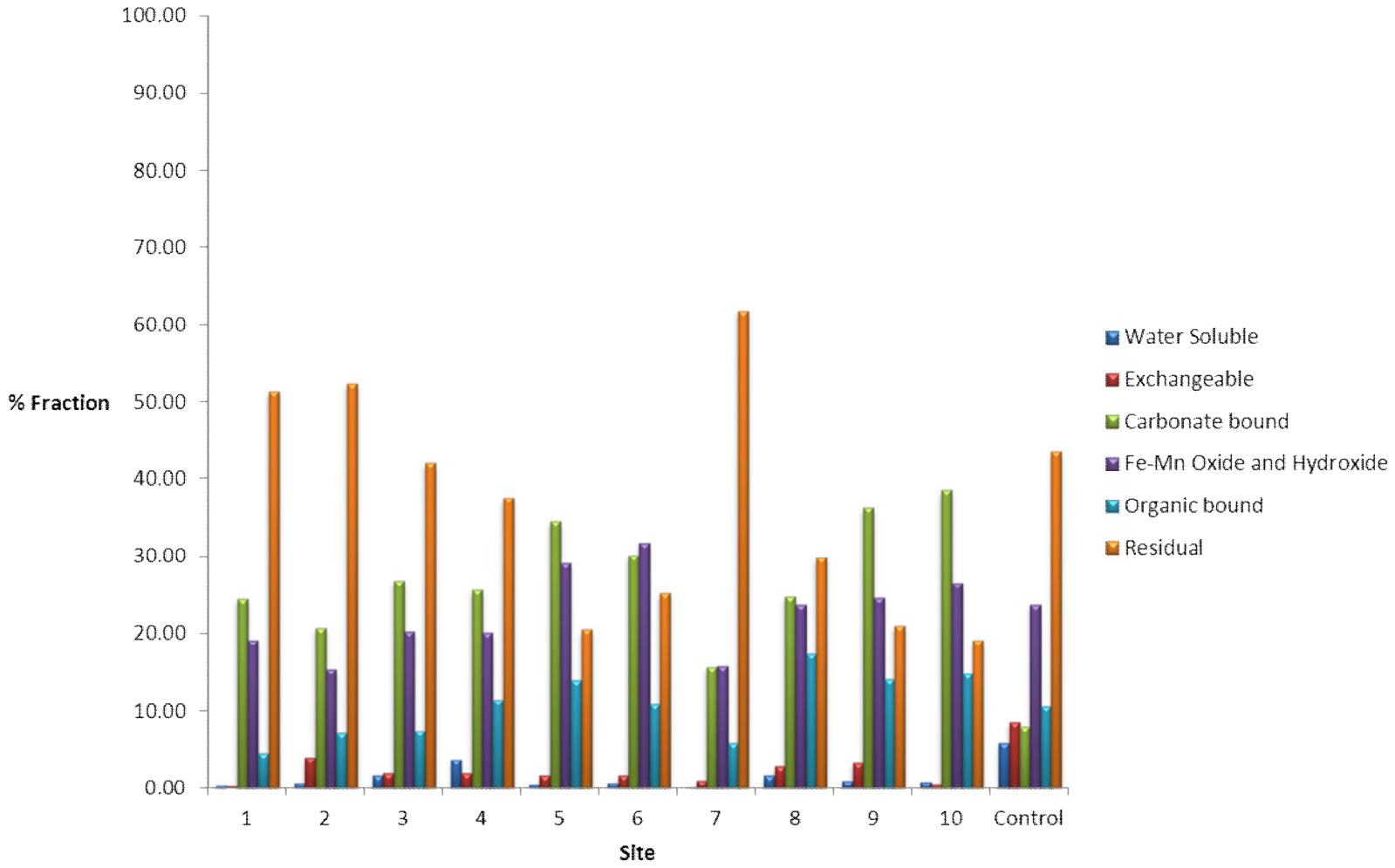


Fig. 4.24c. Percentage Zn in each operationally fraction of roadside soils particle size 355µm (Warm and Dry Season).

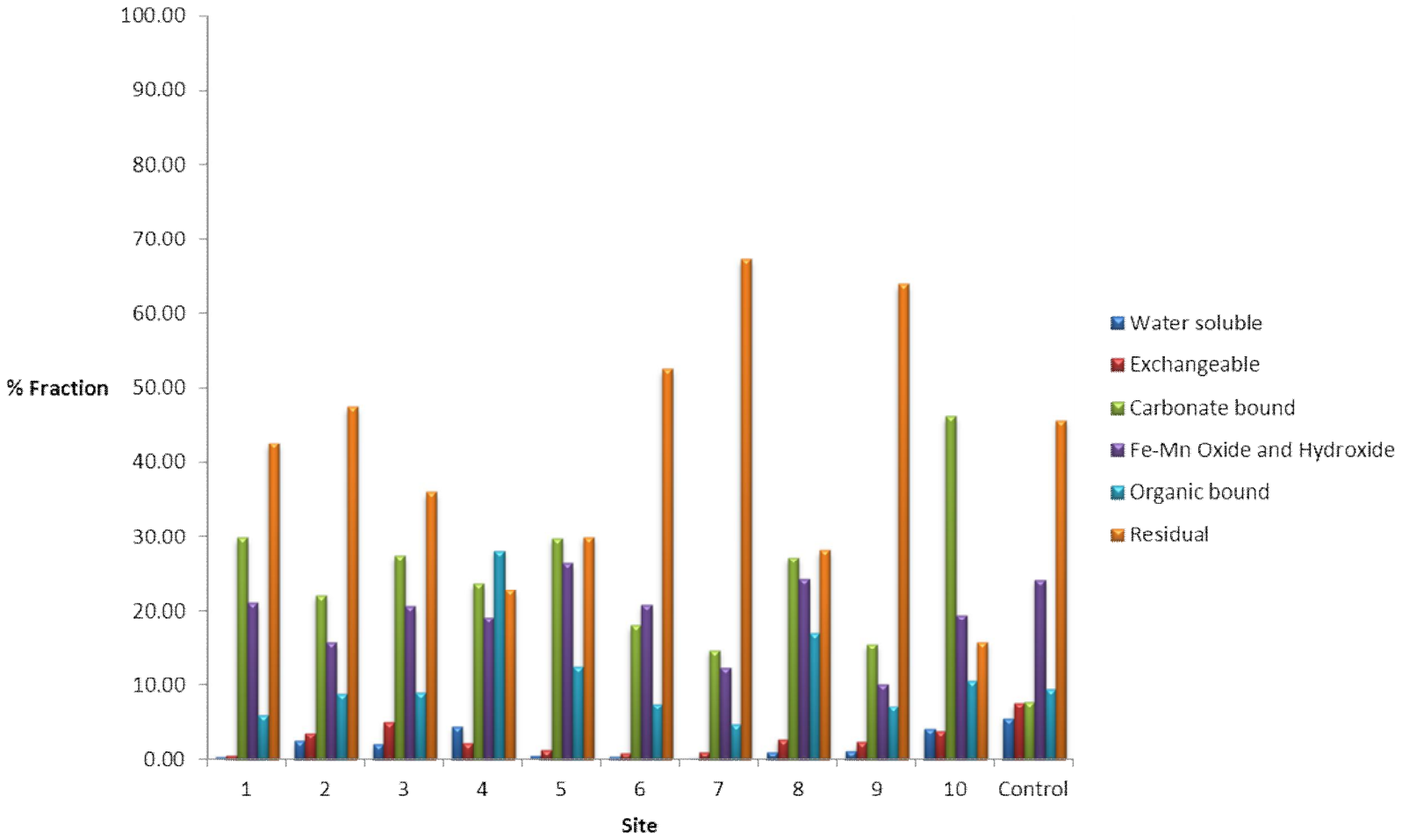


Fig. 4.24c. Percentage Zn in each operationally fraction of roadside soils particle size 150µm (Warm and Dry Season).

The highest percentages of Cd were associated with the carbonate bound, Fe-Mn oxide bound and organic bound fractions, making up > 40% of the total Cd content, although Site 7 and control has their highest percentage fraction associated with exchangeable phase during the Warm and Wet and Warm and Dry Season. The results generally indicate soil fractions FI – FV are the major carriers of Cd in soils across the Sites. This is similar to the findings of Oluwatosin *et al*. (2008). Also, this is supported by the fact that Cd is a very mobile metal that is more easily desorbs by ionic exchange processes (Pagotto *et al*., 2001; Diamantino, 2002), which is observed in samples with 355µm and 150µm grain size in this study. Among the non-residual phases, there is evidence that the speciation pattern of Cd in the soils were variable with sites and is similar with reported results (Stones and Marsalek, 1996) and contradicts with others (Karathanasis and Pils, 2005) where Fe-Mn oxide bound and residual fractions made up about 2/3 of the overall total Cd.

Furthermore, as found in the total metal studies (Table 4.10), high amount of Cd was found in samples from Site 8. However, the present study showed that Cd in Site 8 samples was mainly concentrated in the residual fraction especially for samples with 355µm and 150µm grain sizes. The positive correlation between EC, CEC and % OM content indicates that these factors control the distribution of Cd among the fractions. For organic matter, the polymerized, solid phase humus acts as a major adsorbent for heavy metals via formation of stable chelates (Massadeh *et al*., 2007) which keeps them immobile and much less bioavailable.

Furthermore, Cd adsorption by Mn oxides has been reported to increase linearly with pH, while organic coatings present Fe-Mn particles with surfaces that may enhance metal retentions (Manceau *et al*., 1992). This implies that toxicity problem attributed to Cd is not expected to occur, unless there is reduction of Fe or Mn, which could result in Cd mobility. In spite of relatively low percentage water soluble and exchangeable fractions, Cd shows stronger association with water soluble (< 30%) and exchangeable (< 45%) fractions (Site 5, 6 and 10) than any other metal especially for samples with 355µm and 150µm grain sizes. This agrees with some studies (Karathanasis and Pils, 2005; Hickey and Kittrick, 1984). Considering that percentage water soluble, exchangeable and carbonate bound fractions are regarded as a sensitive indicator of plant-uptake and bioavailability (Ma and Rao, 1997; Onianwa, 2001), the Cd concentration found in this study are considerably low than the lowest reported toxic level ($8mgkg^{-1}$) (Kabata-Pendias, 1995) (except Site 8).

The results of chemical fractionation of Cr in Figs. 4.5 – 4.8a-c show that Cr was primarily bound to the residual fraction (FVI) (except for Site 2) accounting on average > 50% of the total Cr, with the organic (FV) and Fe-Mn oxide (FIV) phases being next to the residual fraction for binding the metal. The results in the roadside soils are comparable to those reports from Seoul, Republic of Korea (Lee *et al*., 2005) and Ibadan Nigeria (Onianwa, 2001). This may probably be due to preferential incorporation of Cr into the silicate lattice (Lee *et al*., 2005). Also, the high level of Cr in the organic bound fraction may be attributed to the ease of complexation and peptisation products formed between the metal and natural organic matter like humic and fulvic acids (Ogunfowokan *et al*., 2009). The level of Cr in the Fe-Mn oxide fraction was probably due to the fact that chromate ions can be easily sorbed to hydrous oxide surfaces at pH levels > 4, while Cr^{3+} tend to co-precipitate with Fe-or Al-hydroxide because its ionic size and geochemical properties are very similar to those of Fe^{3+} and Al^{3+} (Kabata-Pendias and Pendias, 1992). This is supported by Pearson's correlation analysis (Table 4.22) showing a strong dependence of Cr on pH, particularly in samples with 1400µm grain size. Regarding the role of pH on

regulating mobility or leaching of Cr species, it is worth recalling that high soil pH tends to favour the mobility of Cr (VI) whereas low pH tends to favour the mobility of Cr (III) (Smith *et al*., 1995).

Generally, the high percentage of Cr in the residual fraction, indicate that the risk of Cr leaching is comparatively small, suggesting that Cr is of minor importance especially with large grain particle size during the Warm and Dry Season and with respect to ecotoxicity. Although toxicity due to Cr seems high especially at Site 5 across the seasons and Site 3 in cool and dry seasons, this could indicate a possible pollution due to Cr from other environmental niches within the site. This is because, metals released from roadside soils can be flushed through drain networks into drainages, thereby contaminating underground water nearby and most important the rivers flowing across Kano Metropolis.

Ni was found in all the fractions, irrespective of the total Ni concentration in all the roadside soils. Ni as observed from the results (Figs. 4.9 – 4.12a-c) was identified as potentially the most bioavailable metal as it had the highest percentage > 50% with grain size 1400µm in all seasons. The majority of Ni is partitioned in the carbonate, Fe-Mn oxide, organic and residual fractions while the proportion of Ni in the exchangeable fraction is low. High percentages of Ni in the residual fraction have also been reported by Sutherland and Tack. (2000), Banerjee (2003) and Lee *et al*. (2005). This is supported with correlation analyses (Tables 4.20 and 4.23) which show that silt was the main soil parameter controlling Ni retention in the residual fraction.

The sorption of Ni on Fe-Mn oxide surfaces usually occur through Ni^{2+} substitutions of Mn (Mckenzie, 1979) which must have been enhanced by the high pH in this study. This is consistent with the findings of other investigators suggesting that Ni mobilized during weathering processes is mainly co-precipitated with Fe-Mn oxides (Kabata-Pendias and Pendias, 1992). Hence, the mobility and bioavailability potentials of this metal should be of concern in the soils studied particularly if the soil pH drops significantly below 5.

Pb levels in the roadside (Figs. 4.13 – 4.16a-c) is of anthropogenic origin because of the positive significant correlation of the total concentration of the metal with traffic density. The non-residual fraction act as a predominant sink for anthropogenic Pb accounting for about 55% of total Pb except at Site 1 (63.29 – 87.98%) where residual fraction dominated. These results also indicate that water soluble, exchangeable, carbonate, Fe-Mn oxide and organic fractions contain significant amount of the Pb in roadside soils in Kano metropolis. Pb in the residual fraction varied widely from 0.00 – 87.98% with the highest at all the sites during Warm and Dry Season. Such variability of the Pb partitioning may be a function of different levels of anthropogenic contamination along the roadsides (Sutherland and Tack, 2000; Norrstrõm and Jacks, 1998).

Lead exists predominantly as Pb^{2+} in the environment, but when oxidized to Pb^{4+} it can be incorporated in clay mineral and Fe-Mn oxide structures (Kabata-Pendias and Pendias, 1992). Especially, for the samples with 355µm and 150µm grain sizes, the Fe-Mn oxide fraction was the second most important sink for Pb across the sites. Karathanasis and Pils (2005) also listed the Fe-Mn oxide as playing a second dominant role for Pb retention to carbonate bound fraction. Chlopecka *et al*. (1996) and Ramos *et al*. (1994), however, found most of the Pb mainly exist in the Fe-Mn oxide and organic fractions. In support of these reports, the fraction of Pb bound to oxides was quite high for most of the studied soils. A strong association of Pb with organic matter especially of samples with 150µm grain size as shown in Tables 4.21 – 4.23 was also described by Kabata-Pendias and

Pendias (1992), based on the results of many investigators. This could explain why Pb is bound to organic fraction.

Also, as shown in the bar graphs (Figs. 4.13 – 4.16a-c), the carbonate Pb is more abundant than any other non-residual fraction in many sites. The association of Pb with carbonate is expected because Pb has often been found in the carbonate fraction of calcareous soils (Sposito *et al*., 1982; Ramos *et al*., 1994; Chlopecka *et al*., 1996). The prominence of Pb in the reducible phase of the roadside soils has also been reported by many researchers (Li *et al*., 2001). Furthermore, level of Pb in each fraction seems to decrease as the surface area increases except during Warm and Wet and Warm and Dry Seasons. This could be related to high organic matter in smaller soil grain sizes compare to larger ones, thereby reducing the amount of Pb available. Similar to this study, other authors (Martinez-Martinez *et al*. 2010) observed that high concentration of Pb occurred in finest fractions is due to highest surface area and negative charges associated with fine particles. Also, small fraction of the total Pb was observed in the water soluble and exchangeable fraction of the soil solution, similar observation were reported by Maiz *et al*. (2000) and Finzgar *et al*. (2007). Hence, with high concentration of Pb in small particles, soluble Pb is more likely to traverse the gastric mucosa and be more efficiently adsorbed in human tissues than for coarse fractions (Lin *et al*., 1998).

The chemical speciation of Cu is dominated by the oxidizable (FV) (0.0 – 100%) and residual (FVI) (ND – 100%) fractions as shown in Figs. 4.17 – 4.20a-c. This is similar to what was found in other studies on roadside soils (Wang *et al*. 1998; Banerjee, 2003; Charlesworth *et al*., 2003) and indicates the effectiveness of organic matter as a scanvenger of Cu in roadside soils (Hickey and Kittrick, 1984). Also, a number of studies on speciation of Cu have shown that Cu is mainly associated with the oxidizable phase, occurring as organically complexed metal species (Pardo *et al*., 1993; Fytianos and Lourantou, 2004). This is because Cu shows high affinity to humic substances, which are natural organic matter chemically active in complexing, such metals (Pempkowiak *et al*., 1999). With the exception of Hot and Dry, and Warm and Dry Seasons, the association of Cu with organic fraction increases with increasing surface area, and highest during Warm and Dry Season in all the grain sizes. The role of water soluble (FI) and exchangeable fractions is not significant, though FI is significant at Site 4 (38.59%) and Site 8 (60- 100%) among the grain sizes but is not enough to cause environmental risk of Cu in the soils.

The association of Cu with Fe-Mn oxides is attributed to Cu^{2+} - Fe^{2+} competitive sorption or co-precipitation processes (Taylor, 1965) which tend to increase in smaller grain sizes (150μm). Since Cu was mainly associated with the organic and residual fractions, which are relatively insoluble under natural conditions, its status in the soils studied is considered stable and may not lead to any risk to the environment.

Zn was the most abundant metal in the soils studied. Unlike other metals chemical partitioning of Zn is majorly dominated by the residual (FVI) fraction accounting for nearly 95% of the total concentration in the soils during Warm and Wet Season. Following the residual fraction was the reducible (FIV) fraction then carbonate fraction (FIII) as shown in Figs. 4.21 – 4.24a-c, indicating that these three fractions are of major importance as Zn carriers in the roadside soils of Kano Metropolis. This is in agreement with previous findings for roadside soils (Banerjee, 2003; Lee *et al*., 2005) and urban city soils in South-Western Nigeria (Oluwatosin *et al*., 2008). Levels of the metal associated with the residual fraction decreases as the grain size of the soils increases from 1400 - 150 μm. The greater percentage of Zn in the residual fraction probably reflects the greater tendency of Zn to

become unavailable once it was in soils. Similar results for Zn were reported for contaminated soils (Ma and Rao, 1997).

Among the non residual fractions for Zn levels, Fe-Mn oxide fraction contained the greatest among the fractions with few exceptions at some sites. This may be partially due to the high stability constants of Zn oxides and the ability of Zn to replace Mn in the oxide surface (Ma and Rao, 1997; Karathanasis and Pils, 2005). Several other workers have also found Zn to be associated with Fe-Mn oxide phase of soil samples (Kuo *et al*., 1983; Ramos *et al*., 1994; Ma and Rao, 1997). The percentage content of the water soluble, exchangeable and organic fractions in these soils on average is relatively low. Although a large percentage of the total Zn was in the residual fraction in these soils, the amount of Zn present in the non-residual fractions was also appreciable from the standpoint of potential Zn mobility and bioavailability especially during Warm and Dry Season. Generally, Zn was present in all geochemical fractions, irrespective of the total Zn.

4.6 MOBILITY OF METALS IN ROADSIDE SOILS

Mobility of metals in soil may be assessed on the basis of absolute and relative content of fractions weakly bound to soil components. Since some of the metal fractions (FIV - FVI) are strongly bound to the soil components (relatively less mobile) than those extracted in FI, FII and FIII, the relative index of metal mobility was calculated as a mobility factor (MF) according Yusuf (2007) and Kabala and Singh (2001) on the basis of the following equation:

$$MF = (FI + FII + FIII) \times 100 \Big/ (FI + FII + FIII + FIV + FV + FVI) \quad \text{---------- 7}$$

The Tables 4.29 – 4.34 show the percentage mobility factor (MF) as evaluated for the metals (Cd, Cr, Ni, Pb, Cu and Zn) per site for roadside soils of different grain sizes across the four seasons. Evidently from the results in Table 4.29, the soil samples from Sites 5 and 7 have the highest vulnerability to Cd with the highest MF (82.47 and 87.35%) recorded during Warm and Wet Season for samples with 150µm and 355µm grain sizes and 83.33% for sample with 1400µm grain size during Warm and Dry Season. However, the MF of Cd in the soil samples across the seasons decreased in the following order:

	1400µm	5 > 7 > 9 > 3 > 10 > 6 > 4 > 8 > 1 > 2
Cool and Dry Season	**355µm**	7 > 9 > 5 > 10 > 6 > 4 > 2 > 3 > 8 > 1
	150µm	7 > 5 > 9 > 6 > 4 > 10 > 8 > 3 > 1 > 2
	1400µm	5 > 7 > 9 > 3 > 10 > 4 > 6 > 8 > 1 > 2
Hot and Dry Season	**355µm**	7 > 5 > 9 > 6 > 10 > 4 > 2 > 3 > 8 > 1
	150µm	7 > 9 > 5 > 6 > 4 > 10 > 8 > 2 > 1 > 3
	1400µm	5 > 7 > 9 > 3 > 10 > 6 > 4 > 8 > 1 > 2
Warm and Wet Season	**355µm**	7 > 9 > 5 > 10 > 6 > 4 > 2 > 8 > 3 > 1
	150µm	7 > 5 > 9 > 6 > 4 > 10 > 8 > 3 > 2 > 1
	1400µm	5 > 7 > 9 > 3 > 10 > 4 > 8 > 6 > 2 > 1
Warm and Dry Season	**355µm**	7 > 5 > 9 > 3 > 4 > 10 > 2 > 3 > 1 > 8

	150µm	7 > 5 > 9 > 6 > 4 > 8 > 10 > 2 > 1 > 3

In a similar manner the values of mobility factor (MF) for Cr (Table 4.30) recorded across the seasons showed that Sites 1, 5, 6 and 10 recorded highest among the sites. Generally, lower MF values were obtained for Cr compared to Cd, hence, Cd is more bioavailable than Cr. However, the following trends were found for Cr across the seasons.

	1400µm	1 > 6 > 8 > 5 > 10 > 7 > 4 > 3 > 2 > 9
Cool and Dry Season	**355µm**	1 > 5 > 10 > 6 > 8 > 4 > 7 > 3 > 2 > 9
	150µm	5 > 1 > 10 > 6 > 3 > 7 > 4 > 8 > 2 > 9
	1400µm	6 > 8 > 10 > 1 > 5 > 7 > 4 > 3 > 2 > 9
Hot and Dry Season	**355µm**	1 > 5 > 10 > 8 > 6 > 4 > 7 > 3 > 2 > 9
	150µm	5 > 1 > 10 > 6 > 4 > 3 > 8 > 7 > 2 > 9
	1400µm	1 > 6 > 8 > 5 > 10 > 7 > 4 > 3 > 2 > 9
Warm and Wet Season	**355µm**	5 > 1 > 10 > 6 > 8 > 4 > 7 > 3 > 2 > 9
	150µm	5 > 1 > 10 > 6 > 3 > 7 > 4 > 8 > 2 > 9
	1400µm	10 > 6 > 8 > 1 = 2 = 3 = 4 = 5 = 7 = 9
Warm and Dry Season	**355µm**	1 > 5 > 10 > 8 > 6 > 2 = 3 = 4 = 7 = 9
	150µm	5 > 1 > 6 > 10 > 4 > 8 > 3 > 2 > 7 = 9

As shown in Table 4.31, the highest mobility factor (72.81, 62.64 and 66.82%) for Ni was recorded during Warm and Wet Season for samples with 1400µm, 355µm and 150µm, respectively.

Table 4.29. Percentage Mobility Factor (MF) of Cd in Roadside Soils

	SITE									
Grain Size	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
	Cool and Dry Season									
1400µm	18.58	0.81	50.41	36.14	79.41	39.13	71.43	32.39	58.84	48.28
355 µm	25.36	36.59	35.00	38.24	65.57	42.86	81.55	32.02	68.89	47.62
150 µm	35.83	35.56	38.39	50.67	62.82	58.33	86.79	43.74	59.85	46.19
	Hot and Dry Season									
1400µm	8.67	8.05	54.90	34.41	81.13	32.86	70.49	31.72	62.59	47.62
355 µm	27.59	38.93	36.44	44.17	67.59	46.29	80.62	30.11	61.87	45.19
150 µm	36.92	38.98	32.10	52.92	61.52	57.81	81.39	44.13	61.80	45.52
	Warm and Wet Season									
1400µm	18.13	0.78	50.11	35.16	80.57	40.92	72.05	35.08	60.46	48.80
355 µm	24.37	36.84	34.84	37.29	66.67	44.98	82.47	34.02	70.86	48.99
150 µm	34.60	36.21	38.13	51.57	64.59	59.47	87.35	45.93	61.22	47.41
	Warm and Dry Season									
1400µm	0.00	12.50	60.00	33.33	83.33	25.00	70.00	30.77	66.67	47.37
355 µm	30.00	41.67	37.50	52.94	70.00	50.00	80.00	27.59	55.00	42.31
150 µm	38.46	42.86	25.00	55.56	60.00	56.52	75.00	44.20	63.56	43.53

Table 4.30. Percentage Mobility Factor (MF) of Cr in Roadside Soils

	SITE									
Grain Size	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
	Cool and Dry Season									
1400µm	44.00	0.88	2.30	2.34	23.63	31.56	9.40	26.25	0.58	22.78
355 µm	38.04	2.49	3.07	10.88	36.34	27.87	8.94	24.82	0.71	31.45
150 µm	45.46	2.78	26.42	14.83	52.10	27.61	14.57	11.15	1.57	33.56
	Hot and Dry Season									
1400µm	26.17	0.45	1.23	1.60	16.10	32.27	3.41	28.95	0.28	27.84
355 µm	35.08	1.27	1.58	6.07	34.49	25.87	5.14	25.97	0.39	30.82
150 µm	39.47	2.13	14.84	23.17	50.34	29.57	7.62	11.30	0.83	32.46
	Warm and Wet Season									
1400µm	41.81	1.05	2.52	2.66	24.13	31.80	10.34	25.08	0.64	21.74
355 µm	35.96	2.87	3.36	11.32	37.79	26.85	10.02	24.23	0.79	30.88
150 µm	43.90	3.03	28.15	15.27	54.27	26.82	15.29	11.02	1.62	32.72
	Warm and Dry Season									
1400µm	0.00	0.00	0.00	0.00	0.00	33.82	0.00	33.33	0.00	35.29
355 µm	32.81	0.00	0.00	0.00	31.15	23.60	0.00	27.59	0.00	29.65
150 µm	33.87	1.51	9.48	30.15	48.96	32.84	0.00	11.81	0.00	30.51

Table 4.31. Percentage Mobility Factor (MF) of Ni in Roadside Soils

	SITE									
Grain Size	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
	Cool and Dry Season									
1400µm	50.91	28.60	36.76	45.72	45.82	42.55	43.43	33.09	48.76	70.60
355 µm	58.73	28.43	47.55	52.30	35.18	39.20	39.91	33.26	59.71	36.79
150 µm	49.86	42.91	54.59	57.18	33.49	36.12	65.94	44.58	52.93	27.80
	Hot and Dry Season									
1400µm	50.96	22.22	35.87	43.41	39.41	25.81	45.78	27.94	49.48	69.26

355 µm	59.32	23.10	48.97	52.59	32.75	34.57	41.18	34.77	52.79	33.21
150 µm	49.95	41.89	55.15	56.62	32.26	33.94	62.56	45.73	51.87	23.69
	Warm and Wet Season									
1400µm	51.22	28.74	37.65	48.54	47.28	43.87	43.90	34.42	50.45	72.81
355 µm	59.68	29.46	48.29	54.70	36.67	41.00	39.14	35.50	62.64	38.59
150 µm	51.51	45.54	55.93	58.88	34.10	37.84	66.82	46.50	54.11	28.29
	Warm and Dry Season									
1400µm	51.35	17.19	34.85	40.35	33.33	9.73	48.52	23.24	51.18	67.66
355 µm	59.58	16.54	50.00	52.34	30.43	30.92	42.38	35.97	44.22	28.41
150 µm	49.55	40.38	54.78	55.32	31.09	32.47	58.62	46.59	51.12	18.16

Table 4.32. Percentage Mobility Factor (MF) of Pb in Roadside Soils

	SITE									
Grain Size	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
	Cool and Dry Season									
1400µm	20.35	20.24	21.34	60.96	36.18	11.37	12.14	32.35	68.42	59.77
355 µm	29.81	29.99	51.36	64.42	68.43	5.48	74.72	36.92	54.93	51.88
150 µm	28.69	44.49	38.31	67.60	35.63	35.30	52.78	56.09	66.88	50.29
	Hot and Dry Season									
1400µm	16.36	13.25	11.18	63.66	35.36	6.22	15.20	38.29	67.44	63.03
355 µm	17.53	20.38	42.24	64.91	65.08	2.93	66.13	25.66	54.44	56.91
150 µm	26.00	41.55	37.81	68.51	37.02	43.76	54.96	47.87	66.95	57.07
	Warm and Wet Season									
1400µm	20.85	19.22	21.77	61.41	36.27	11.32	11.42	34.09	69.29	62.00
355 µm	29.90	29.19	50.33	65.23	69.46	6.11	73.64	38.15	56.53	54.27
150 µm	28.80	43.27	37.47	67.12	34.53	35.53	51.89	55.86	68.93	52.20
	Warm and Dry Season									
1400µm	12.02	0.00	0.00	67.19	34.81	0.00	25.00	47.01	66.67	66.40
355 µm	7.34	0.00	35.61	65.34	61.54	0.00	58.33	20.28	53.56	60.85

150 µm	24.30	39.17	38.27	69.37	36.84	50.93	56.46	42.84	66.46	62.95

Table 4.33. Percentage Mobility Factor (MF) of Cu in all Studied Seasons

	SITE									
Grain Size	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
	Cool and Dry Season									
1400µm	3.03	6.59	0.00	50.27	100.00	48.34	17.91	24.30	3.10	7.09
355 µm	17.51	4.87	13.11	22.03	37.39	28.20	28.63	5.44	15.79	6.25
150 µm	49.54	24.34	11.22	8.04	23.72	27.14	11.67	18.92	11.64	9.04
	Hot and Dry Season									
1400µm	1.43	3.70	0.00	43.91	4.44	48.31	18.15	33.94	1.78	7.07
355 µm	13.69	2.91	15.90	22.00	11.27	57.81	25.67	2.21	12.71	5.40
150 µm	49.30	23.80	13.75	8.17	21.89	27.43	11.97	14.51	10.71	7.36
	Warm and Wet Season									
1400µm	3.18	7.22	0.00	52.03	100.00	46.61	17.62	25.50	3.55	7.35
355 µm	19.04	5.13	14.32	23.13	38.59	26.64	27.87	5.81	17.05	7.00
150 µm	51.24	25.37	12.37	8.25	24.75	28.57	11.68	18.85	12.70	8.78
	Warm and Dry Season									
1400µm	0.00	0.00	0.00	35.19	0.00	0.00	18.58	60.00	0.00	0.00
355 µm	0.00	0.00	17.86	21.20	7.45	100.00	22.71	0.00	8.82	0.00
150 µm	49.32	22.03	15.46	7.62	17.61	26.07	11.61	9.57	9.17	5.71

Table 4.34. Percentage Mobility Factor (MF) of Zn in all Studied Seasons

	SITE									
Grain Size	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
	Cool and Dry Season									
1400µm	1.21	0.64	5.06	2.92	6.08	5.17	1.57	0.12	11.55	6.59
355 µm	1.26	2.09	4.10	2.76	4.69	6.64	2.22	0.48	0.50	5.20
150 µm	14.65	7.09	30.04	4.12	18.31	18.85	2.91	0.54	1.09	6.03
	Hot and Dry Season									
1400µm	2.43	2.25	6.43	4.14	7.89	7.12	3.78	0.76	15.29	7.01
355 µm	2.49	3.70	6.59	4.53	7.05	9.01	4.86	1.59	1.56	6.32
150 µm	17.44	7.89	30.97	5.68	18.75	18.56	4.83	1.47	1.91	7.34
	Warm and Wet Season									
1400µm	1.12	0.59	4.69	2.69	5.67	4.84	1.47	0.11	11.08	6.10
355 µm	1.16	1.93	3.82	2.57	4.43	6.20	2.06	0.45	0.48	4.81
150 µm	14.10	6.58	30.02	3.84	17.34	17.85	2.71	0.52	1.04	5.60
	Warm and Dry Season									
1400µm	23.77	19.38	17.87	20.81	29.17	26.28	16.33	21.88	24.01	24.71
355 µm	25.07	25.11	30.18	31.00	36.52	32.33	16.74	29.06	40.33	39.75
150 µm	30.59	28.02	34.39	30.14	31.34	19.31	15.69	30.65	18.81	54.16

Also, as shown in the Mf pattern across the seasons, it was also observed that inhabitants of Sites 1, 7, 9 and 10 were more vulnerable to Ni, while those living around Sites 2, 6 and 10 had the least vulnerability.

	1400µm	10 > 1 > 9 > 5 > 4 > 7 > 6 > 3 > 8 > 2
Cool and Dry Season	**355µm**	9 > 1 > 4 > 3 > 7 > 6 > 10 > 5 > 8 > 2

	150µm	7 > 4 > 3 > 9 > 1 > 8 >2 > 6 > 5 > 10
	1400µm	10 > 1 > 9 > 7 > 4 > 5 > 3 > 8 > 6 > 2
Hot and Dry Season	**355µm**	1 > 9 > 4 > 3 > 7 > 8 > 6 > 10 > 5 > 2
	150µm	7 > 4 > 3 > 9 > 1 > 8 > 2 > 6 > 5 > 10
	1400µm	10 > 1 > 9 > 4 > 5 > 7 > 6 > 3 > 8 > 2
Warm and Wet Season	**355µm**	9 > 1 > 4 > 3 > 6 > 7 > 10 > 5 > 8 > 2
	150µm	7 > 4 > 3 > 9 > 1 > 8 > 2 > 6 > 5 > 10
	1400µm	10 > 1 > 9 > 7 > 4 > 3 > 5 > 8 > 2 > 6
Warm and Dry Season	**355µm**	1 > 4 > 3 > 9 > 7 > 8 > 6 > 5 > 10 > 2
	150µm	7 > 4 > 3 > 9 > 1 > 8 > 2 > 6 > 5 > 10

The values of mobility factor (MF) for Pb (Table 4.32) revealed highest MF at Sites 7 (69.29%) and 9 (73.64%) during Warm and Wet Season and lowest at Sites 1 and 6 during Cool and Dry Season. Also across the seasons, population living or working around Sites 4, 7 and 9 showed highest vulnerability to Pb exposure compared to Sites 1 and 6. Furthermore, MF value of Pb across the seasons decreased in the following order:

	1400µm	9 > 4 > 10 > 5 > 8 > 3 > 1 > 2 > 7 > 6
Cool and Dry Season	**355µm**	7 > 5 > 4 > 9 > 10 > 3 > 8 > 2 > 1 > 6
	150µm	4 > 9 > 8 > 7 > 10 > 2 > 3 > 5 > 6 > 1
	1400µm	9 > 4 > 10 > 8 > 5 > 1 > 7 > 2 > 3 > 6
Hot and Dry Season	**355µm**	7 > 5 > 4 > 9 > 10 > 3 > 8 > 2 > 1 > 6
	150µm	4 > 9 > 10 > 7 > 8 > 6 > 2 > 3 > 5 > 1
	1400µm	9 > 10 > 4 > 5 > 8 > 3 > 1 > 2 > 7 > 6
Warm and Wet Season	**355µm**	7 > 5 > 4 > 9 > 10 > 3 > 8 > 1 > 2 > 6
	150µm	9 > 4 > 8 > 10 > 7 > 2 > 3 > 6 > 5 > 1
	1400µm	4 > 9 > 10 > 8 > 5 > 7 > 1 > 2 = 3 = 6
Warm and Dry Season	**355µm**	4 > 5 > 10 > 7 > 9 > 3 > 8 > 1 > 2 = 6
	150µm	4 > 9 > 10 > 7 > 6 > 8 > 2 > 3 > 5 > 1

Cu in contrast to other metals recorded the highest mobility factor in samples of different grain sizes during all the seasons. The highest MF (Site 5, 100%) for 1400µm grain size was recorded during Cool and Dry, and Warm and Wet Season. 100% was also recorded at Site 6 for 355µm grain size samples during Warm and Dry Season , and 49.54% (Site 1) for 150µm grain size samples during Cool and Dry Season. However, across the seasons the bioavailability of Cu declined in the following order:

1400µm 5 > 4 > 6 > 8 > 7 > 10 > 2 > 9 > 1 > 3

Cool and Dry Season	**355µm**	5 > 7 > 6 > 4 > 1 > 9 > 3 > 10 > 8 > 2
	150µm	1 > 6 > 2 > 5 > 8 > 7 > 9 > 3 > 10 > 4
	1400µm	6 > 4 > 8 > 7 > 10 > 5 > 2 > 9 > 1 > 3
Hot and Dry Season	**355µm**	6 > 7 > 4 > 3 > 9 > 1 > 5 > 10 > 2 > 8
	150µm	1 > 6 > 2 > 5 > 8 > 3 > 7 > 9 > 4 > 10
	1400µm	5 > 4 > 6 > 7 > 8 > 10 > 2 > 9 > 1 > 3
Warm and Wet Season	**355µm**	5 > 7 > 6 > 4 > 1 > 9 > 3 > 10 > 7 > 2
	150µm	1 > 6 > 2 > 5 > 8 > 9 > 3 > 7 > 10 > 4
	1400µm	8 > 4 > 7 > 1 = 2 = 3 = 5 = 6 = 9 = 10
Warm and Dry Season	**355µm**	6 > 7 > 4 > 3 > 9 > 5 > 1 = 2 = 8 = 10
	150µm	1 > 6 > 2 > 5 > 7 > 3 > 8 > 9 > 4 > 10

Apart from Warm and Dry Season, Zn revealed the least MF among the metals, with MF showing in similar pattern to Cu in among the grain sizes. This indicates that Zn was least bioavailable to the environment, since most Zn was concentrated in the residual fraction. Generally, highest MF 29.17, 40.33 and 54.16% were recorded at Sites, 5, 9 and 10, respectively, for the grain sizes in decreasing order during Warm and Dry Season. This indicates that Zn was more bioavailable to the environment after rains. However the MF pattern for Zn across the seasons was:

	1400µm	9 > 10 > 5 > 6 > 3 > 4 > 7 > 1 > 2 > 8
Cool and Dry Season	**355µm**	6 > 10 > 5 > 3 > 4 > 7 > 2 > 1 > 9 > 8
	150µm	3 > 6 > 5 > 1 > 2 > 10 > 4 > 7 > 9 > 8
	1400µm	9 > 5 > 6 > 10 > 3 > 4 > 7 > 1 > 2 > 8
Hot and Dry Season	**355µm**	6 > 5 > 3 > 10 > 7 > 4 > 2 > 1 > 8 > 9
	150µm	3 > 5 > 6 > 1 > 2 > 10 > 4 > 7 > 9 > 8
	1400µm	9 > 10 > 5 > 3 > 6 > 4 > 1 > 7 > 2 > 8
Warm and Wet Season	**355µm**	6 > 10 > 5 > 3 > 4 > 7 > 2 > 1 > 9 > 8
	150µm	3 > 6 > 5 > 1 > 2 > 10 > 4 > 7 > 9 > 8
	1400µm	5 > 6 > 10 > 9 > 1 > 8 > 4 > 2 > 3 > 7
Warm and Dry Season	**355µm**	9 > 10 > 5 > 6 > 4 > 3 > 8 > 2 > 1 > 7
	150µm	10 > 3 > 5 > 8 > 1 > 4 > 2 > 6 > 9 > 7

Overall, the results of the present study suggest that the mobility and bioavailability of the metals declined in the following order across the seasons.

Cool and Dry Season
1400µm : Ni > Cd > Pb > Cu > Cr > Zn
355µm : Cd > Pb > Ni > Cr > Cu > Zn
150µm : Cd > Pb > Ni > Cr > Cu > Zn
Hot and Dry Season
1400µm : Cd > Ni > Pb > Cu > Cr > Zn
355µm : Cd > Pb > Ni > Cu > Cr > Zn
150µm : Cd > Pb > Ni > Cr > Cu > Zn
Warm and Wet Season
1400µm : Ni > Cd > Pb > Cu > Cr > Zn
355µm : Cd > Pb > Ni > Cu > Cr > Zn
150µm : Cd > Ni > Pb > Cr > Cu > Zn
Warm and Dry Season
1400µm : Cd > Ni > Pb > > Zn > Cu > Cr
355µm : Cd > Ni > Pb > Zn > Cu > Cr
150µm : Cd > Pb > Ni > Zn > Cr > Cu

From the results, highest MF for all studied metals was obtained in Warm and Wet Season, with exception of Cu and Zn which had highest MF in Hot and Dry, and Warm and Dry Season, respectively. This indicates that during rains, mobility of these metals increases. Also, apart from reflecting levels of water soluble, exchangeable and carbonate bound of these metals, high MF values, an indication of lability and biological availability of heavy metals (Ahumada *et al*., 1999; Kabala and Singh, 2001; Yusuf, 2007), showed the extent of the vulnerability of living things generally to heavy metals (Ogunfowokan *et al*., 2009). From this study, it is evident that the inhabitants of Sites 1, 4, 5, 6, 7 and 9 had the highest vulnerability to Cd, Cr, and Pb exposure, while those living around sites 2, 3, 8 and 10 had low vulnerability compared to others. The low MF value for some metals in this study could be an index of the high stability of these metals in the sample (Ogunfowokan *et al*., 2009). In terms of toxicity, however, levels of Cd and Pb may give serious concern. Generally, the results of the present study confirmed the contamination of the roadside soils of Kano Metropolis by Cd, Pb, Ni, Cr, Cu and Zn and the presence of Cd, Ni and Pb in the mobile phases. Therefore, Cd, Ni and Pb represent the highest potential risk for the surrounding environment.

4.7 GEOCHEMISTRY OF HEAVY METALS IN ATMOSPHERIC PARTICULATE DUST

4.7.1 Results

The total contents of metals namely Cd, Cr, Ni, Pb, Cu and Zn in particulate dust samples from the sites studied are presented in Table 4.35. In each case the presented value is a mean observed in three determinations. Analysis of variance (ANOVA) revealed significant differences ($p < 0.05$) in the contents of the heavy metals across sites and seasons.

The concentrations across the seasons varied to a greater extent among the samples: 2.89 (Site 3) – 13.93 (Site 8), 5.27 (Site 3) – 26.00 (Site 8),

Table 4.35. Concentrations ($mgkg^{-1}$) of heavy metals in atmospheric particulate dust samples across the seasons

Metal	SN	SITE									
		1	2	3	4	5	6	7	8	9	10
Cd	A	4.89±0.15^{b}	5.74±0.36^{c}	2.89±0.16^{a}	10.80±0.29^{f}	10.49±0.01^{f}	8.92±0.12^{e}	6.68±0.45^{d}	13.93±0.10^{h}	8.77±0.33^{e}	12.88±0.17^{g}
	B	9.49±0.01^{b}	10.81±0.02^{c}	5.27±0.32^{a}	20.39±0.02^{h}	18.84±0.23^{f}	15.38±0.17^{e}	11.89±0.02^{d}	26.00±0.01^{i}	15.27±0.38^{e}	19.70±0.71^{g}
	C	12.01±0.01^{b}	13.58±0.60^{c}	7.06±0.06^{a}	24.82±0.26^{g}	25.18±0.16^{gh}	19.55±0.63^{e}	14.92±0.11^{d}	32.95±0.07^{i}	20.72±0.12^{f}	25.85±0.21^{h}
	D	2.76±0.34^{b}	3.39±0.16^{b}	1.53±0.05^{a}	7.59±0.58^{e}	6.86±0.20^{d}	6.43±0.24^{d}	5.30±0.28^{c}	8.81±0.13^{f}	5.59±0.02^{c}	8.69±0.43^{f}
Cr	A	19.78±0.32^{a}	36.96±0.05^{f}	61.28±0.32^{h}	33.89±0.15^{e}	29.53±0.66^{d}	20.00±0.14^{a}	24.67±0.47^{b}	38.85±0.21^{g}	87.79±0.30^{i}	28.14±0.09^{c}
	B	19.78±0.31^{a}	56.57±0.60^{h}	44.50±0.14^{d}	47.79±0.30^{f}	29.96±0.06^{b}	42.13±0.10^{c}	47.07±0.05^{e}	171.46±0.05^{j}	151.82±0.26^{i}	52.92±0.11^{g}
	C	24.57±0.61^{a}	70.98±0.03^{f}	98.28±2.44^{g}	66.85±0.21^{de}	36.90±0.14^{b}	43.69±0.44^{c}	67.62±0.54^{e}	220.76±0.35^{i}	188.52±0.68^{h}	64.94±0.09^{d}
	D	8.74±0.37^{a}	27.61±0.55^{f}	22.06±0.06^{e}	21.55±0.08^{e}	19.95±0.07^{c}	16.80±0.29^{b}	19.96±0.05^{c}	72.58±0.60^{h}	67.94±0.08^{g}	20.73±0.39^{d}
Ni	A	134.75±0.35^{g}	71.91±0.13^{bc}	80.67±0.47^{d}	66.83±0.23^{b}	90.69±0.43^{e}	79.82±0.26^{d}	66.88±0.18^{b}	72.88±1.25^{c}	46.54±0.64^{a}	121.14±1.21^{f}
	B	236.61±1.97^{j}	34.66±0.48^{b}	43.73±0.38^{c}	26.27±0.39^{a}	72.29±0.41^{f}	49.89±0.15^{d}	129.13±0.19^{h}	183.88±0.16^{i}	64.80±0.29^{e}	86.65±0.50^{g}
	C	327.14±2.62^{j}	47.98±0.03^{b}	53.85±0.22^{c}	37.63±0.53^{a}	99.67±0.47^{f}	88.86±0.19^{d}	196.65±0.50^{h}	237.54±0.65^{i}	94.64±0.51^{e}	121.52±0.67^{g}
	D	254.85±0.21^{i}	38.81±0.26^{b}	47.55±0.64^{c}	38.00±0.00^{b}	47.10±0.14^{c}	35.96±0.06^{a}	166.95±0.07^{g}	172.69±0.44^{h}	89.50±0.70^{f}	74.78±0.31^{d}
Pb	A	133.71±0.41^{b}	167.49±0.72^{c}	189.05±1.35^{f}	129.13±1.60^{a}	188.89±0.16^{f}	156.77±0.32^{c}	215.39±0.86^{g}	213.76±0.34^{g}	161.23±1.09^{d}	219.52±0.68^{h}
	B	90.35±0.50^{a}	135.22±1.11^{c}	151.23±1.09^{f}	218.58±0.59^{h}	1068.01±1.39^{i}	118.97±0.04^{b}	137.60±0.70^{d}	135.06±0.08^{c}	143.22±1.10^{c}	164.08±1.30^{g}
	C	127.53±0.67^{a}	182.75±0.35^{c}	196.28±0.40^{g}	291.10±1.28^{h}	1408.57±0.61^{i}	178.77±0.32^{b}	253.69±0.44^{d}	247.86±0.19^{e}	197.24±1.08^{c}	254.98±0.02^{g}
	D	61.59±0.57^{a}	80.89±0.15^{e}	95.18±1.16^{g}	121.79±0.30^{h}	640.68±0.96^{i}	75.80±1.13^{b}	78.12±1.59^{d}	78.62±0.88^{c}	86.52±0.74^{c}	101.98±2.81^{g}
Cu	A	26.51±0.69^{a}	50.71±0.41^{d}	44.51±0.70^{c}	55.10±0.56^{e}	56.21±0.69^{e}	71.54±0.77^{f}	131.64±2.31^{g}	36.71±1.01^{b}	36.59±0.83^{b}	37.44±0.62^{b}
	B	16.15±0.50^{a}	39.16±0.48^{d}	40.21±0.55^{d}	205.21±1.11^{h}	57.34±0.93^{e}	61.95±0.07^{f}	116.76±2.48^{g}	31.66±0.47^{c}	30.54±0.93^{c}	25.05±0.08^{b}
	C	20.54±0.65^{a}	53.87±0.18^{d}	51.28±1.81^{d}	267.39±3.37^{h}	66.32±0.46^{c}	81.84±1.19^{f}	149.28±1.81^{g}	41.05±1.49^{c}	40.19±0.27^{c}	31.47±2.08^{b}
	D	13.30±0.43^{a}	23.91±0.13^{e}	21.51±0.70^{d}	98.62±0.88^{i}	31.72±1.01^{f}	36.70±0.42^{g}	64.79±0.29^{h}	17.71±0.41^{bc}	18.25±1.06^{c}	16.61±0.55^{b}
Zn	A	153.98±1.38^{a}	295.82±8.23^{h}	259.85±2.61^{b}	507.07±5.76^{g}	429.23±1.74^{f}	372.08±2.94^{e}	192.13±3.01^{c}	2028.42±2.01^{j}	675.45±7.70^{i}	213.49±4.94^{d}
	B	2312.28±3.22^{a}	11711.20±15.84^{h}	2371.19±1.68^{b}	10892.70±3.82^{g}	9435.83±8.25^{f}	7999.74±0.36^{e}	5694.99±7.06^{c}	23515.52±21.94^{j}	14673.83±5.4^{i}	7405.33±7.54^{d}
	C	2083.70±5.23^{a}	8781.65±2.34^{h}	2263.52±4.97^{b}	8451.63±2.31^{g}	7135.12±7.24^{f}	6354.11±0.16^{e}	4932.63±3.72^{c}	17401.77±2.50^{j}	11204.80±6.79^{i}	5506.89±4.39^{d}
	D	211.52±2.15^{b}	1261.07±1.52^{h}	201.82±2.58^{a}	1211.31±1.85^{g}	883.05±4.32^{f}	741.49±2.10^{d}	608.18±4.49^{c}	3152.32±3.29^{j}	1493.91±5.53^{i}	770.06±1.50^{e}

SN: Season; A: Cool and Dry Season; B: Hot and Dry Season; C: Warm and Wet Season; D: Warm and Dry Season

Values are mean±SD of triplicate determinations of a sample mixed from three simultaneous soil collections at each site.

Mean values in the same row followed by the same superscript letters are not significantly different ($p > 0.05$)

7.06 (Site 3) – 32.95 (Site 8) and 1.53 (Site 3) – 8.81mgkg^{-1} (Site 8) for Cd, 19.78 (Site 1) – 87.79 (Site 9), 19.78 (Site 1) – 171.46 (Site 8), 24.57 (Site 1) – 220.76 (Site 8) and 8.74 (Site 1) – 72.58 mgkg^{-1} (Site 8) for Cr, 46.54 (Site 8) – 134.75 (Site 1), 34.66 (Site 2) – 236.61 (Site 1), 37.63 (Site 4) – 327.14 (Site 1) and 35.96 (Site 6) – 254.85mgkg^{-1}(Site 1) for Ni, 129.13 (Site 4) – 219.52 (Site 10), 90.35 (Site 1) – 1068.01 (Site 5), 37.63 (Site 4) – 327.14 (Site 1) and 35.96 – 254.85mgkg^{-1} (Site 1) for Pb, 26.51 (Site 1) – 131.64 (Site 7), 16.15 (Site 1) – 205.21 (Site 4), 20.54 (Site 1) – 267.39 (Site 4) and 13.30 (Site 1) – 98.62 mgkg^{-1} (Site 4) for Cu, and 153.98 (Site 1) – 2028.42 (Site 8), 2312.28 (Site 1) – 23515.52 (Site 8), 2083.70 (Site 1) – 17401.77 (Site 8) and 201.82 (Site 3) – 3152.32mgkg^{-1} (Site 8) for Zn in Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons, respectively. Irrespective of sampling site, the distribution of total metals in the atmospheric particulate dust samples generally followed the order: Zn > Pb > Ni > Cu > Cr > Cd. Highest levels of Cd, Cr and Zn were found at Site 8, while highest concentration of Ni and Pb, and Cu were found at Sites 1 and 4 respectively. Also, in contrast to levels of metals in roadside soils highest concentrations of all studied metals were recorded in Warm and Wet Season with exception of Pb and Zn that has highest concentration recorded in Hot and Dry Season.

Correlation analysis as shown in Table 4.36a-d indicates significant positive correlation ($p < 0.05$) between Zn_p and Cr_p (Cool and Dry Season), and Zn_p: Cd_p and Cr_p (Warm and Wet, and Warm and Dry Seasons). Positive correlation of metals indicate common source of metals. Correlation coefficients between the levels of heavy metals in roadside soil and in particulate dust are presented in Table 4.37a-d. Correlations between metals indicate whether there is any common source of pollution. In Cool and Dry Season, positive correlations were observed between Cd_p: CdA and CdB and CdC, Cr_P: CrC, Ni_P:

Table 4.36a. Relationships among heavy metals in air particulate dust (Cool and Dry Season)

Parameters	Cd_P	Cr_P	Ni_P	Pb_P	Cu_P	Zn_P
Cd_P	1.000					
Cr_P	0.377	1.000				
Ni_P	-0.120	0.092	1			
Pb_P	0.208	-0.157	-0.286	1.000		
Cu_P	0.210	-0.270	-0.240	0.030	1.000	
Zn_P	0.611	0.846**	0.079	-0.066	-0.070	1.000

Mp: air particulate dust metal ion

Table 4.36b. Relationships among heavy metals in air particulate dust (Hot and Dry Season)

Parameters	Cd_P	Cr_P	Ni_P	Pb_P	Cu_P	Zn_P
Cd_P	1.000					
Cr_P	-0.147	1.000				
Ni_P	-0.062	-0.577	1.000			
Pb_P	0.323	-0.031	-0.030	1.000		
Cu_P	-0.147	-0.315	-0.336	0.307	1.000	
Zn_P	0.600	0.198	-0.381	0.275	-0.249	1.000

Mp: air particulate dust metal ion

Table 4.36c. Relationships among heavy metals in air particulate dust (Warm and Wet Season)

Parameters	Cd_P	Cr_P	Ni_P	Pb_P	Cu_P	Zn_P
Cd_P	1.000					
Cr_P	0.522	1.000				
Ni_P	0.092	0.142	1.000			
Pb_P	0.238	-0.243	-0.168	1.000		

Cu_P	0.199	-0.230	-0.362	0.047	1.000	
Zn_P	0.776**	0.859**	0.045	0.010	-0.030	1.000

Mp: air particulate dust metal ion

Table 4.36d. Relationships among heavy metals in air particulate dust (Warm and Dry Season)

Parameters	Cd_P	Cr_P	Ni_P	Pb_P	Cu_P	Zn_P
Cd_P	1.000					
Cr_P	0.425	1.000				
Ni_P	0.062	0.057	1.000			
Pb_P	0.322	-0.243	-0.152	1.000		
Cu_P	0.129	-0.199	-0.350	0.015	1.000	
Zn_P	0.748*	0.800**	-0.005	0.026	0.003	1.000

Mp: air particulate dust metal ion

Table 4.37a. Relationships between heavy metals in air particulate dust and roadside soil of different grain sizes (Cool and Dry Season)

Parameters	Cd_P	Cr_P	Ni_P	Pb_P	Cu_P	Zn_P
CdA	0.864**	0.658*	0.155	0.089	-0.015	0.816**
CdB	0.919**	0.412	-0.066	0.308	0.283	0.684*
CdC	0.990**	0.418	-0.088	0.178	0.159	0.679*
CrA	0.350	0.729*	-0.375	-0.211	-0.259	0.496
CrB	0.449	0.974**	0.207	-0.239	-0.283	0.816**
CrC	0.389	0.992**	0.130	-0.191	-0.328	0.838**
NiA	-0.317	-0.325	0.768**	-0.195	-0.303	-0.328
NiB	-0.094	-0.221	0.518	-0.275	-0.210	-0.113
NiC	-0.122	0.118	0.999**	-0.283	-0.234	0.092
PbA	0.255	-0.045	0.406	0.239	-0.005	-0.157
PbB	0.342	-0.032	0.180	0.529	0.001	-0.146
PbC	0.198	-0.164	-0.284	1.000**	0.033	-0.072
CuA	-0.178	-0.121	0.463	-0.418	0.586	-0.176
CuB	0.013	0.303	0.224	-0.345	0.635*	0.254
CuC	0.221	-0.268	-0.234	0.023	0.999**	-0.071
ZnA	0.166	-0.188	0.426	-0.056	0.180	0.233
ZnB	0.551	0.384	0.113	-0.186	-0.364	0.328
ZnC	0.620	0.860**	-0.056	-0.039	-0.021	0.962**
Traffic	0.156	-0.247	-0.068	0.104	-0.079	-0.174

Mp: Particulate dust metal ion
A: Cool and Dry Season
B: Hot and Dry Season
C: Warm and Wet Season
D: Warm and Dry Season

Table 4.37b. Relationships between heavy metals in air particulate dust and roadside

soil of different grain sizes (Hot and Dry Season)

Parameters	Cd_P	Cr_P	Ni_P	Pb_P	Cu_P	Zn_P
CdA	0.908**	0.000	-0.161	0.485	-0.163	0.775**
CdB	0.890**	0.090	-0.096	0.540	-0.190	0.657*
CdC	0.993**	-0.120	-0.007	0.359	-0.196	0.570
CrA	0.048	0.625	-0.625	0.240	0.163	0.145
CrB	0.106	0.243	-0.446	-0.193	-0.044	0.290
CrC	0.221	0.762*	-0.594	0.197	-0.349	0.771**
NiA	-0.262	-0.342	0.770**	-0.324	-0.344	-0.204
NiB	-0.191	-0.379	0.587	-0.197	-0.174	0.067
NiC	-0.112	-0.210	0.330	0.027	0.052	0.182
PbA	0.414	0.047	0.410	0.427	-0.160	-0.107
PbB	0.457	-0.066	0.190	0.728*	0.122	0.303
PbC	0.288	-0.177	0.069	0.229	0.078	0.016
CuA	-0.253	-0.199	0.014	-0.179	0.475	-0.301
CuB	0.253	0.162	-0.512	0.202	0.293	0.444
CuC	0.094	-0.204	-0.370	-0.283	0.505	-0.115
ZnA	-0.573	-0.254	-0.198	-0.097	0.729*	-0.396
ZnB	-0.406	-0.231	-0.315	0.139	0.835**	-0.111
ZnC	-0.241	0.043	-0.659*	-0.054	0.790**	0.032
Traffic	0.097	-0.409	0.125	-0.177	0.232	-0.145

Mp: air particulate dust metal ion
A: Cool and Dry Season
B: Hot and Dry Season
C: Warm and Wet Season
D: Warm and Dry Season

Table 4.37c. Relationships between heavy metals in air particulate dust and roadside soil of different grain sizes (Warm and Wet Season)

Parameters	Cd_P	Cr_P	Ni_P	Pb_P	Cu_P	Zn_P
CdA	0.900**	0.687*	0.247	0.103	0.032	0.781**
CdB	0.946**	0.468	0.068	0.276	0.296	0.739*

CdC	0.980**	0.457	0.038	0.180	0.188	0.692*
CrA	0.316	0.719*	-0.404	-0.226	-0.236	0.600
CrB	0.575	0.676*	-0.112	-0.509	0.186	0.666*
CrC	0.519	0.991**	0.143	-0.198	-0.290	0.858**
NiA	-0.254	-0.279	0.771**	-0.210	-0.320	-0.395
NiB	-0.083	-0.025	0.945**	-0.228	-0.305	-0.111
NiC	-0.026	0.179	0.958**	-0.287	-0.266	0.005
PbA	0.085	-0.031	0.369	0.232	-0.038	-0.165
PbB	0.204	-0.054	0.200	0.509	0.004	-0.133
PbC	0.217	-0.259	-0.160	1.000**	0.029	-0.010
CuA	-0.216	-0.082	0.254	-0.408	0.540	-0.218
CuB	0.099	0.310	0.076	-0.331	0.658*	0.201
CuC	0.181	-0.259	-0.339	0.042	0.996**	-0.062
ZnA	0.326	-0.115	0.537	-0.040	0.181	0.131
ZnB	0.464	0.840**	0.329	-0.170	-0.198	0.702*
ZnC	0.751*	0.862**	-0.015	-0.021	0.003	0.989**
Traffic	0.053	-0.216	0.012	0.092	-0.127	-0.120

Mp: air particulate dust metal ion
A: Cool and Dry Season
B: Hot and Dry Season
C: Warm and Wet Season
D: Warm and Dry Season

Table 4.37d. Relationships between heavy metals in particulate dust and roadside soil of different grain sizes (Warm and Dry Season)

Parameters	Cd_P	Cr_P	Ni_P	Pb_P	Cu_P	Zn_P
CdA	0.917**	0.628	0.176	0.118	0.039	0.784**
CdB	0.943**	0.490	0.090	0.291	0.112	0.739*
CdC	0.984**	0.352	0.026	0.274	0.113	0.669*
CrA	0.177	0.637*	-0.344	-0.298	-0.218	0.504
CrB	0.352	0.568	-0.130	-0.660*	0.176	0.605
CrC	0.428	0.984**	0.036	-0.186	-0.256	0.815**

NiA	-0.253	-0.312	0.782**	-0.216	-0.333	-0.402
NiB	-0.119	-0.087	0.937**	-0.201	-0.305	-0.150
NiC	-0.048	0.136	0.964**	-0.259	-0.265	-0.004
PbA	0.251	-0.052	0.359	0.369	-0.234	-0.148
PbB	0.391	0.101	0.359	0.505	-0.128	0.019
PbC	0.301	-0.255	-0.140	0.999**	-0.006	0.008
CuA	-0.243	-0.222	0.353	-0.025	0.497	-0.248
CuB	0.260	0.393	-0.014	0.203	0.619	0.363
CuC	0.106	-0.228	-0.315	-0.006	0.996**	-0.028
ZnA	0.229	-0.136	0.482	-0.023	0.228	0.079
ZnB	0.718*	0.783**	-0.073	-0.003	0.041	0.986**
ZnC	0.732*	0.787**	-0.059	0.003	0.016	0.989**
Traffic	0.054	-0.341	0.086	0.097	-0.132	-0.116

Mp: air particulate dust metal ion
A: Cool and Dry Season
B: Hot and Dry Season
C: Warm and Wet Season
D: Warm and Dry Season

NiA and ZnC, Pb_p: PbB, Cu_p: ZnA, ZnB and ZnC, and Zn_p: CdA, CdB and CrC. In Hot and Dry Season, positive correlations were observed between: Cd_p: CdA, CdB and CdC, Cr_p: CdA, CrA, CrB, CrC and ZnC, Ni_p: NiA and NiB, Pb_p: CuA, Cu_p:CuB and CuC, and Zn_p: CdA, CdB, CdC, CrC, and ZnC.

In Warm and Wet Season positive correlations were found between: Cd_P: CdA, CdB, CdC and ZnC; Cr_P: CdA, CrA, CrB, CrC, ZnB and ZnC; Ni_p: NiA, NiB and NiC; Pb_p: PbC; Cu_p: CuB and CuC; and Zn_p: CdA, CdB, CdC, CrB, CrC and ZnB. Similar to Warm and Wet Season, Warm and Dry Season had positive correlation observed between the following metals: Cd_p: CdA, CdB, CdC, ZnB and ZnC, Cr_p: CrA, CrC, ZnB and ZnC, Ni_p: NiA, NiB and NiC, Pb_p: CrB and PbC, Cu_p: CuC, and Zn_p: CdA, CdB, CdC, CrC, ZnB and ZnC. The positive relationships between roadside soils and particulate dust indicate that contaminations by these metals originated from a common anthropogenic source, with probably automobiles as a major common source since particulate contaminants emitted from traffic mostly tend to disperse into nearby roadside soils (Saeedi *et al*., 2009).

The distribution of heavy metals Cd, Cr, Ni, Pb, Cu and Zn in the six fractions (water soluble (FI) exchangeable (FII), carbonate bound (FIII), Fe-Mn oxide (FIV), organic bound (FV) and residual (FVI)) for all the samples are summarized in Figs. 4.25 – 4.40

(raw results are presented in Appendix XXV - XXX). The results obtained showed that the amounts of heavy metals extracted from each fraction varied widely among the sites across seasons ($p < 0.05$).

As observed in Figs. 4.25 – 4.28, Cd dominance in different dust fractions varied in sites from one season to another. However, dominant fractions of Cd in the dust samples among the sites across the seasons revealed: water soluble (Site 5), exchangeable (Site 7), carbonate bound (Site 1, 4 and 9), Fe-Mn oxide (Site 3), organic bound (Site 10) and

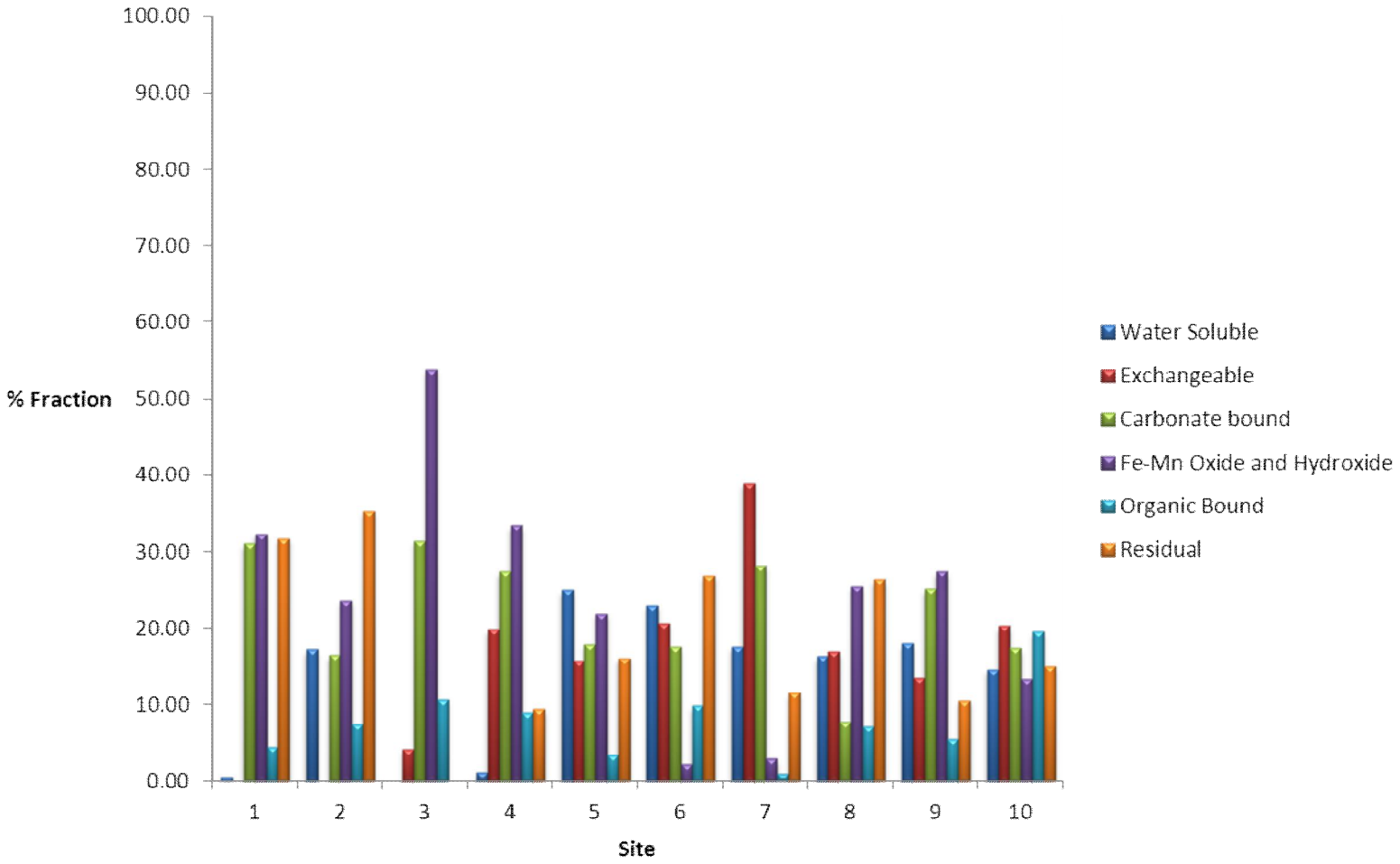


Fig. 4.25. Percentage Cd in each operationally fraction of atmospheric particulate dust (Cool and Dry Season).

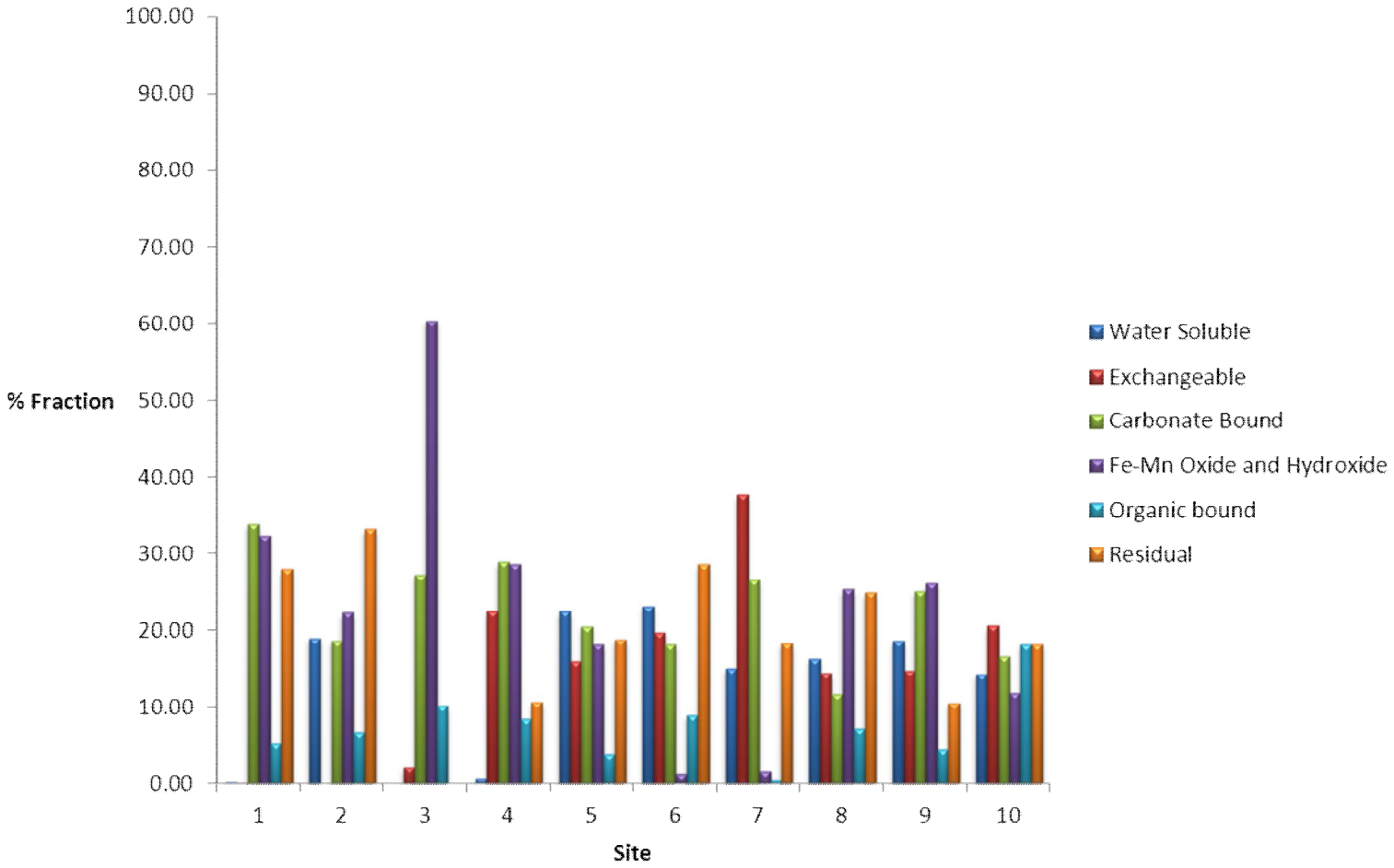


Fig. 4.26. Percentage Cd in each operationally fraction of atmospheric particulate dust (Hot and Dry Season).

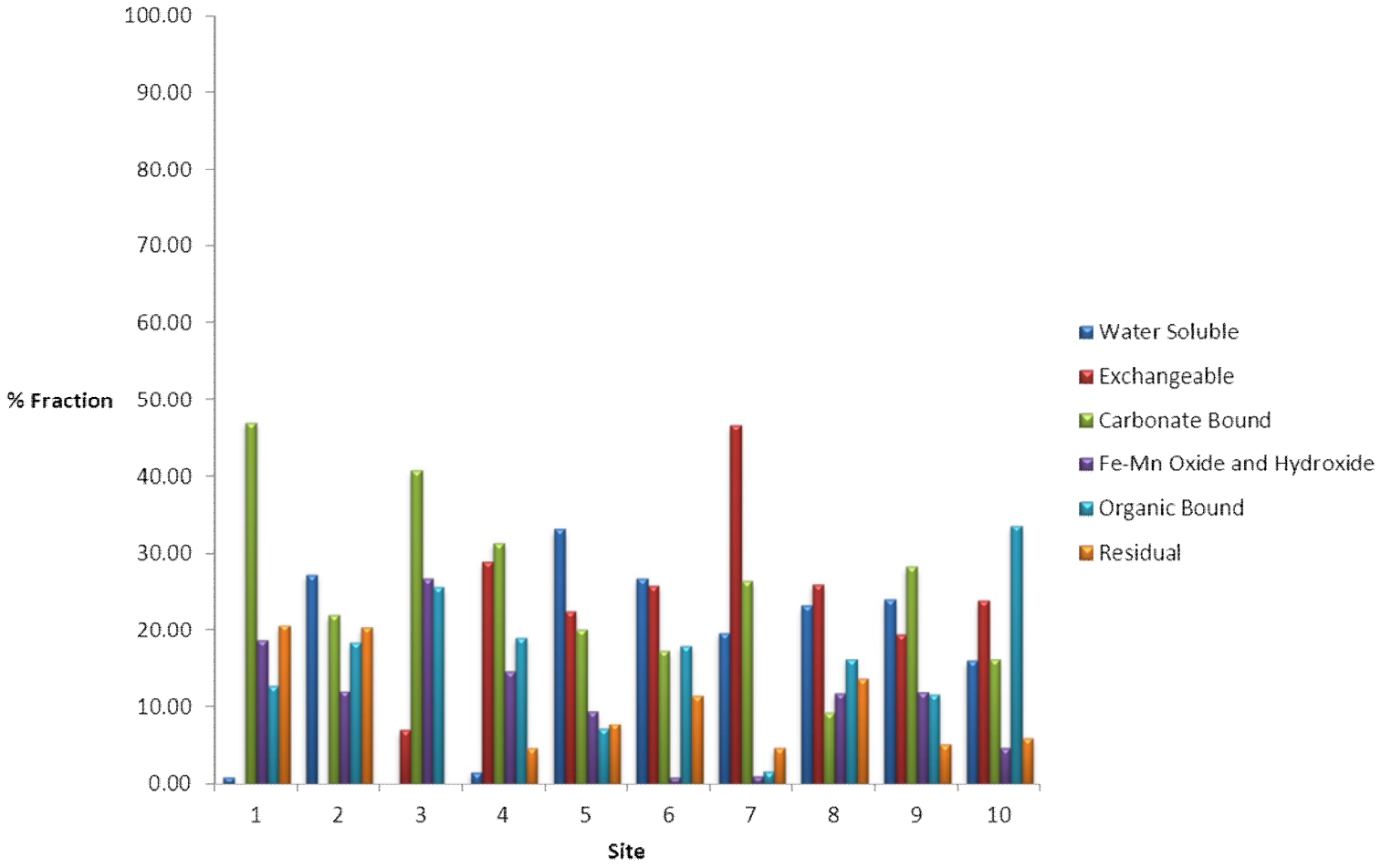


Fig. 4.27. Percentage Cd in each operationally fraction of atmospheric particulate dust (Warm and Wet Season).

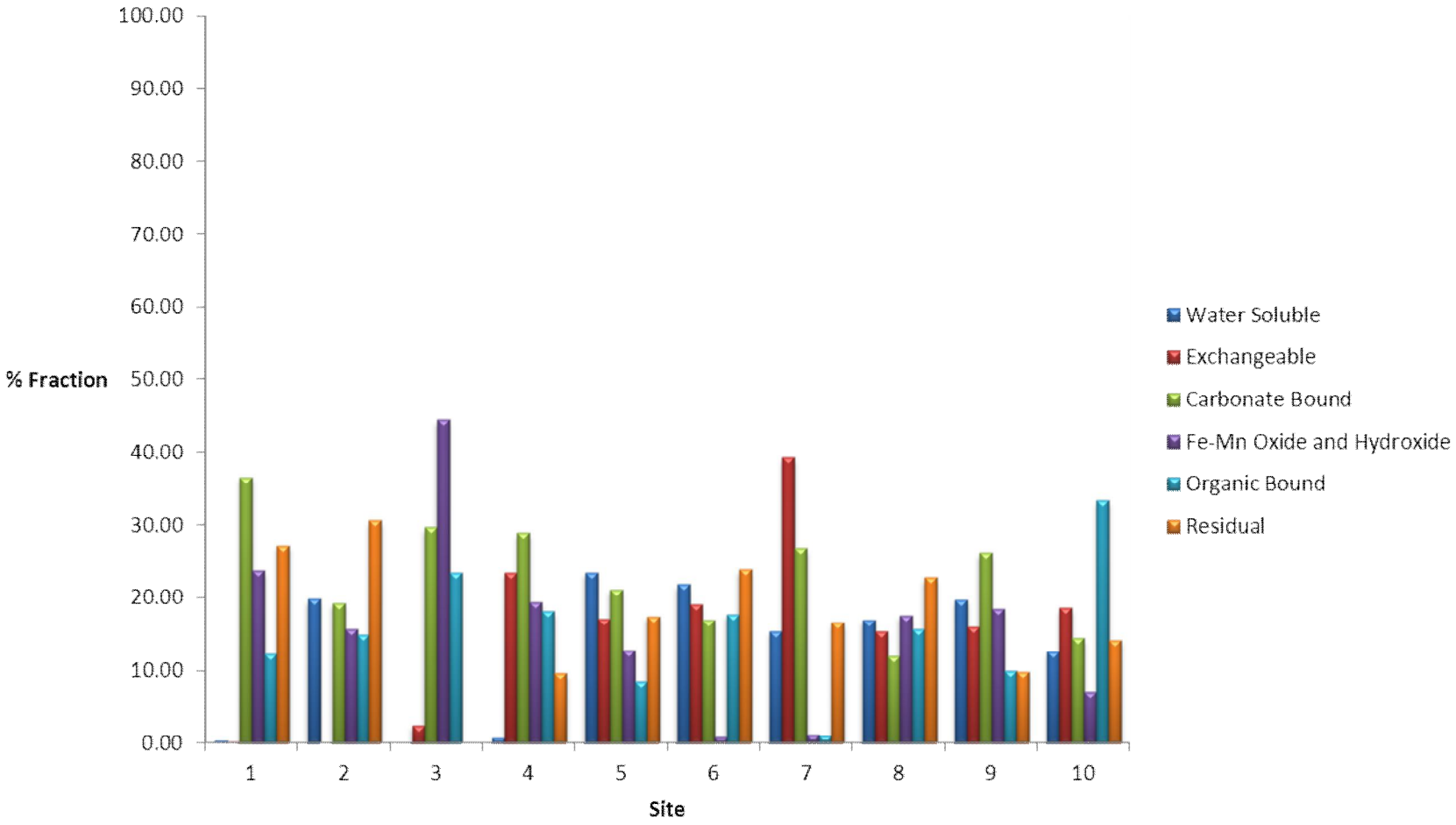


Fig. 4.28. Percentage Cd in each operationally fraction of atmospheric particulate dust (Warm and Dry Season).

Residual (Sites 2, 6 and 8) in Cool and Dry Season. With the exception of Sites 1, 7 and 10, similar dominance were found in Hot and Dry and Warm and Dry Seasons. However, in Warm and Wet Season, Cd dominance were found in exchangeable (Site 2, 5 and 6), Fe-Mn oxide (Sites 3, 4 and 9) and organic bound (Site 10). Highest percentage in Fe-Mn oxide was obtained at Site 3 during the Hot and Dry Season. Averagely, Cd distribution among the geochemical fractions of the particulate dust in the four seasons was:
Cool and dry season: FIV > FIII > FVI > FII > FI > FV
Hot and dry Season: FIV > FIII > FVI > FII > FI > FV
Warm and Wet Season: FIII > FII > FIV > FV > FI > FVI
Warm and dry season: FIII > FVI > FIV > FV > FII > FI

For Cr (Figs. 4.29 – 4.32), the residual (Sites 1, 2, 5, 8 and 9) and organic bound (Sites 3, 4, 6, 7 and 10) fractions exhibited the highest percentage at the sites. Dominant level of Cr in the exchangeable phase at Site 5 was observed, while in Warm and Dry Season, the carbonate bound fraction dominated at Sites 6 and 10. Thus, during rains (Warm and Wet Season) and after rains (Warm and Dry Season), Cr becomes labile at the sites, an indication that leaching of Cr from the particulate dust samples may occur readily. However, despite the mobility of these metals in these seasons, the residual fraction exhibited the highest percentage (90.05%) in samples from Site 9. The Average patterns of Cr distribution among the fractions of the atmospheric particulate dust in the four seasons were:
Cool and dry season: FVI > FV > FIV > FIII > FII > FI
Hot and dry season: FVI > FV > FIV > FIII > FII > FI
Warm and wet season: FVI > FV > FIV > FII > FI > FIII
Warm and dry season: FIII > FVI > FIV > FV > FII > FI

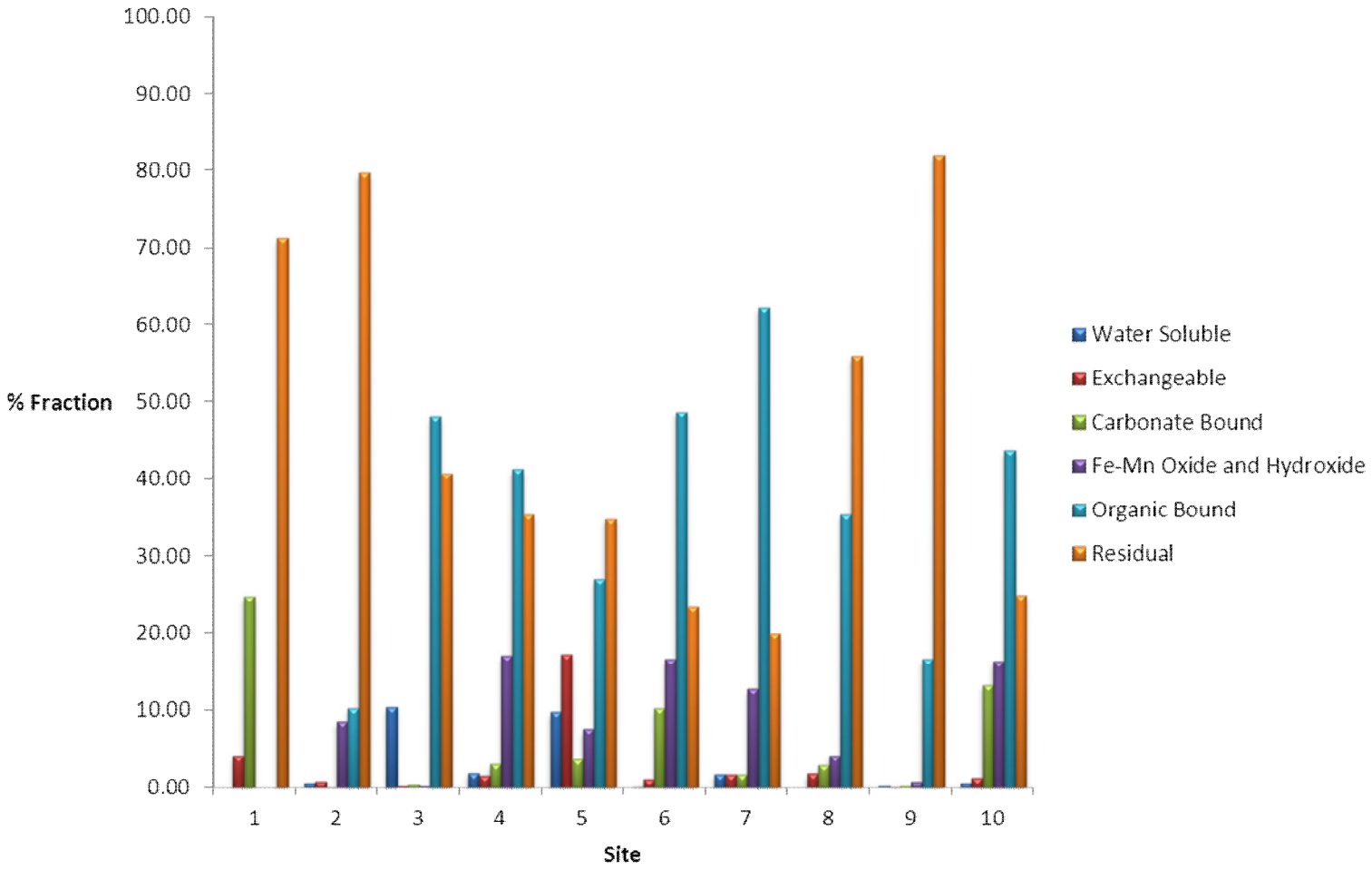


Fig. 4.29. Percentage Cr in each operationally fraction of atmospheric particulate dust (Cool and Dry Season).

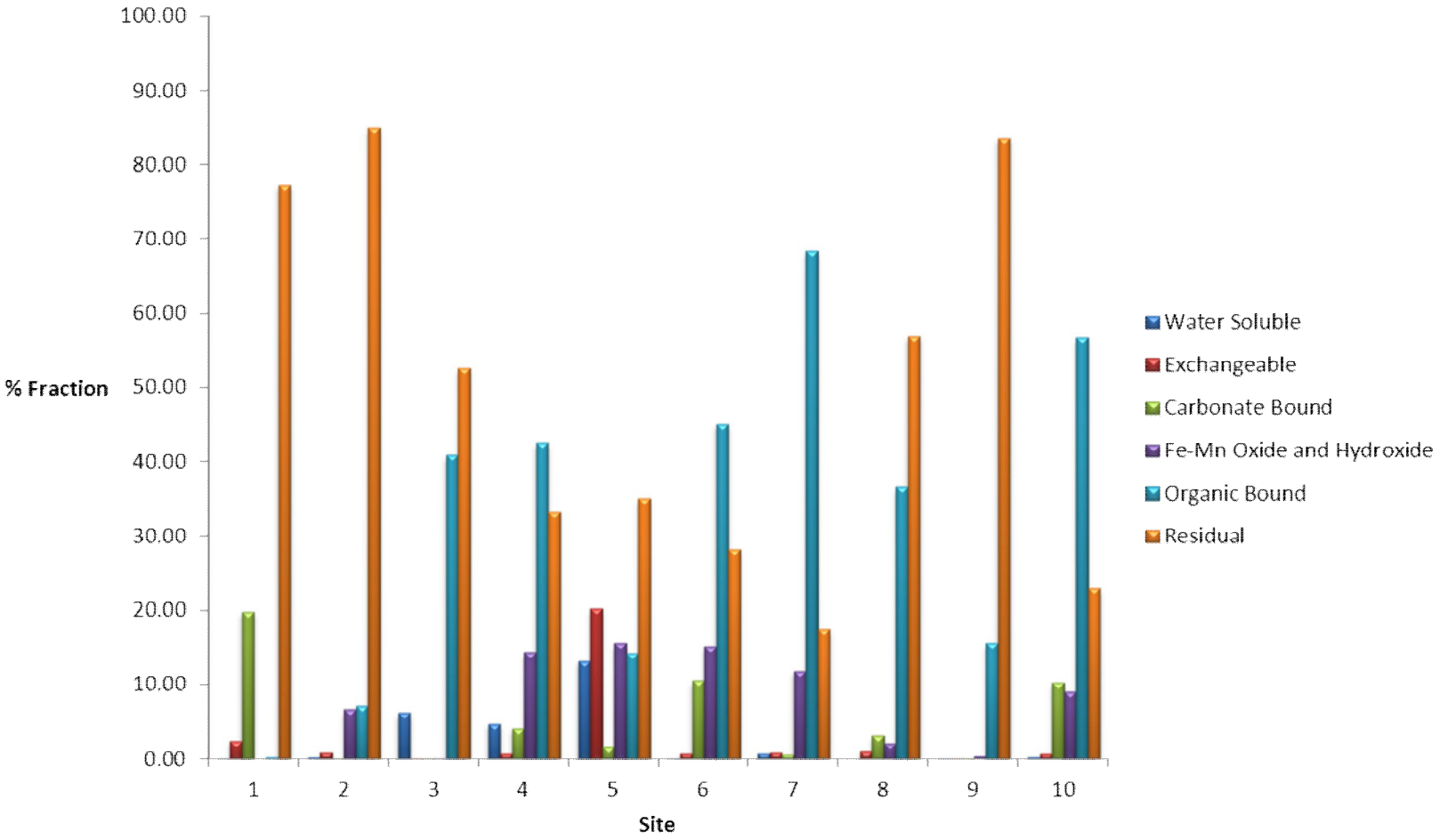


Fig. 4.30. Percentage Cr in each operationally fraction of atmospheric particulate dust (Hot and Dry Season).

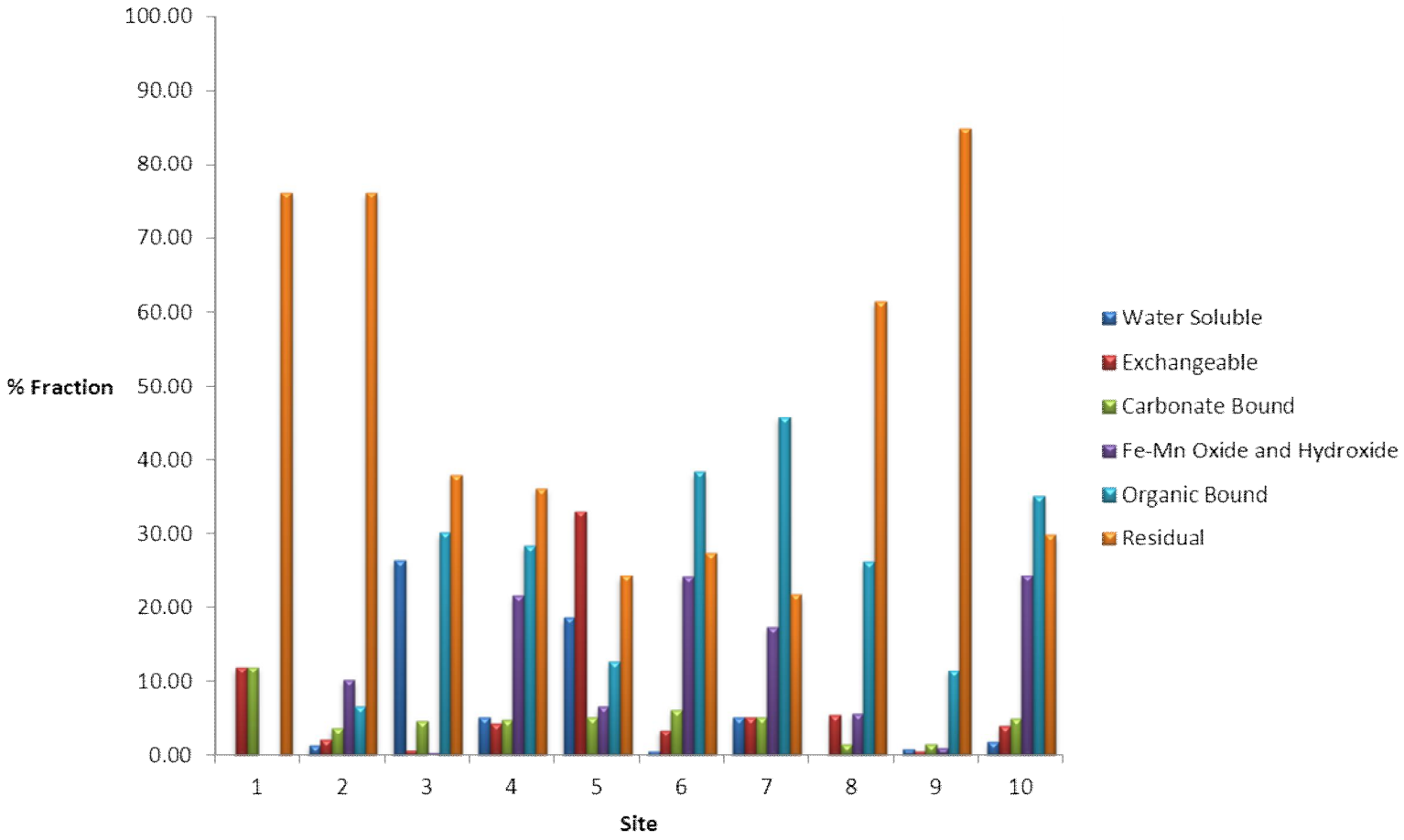


Fig. 4.31. Percentage Cr in each operationally fraction of atmospheric particulate dust (Warm and Wet Season).

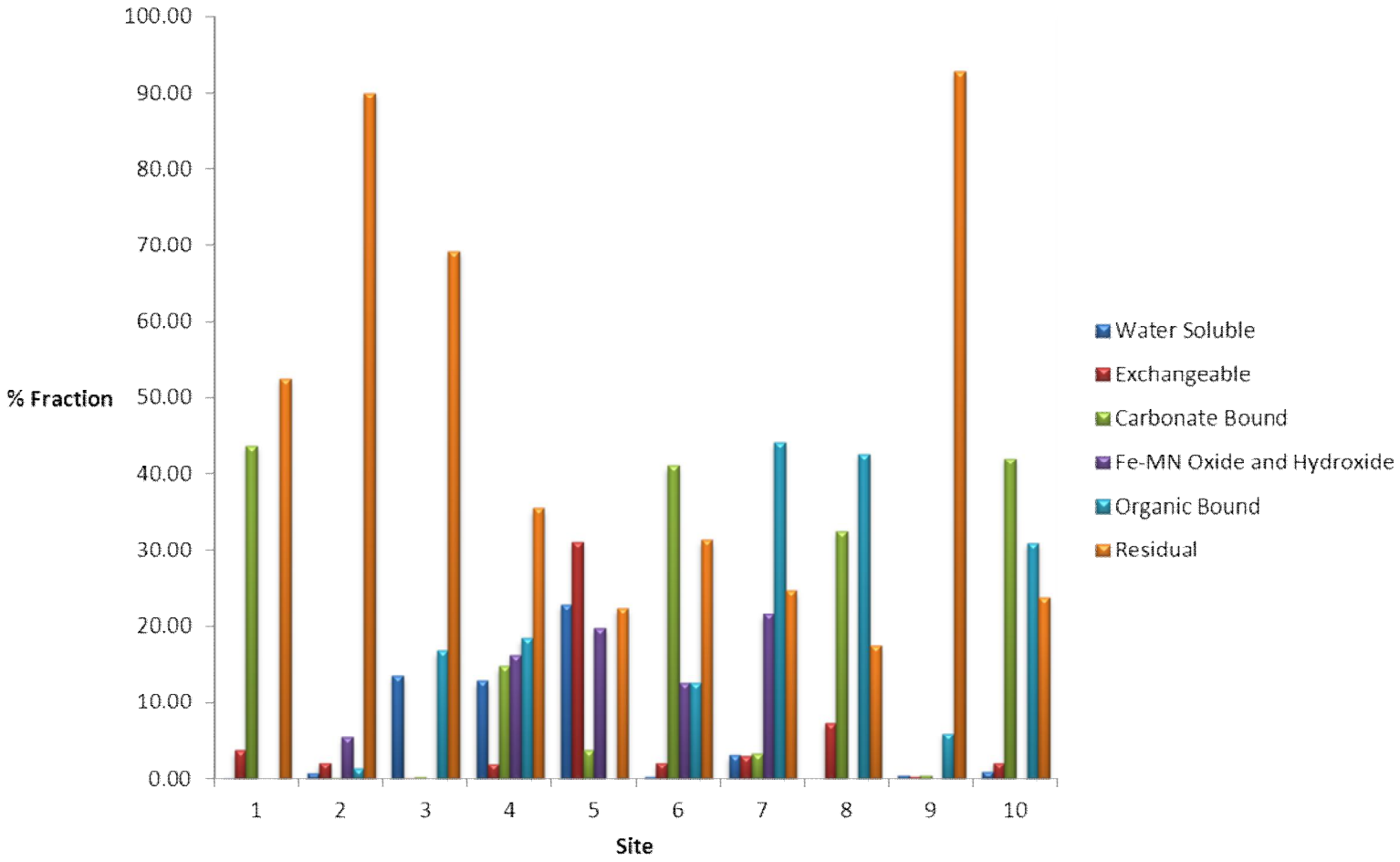


Fig. 4.32. Percentage Cr in each operationally fraction of atmospheric particulate dust (Warm and Dry Season).

Ni across the sites was also associated mostly with the residual phase followed by organic bound and Fe-Mn oxide fractions except in Warm and Wet Season that the exchangeable fractions becomes dominant at Sites 1, 3, 4 , 7 and 8 as shown in Figs. 4.33 – 4.36. This suggests that during rains, more of Ni in the residual fractions relocate to the non-residual fractions, with highest percentage associated with Fe-Mn oxide phase at Sites 9 (42.11%), 10 (56.42%), carbonate bound (29.97%) at Site 9, exchangeable phase (25.54%) at Site 1 and water soluble phase (22.55%) at Site 7. Based on the results found, averagely the profiles of Ni across the seasons were:

Cool and dry season: FVI > FV > FIV > FIII > FII > FI
Hot and dry season: FVI > FV > FIV > FIII > FI > FII
Warm and wet season: FV > FII > FIV > FVI > FI > FIII
Warm and dry season: FVI > FIV > FIII > FV > FI > FII

As observed from the bar graphs (Figs. 4.37 – 4.40), Pb levels in the particulate dust samples were significantly associated with the carbonate fraction (Sites 2, 3, 4, 6, 7, 8 and 10) ranging from 8.81 – 64.69% across the seasons as shown in Figs. 4.37 – 4.40. However, in Warm and Wet Season, Sites 6 and 10 were dominated by Fe-Mn oxide fraction at the expense of carbonate bound fraction. Also, of the ten samples across the seasons, organic bound and residual fractions dominate Pb at Sites 5 and 1, respectively. On the average percent of total Pb associated with different fractions across the site was in the following order:

Cool and dry season: FIII > FVI > FIV > FV > FI > FII
Hot and dry season: FIII > FVI > FIV > FV > FI > FII
Warm and wet season: FIII > FVI > FIV > FV > FI > FII
Warm and dry season: FIII > FVI > FIV > FV > FII > FI

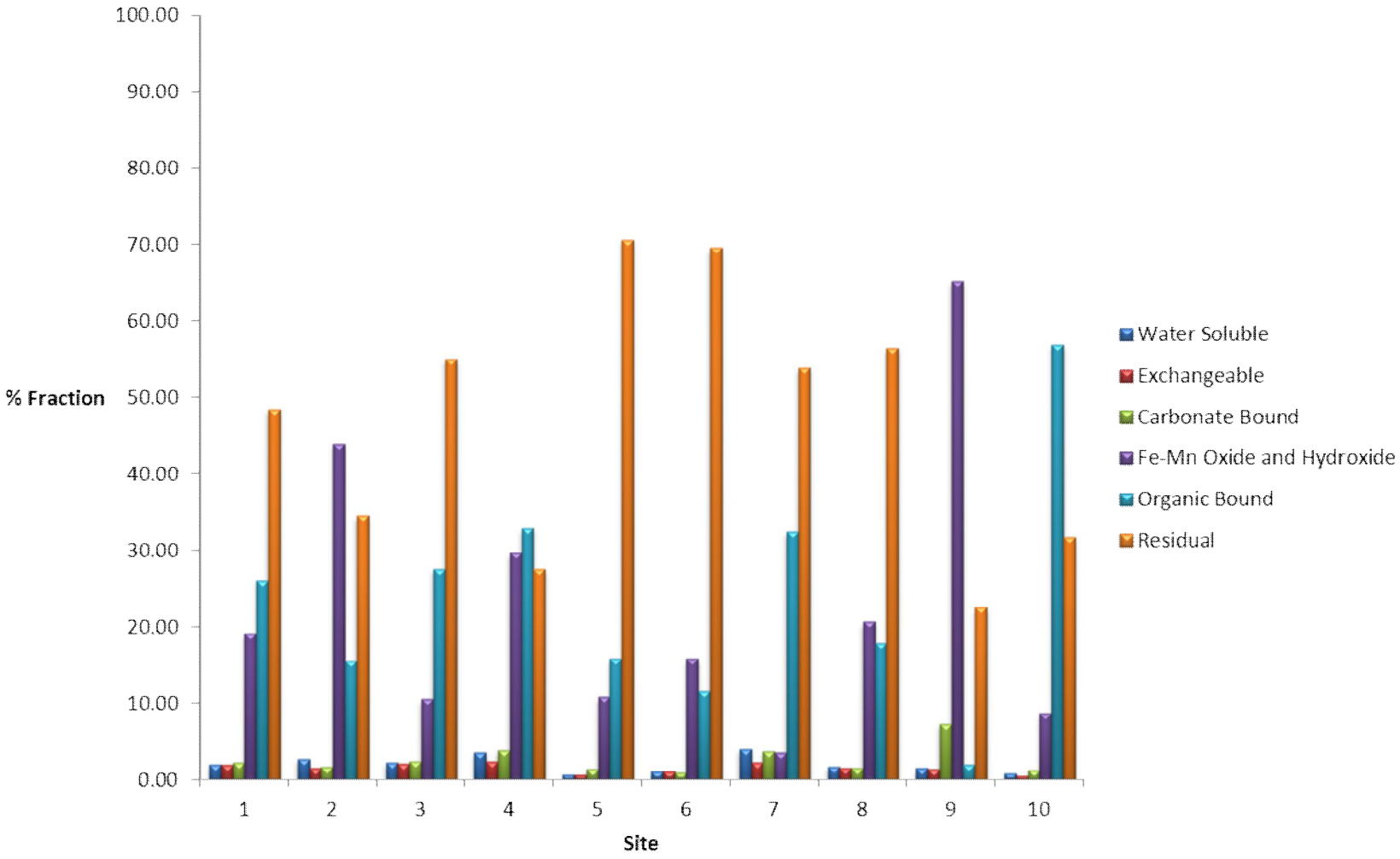


Fig. 4.33. Percentage Ni in each operationally fraction of atmospheric particulate dust (Cool and Dry Season).

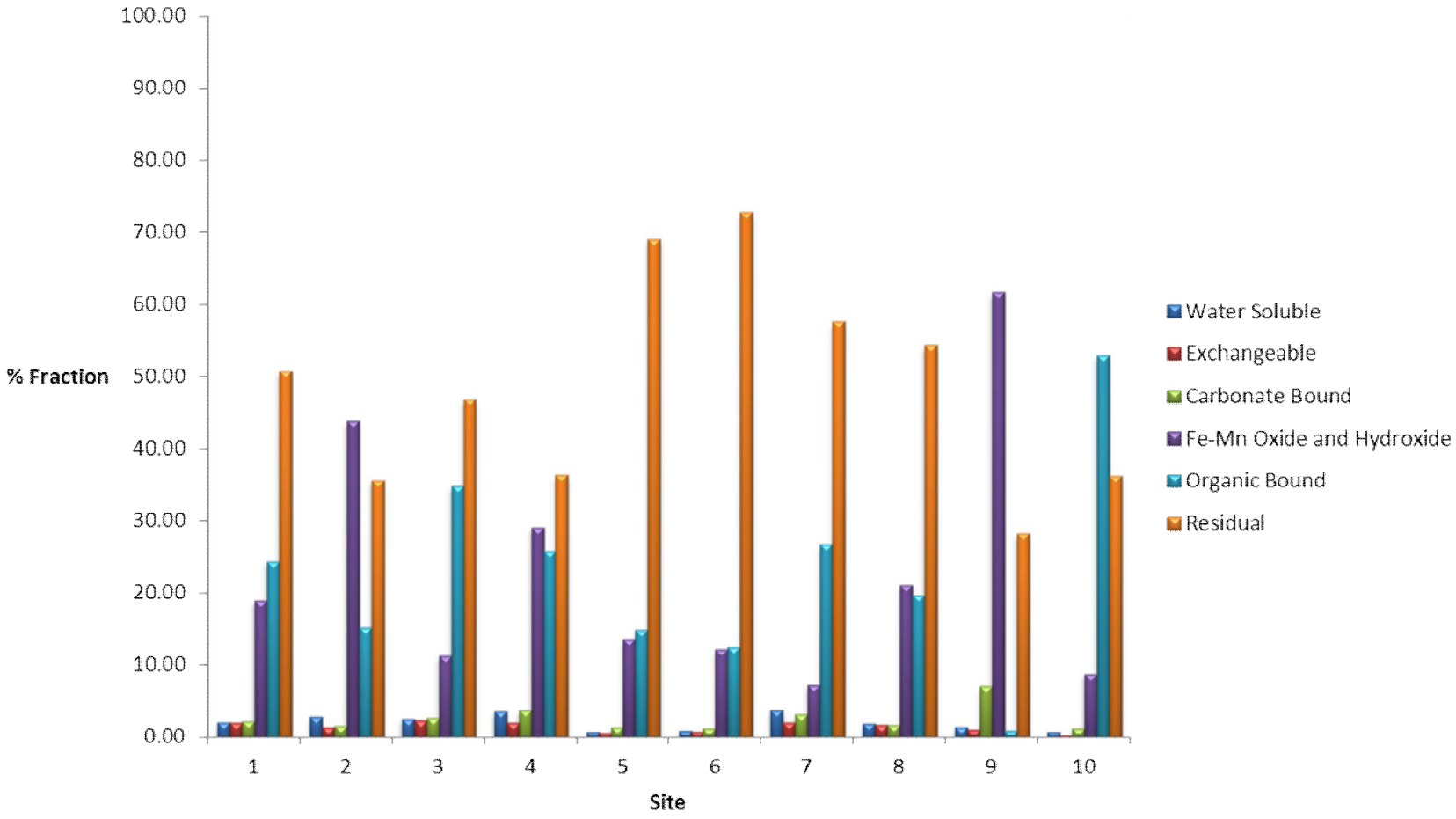


Fig. 4.34. Percentage Ni in each operationally fraction of atmospheric particulate dust (Hot and Dry Season).

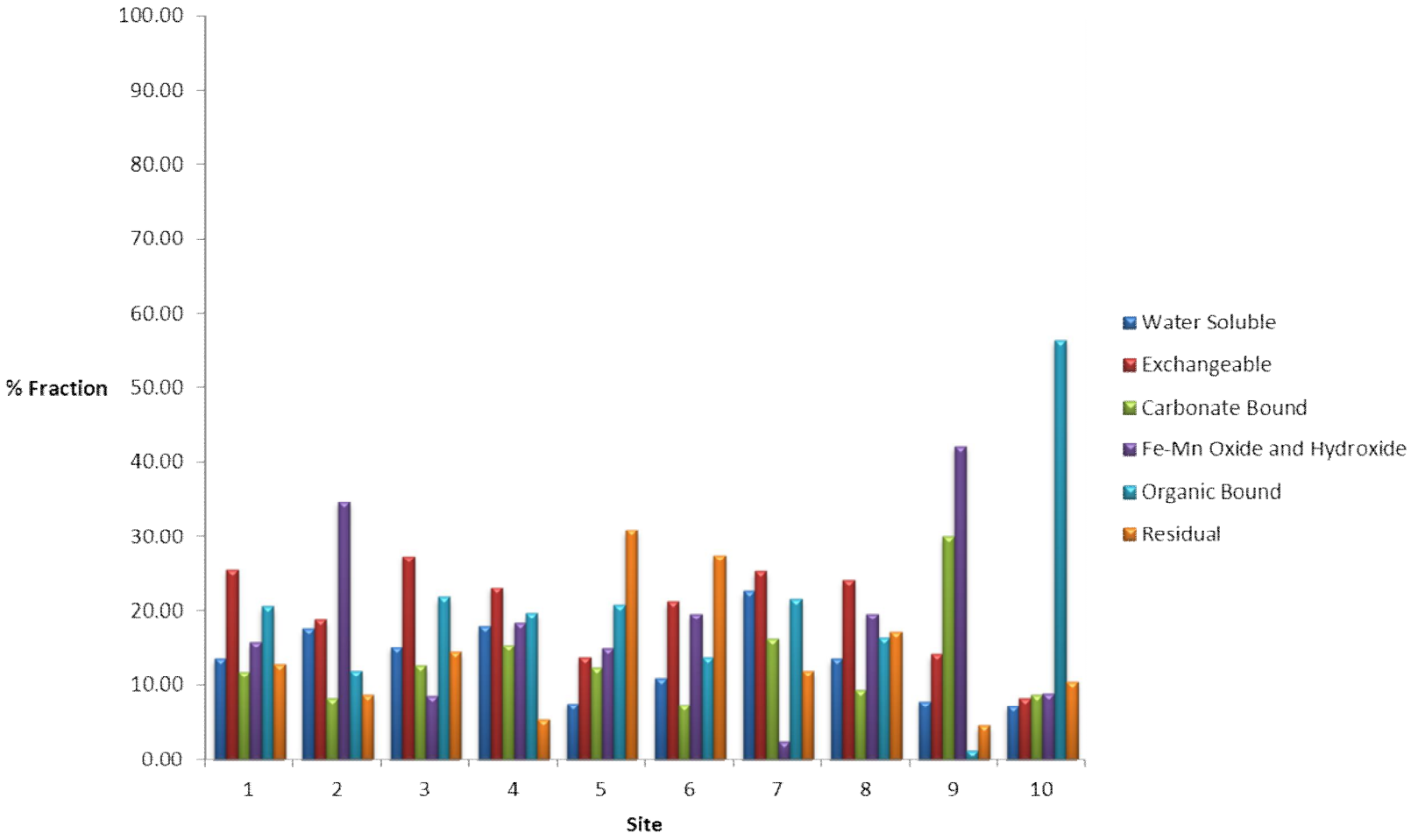


Fig. 4.35. Percentage Ni in each operationally fraction of atmospheric particulate dust (Warm and Wet Season).

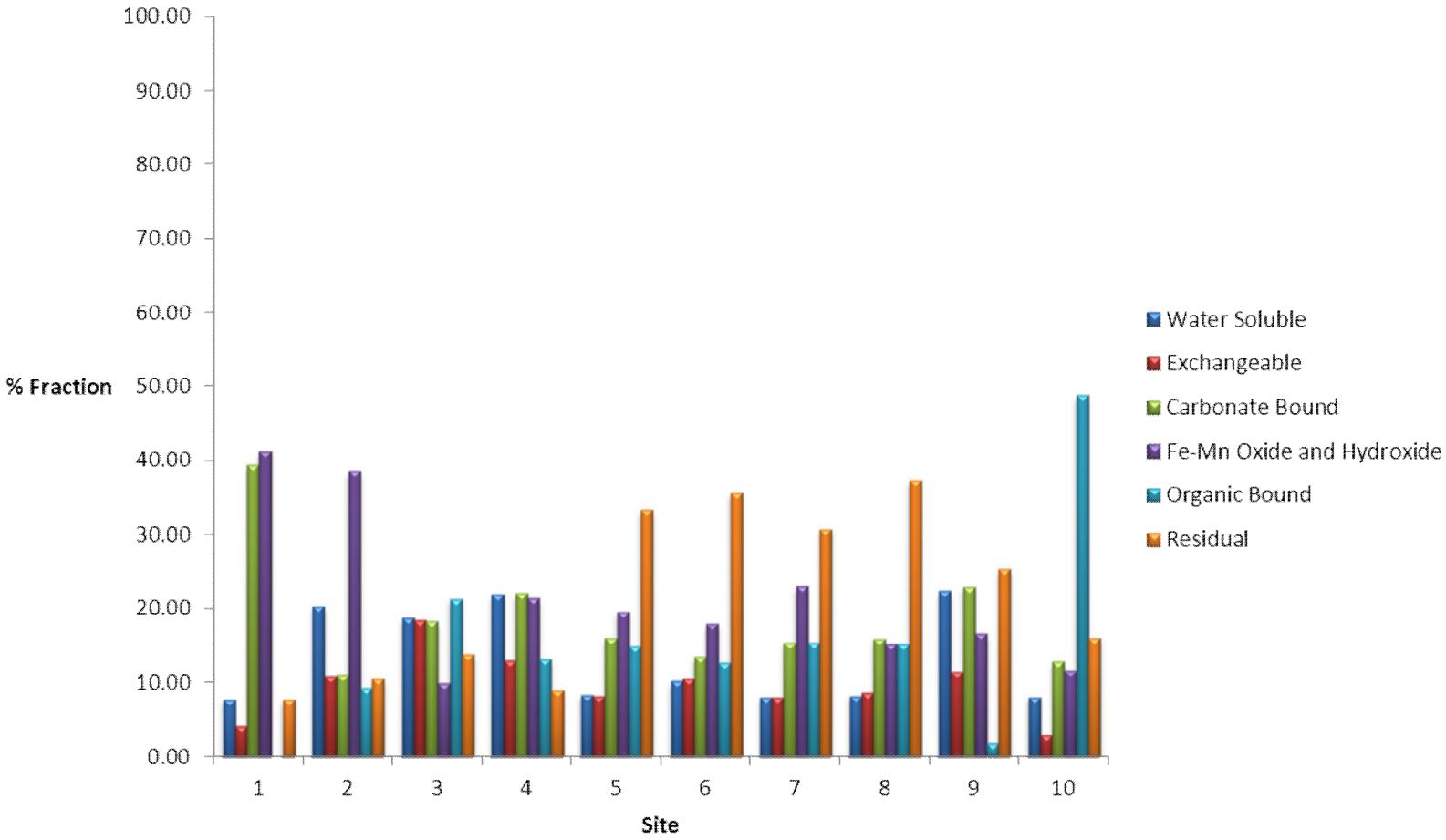


Fig. 4.36. Percentage Ni in each operationally fraction of atmospheric particulate dust (Warm and Dry Season).

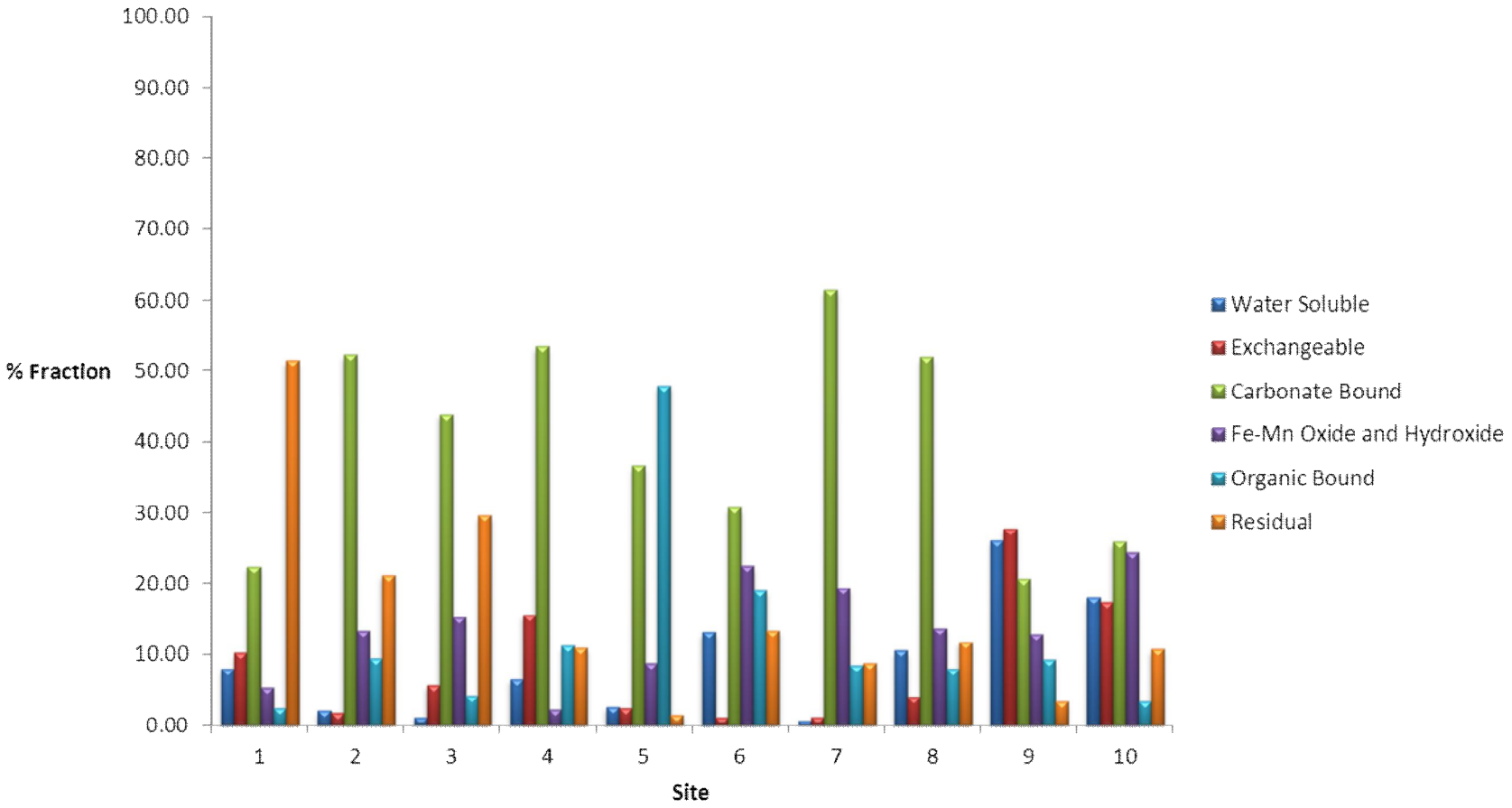


Fig. 4.37. Percentage Pb in each operationally fraction of atmospheric particulate dust (Cool and Dry Season).

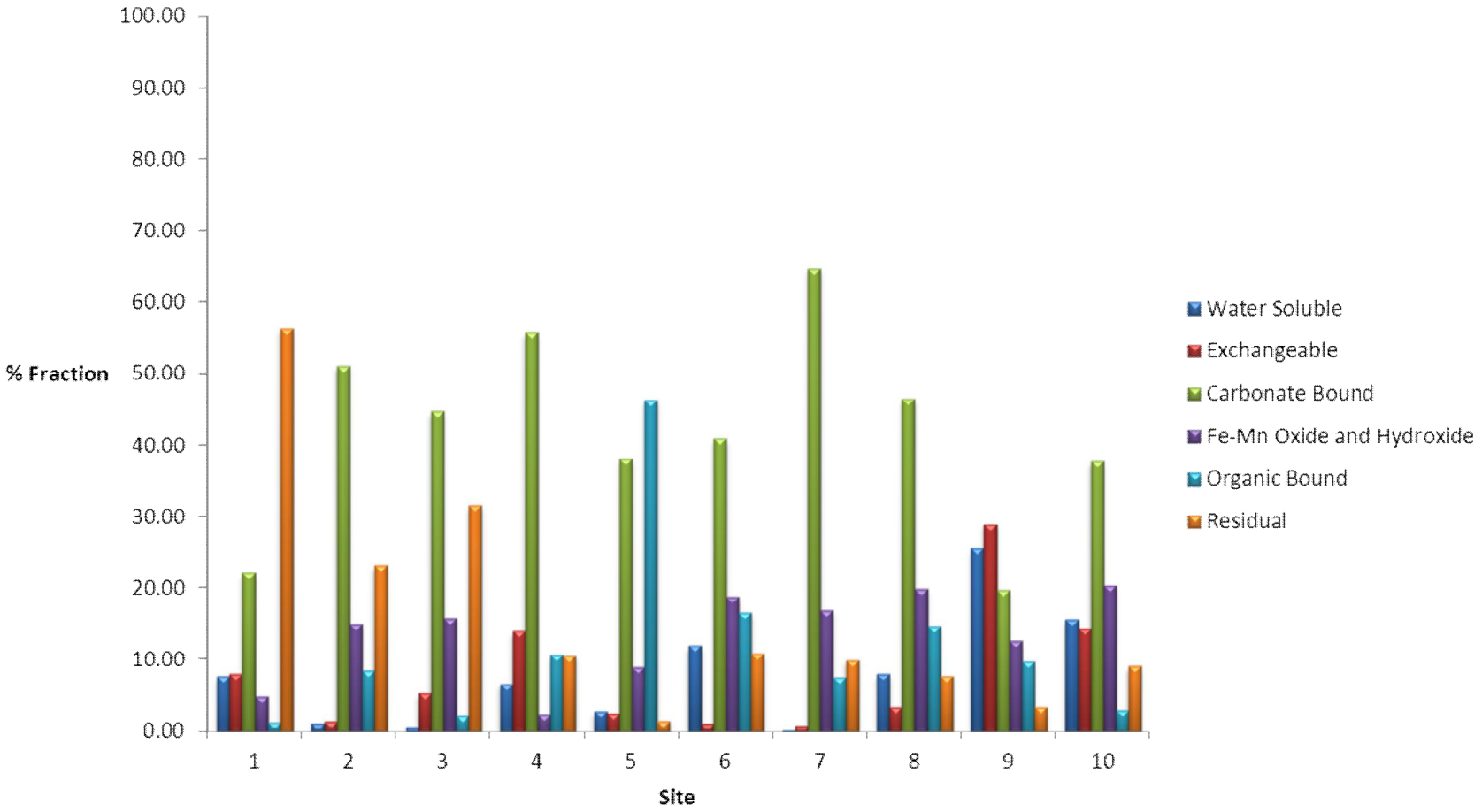


Fig. 4.38. Percentage Pb in each operationally fraction of atmospheric particulate dust (Hot and Dry Season).

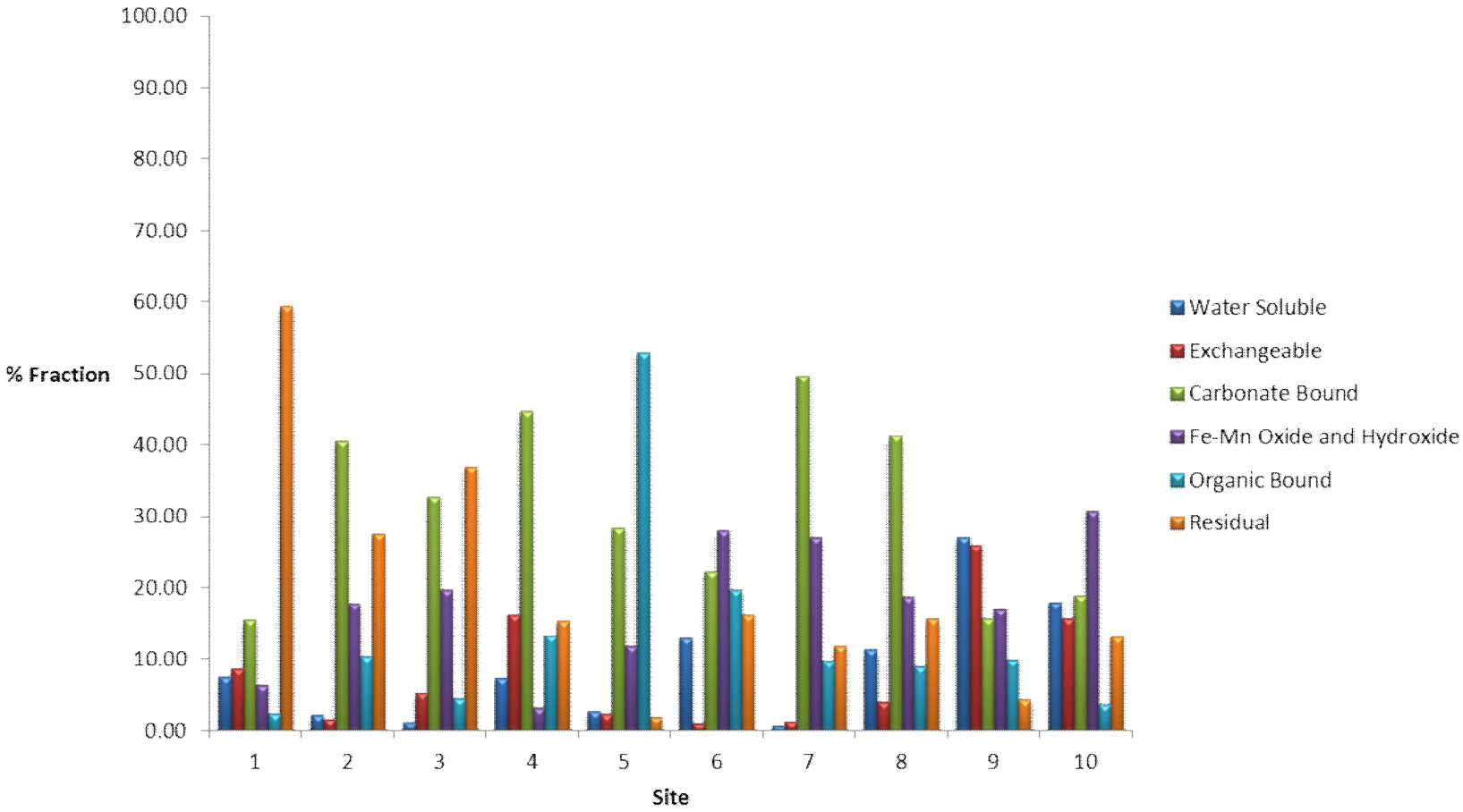


Fig. 4.39. Percentage Pb in each operationally fraction of atmospheric particulate dust (Warm and Wet Season).

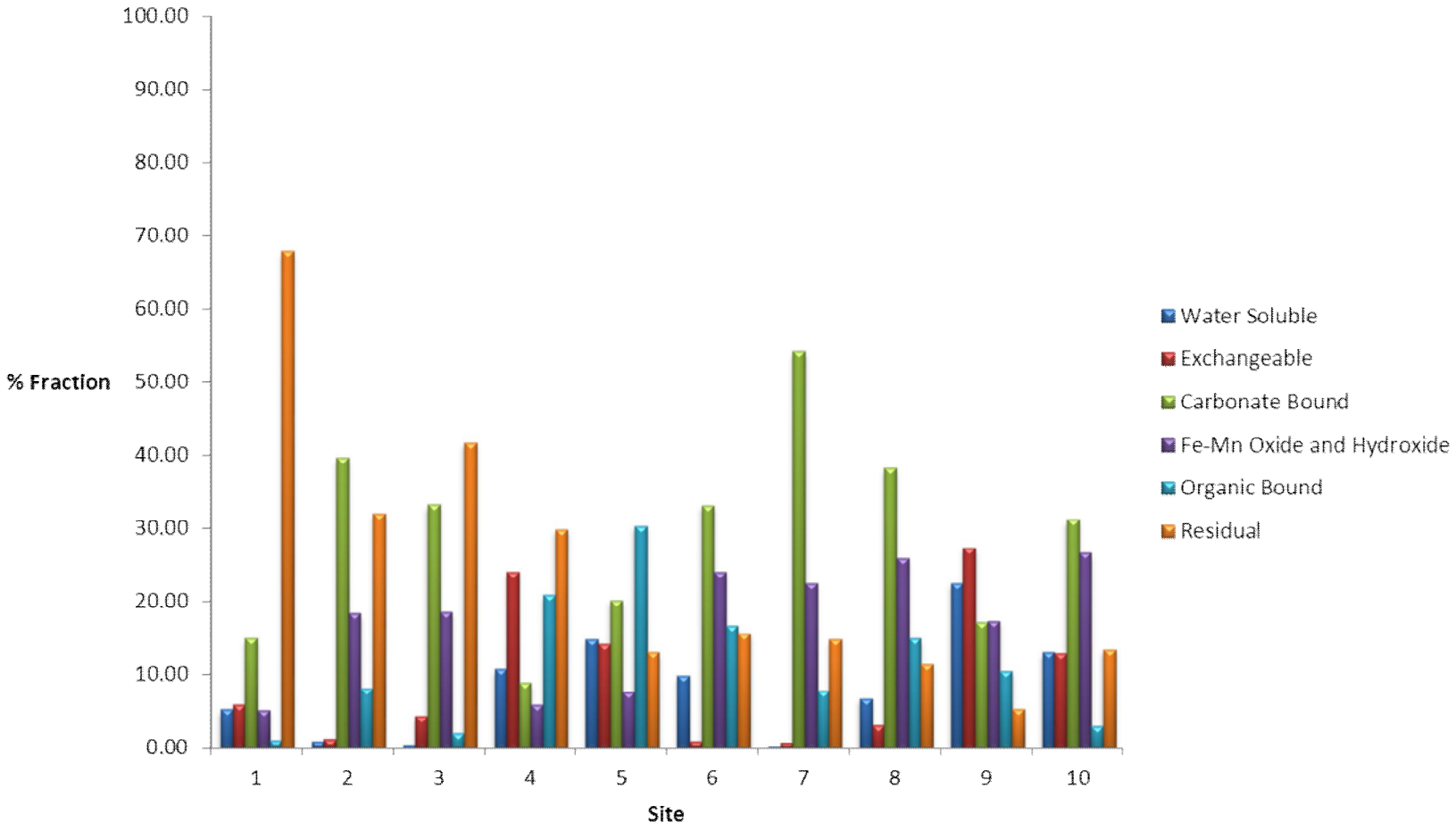


Fig. 4.40. Percentage Pb in each operationally fraction of atmospheric particulate dust (Warm and Dry Season).

With exception of Sites 10 (concentrated in residual fraction) and 1 (concentrated in residual, Fe-Mn oxide and exchangeable fractions across the seasons), the behaviour of Cu was quite different from other metals in that percentage fractions were mainly associated with the organic bound fraction of the soil samples (Site 2, 3, 4, 5, 6, 7, 8 and 9) ranging from 3.62 – 89.62% (Figs. 4.41 – 4.44). The highest percentage 89.62% in organic fraction was found at Site 4. Based on the results found, the profile obtained for Cu was:
Cool and dry season: FV > FVI > FIV > FI > FII > FIII
Hot and dry season: FV > FVI > FIV > FI > FII > FIII
Warm and wet season: FV > FVI > FIV > FI > FIII > FII
Warm and dry season: FV > FVI > FIV > FI > FIII > FII

As for Zn, significant amounts of the metal were associated with the residual fractions (Figs. 4.45 – 4.48) especially in Cool and Dry, Hot and Dry, and Warm and Wet Seasons, except at Sites 1, 3 and 8 where the metal was mainly found in organic bound and Fe-Mn oxide bound fractions across the seasons. In Warm and Dry Season, the dominant fractions across the sites were carbonate bound (Site 2, 5 and 6), Fe-Mn oxide (Site 1, 3, 7, 9 and 10) and organic bound (Site 4 and 8). This suggests relative mobility of Zn at these sites during the seasons. Zn association with the chemically reactive fractions such as Zn in water soluble and exchangeable forms generally represented less than 10% of the total fractions of Zn in the samples. Averagely, the distribution of Zn among the particulate dust fractions across the seasons was:
Cool and dry season: FVI > FIV > FIII > FV > FI > FII
Hot and dry season: FVI > FIV > FIII > FV > FII > FI
Warm and wet season: FVI > FIV > FIII > FV > FI > FII

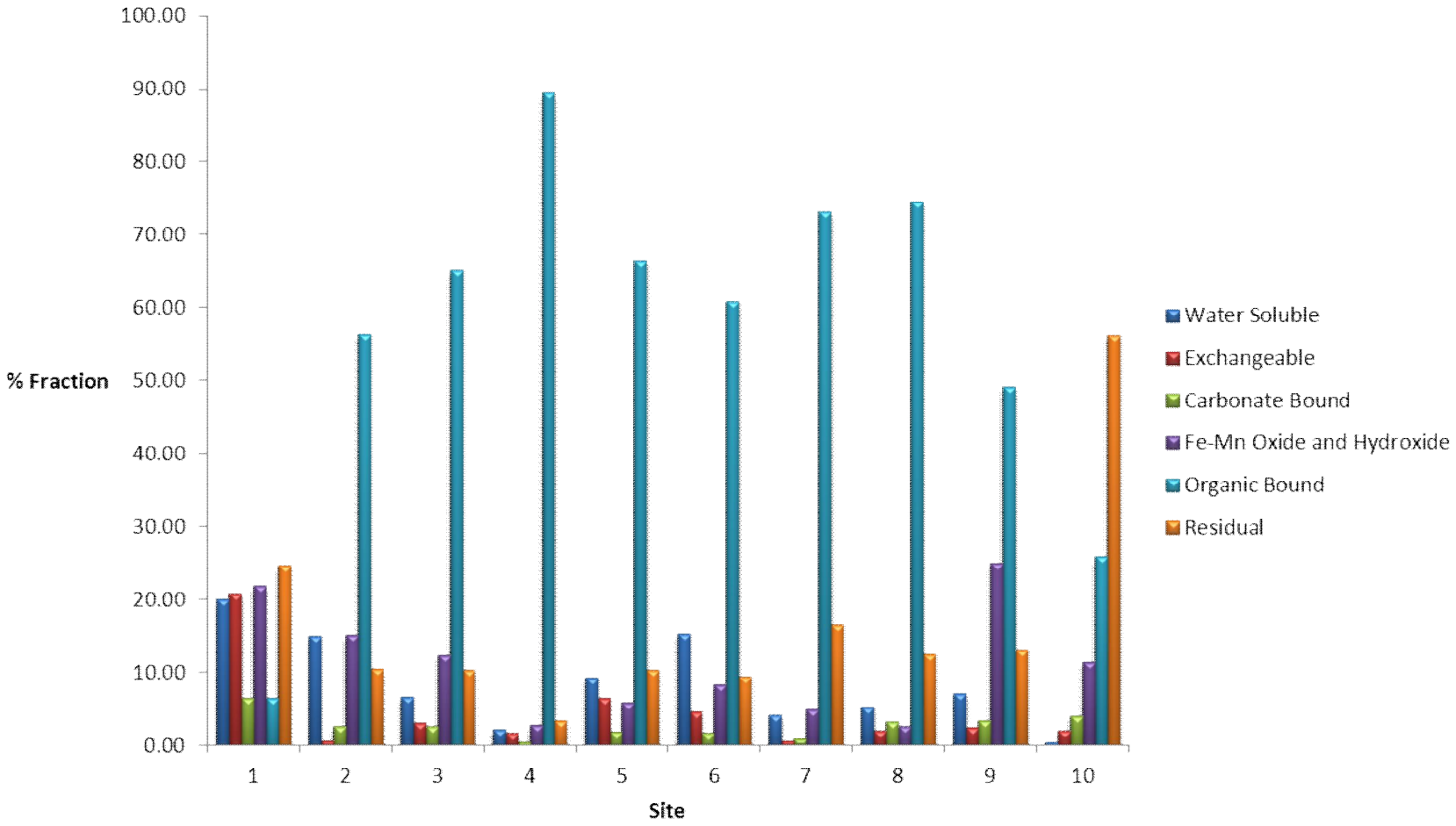


Fig. 4.41. Percentage Cu in each operationally fraction of atmospheric particulate dust (Cool and Dry Season).

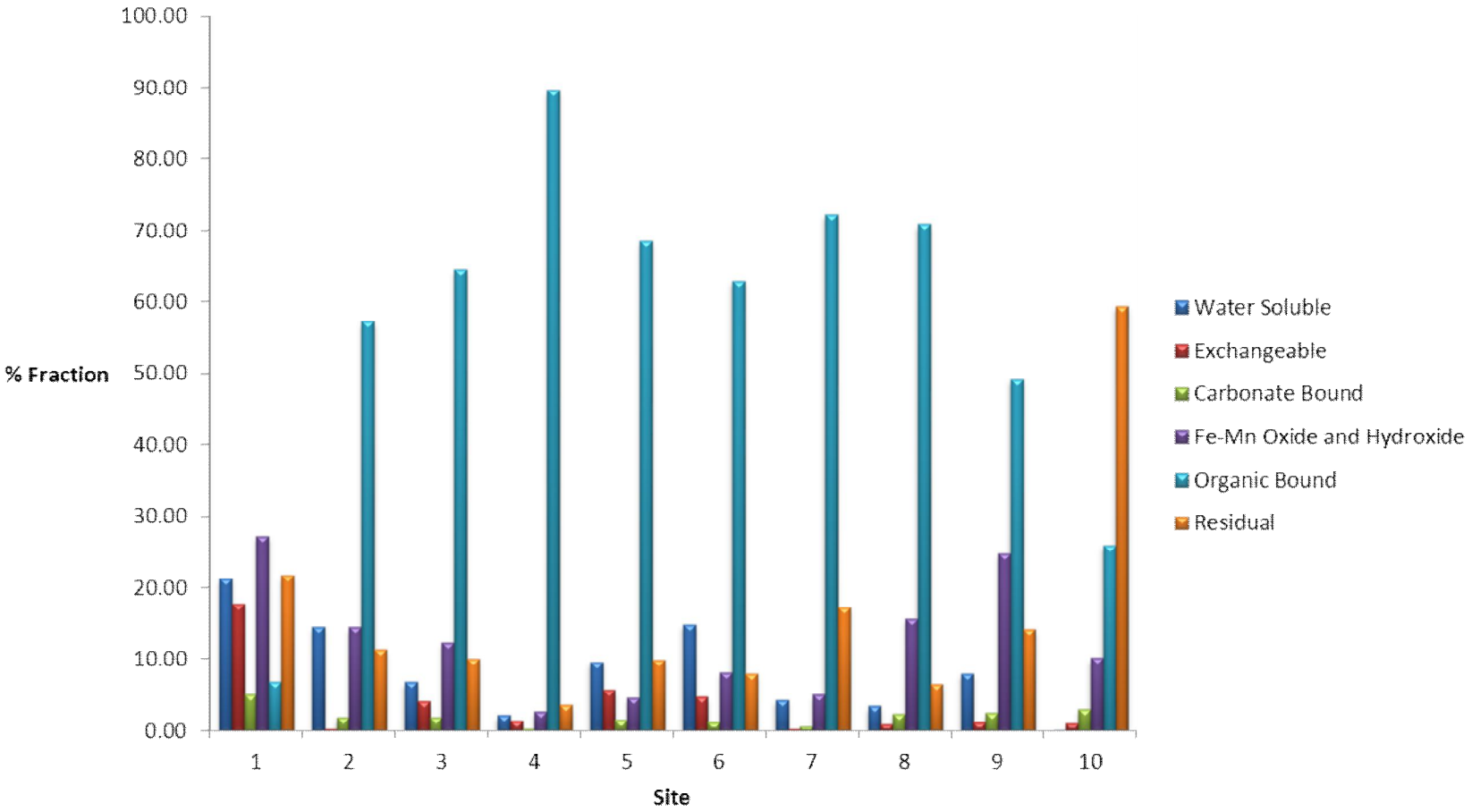


Fig. 4.42. Percentage Cu in each operationally fraction of atmospheric particulate dust (Hot and Dry Season).

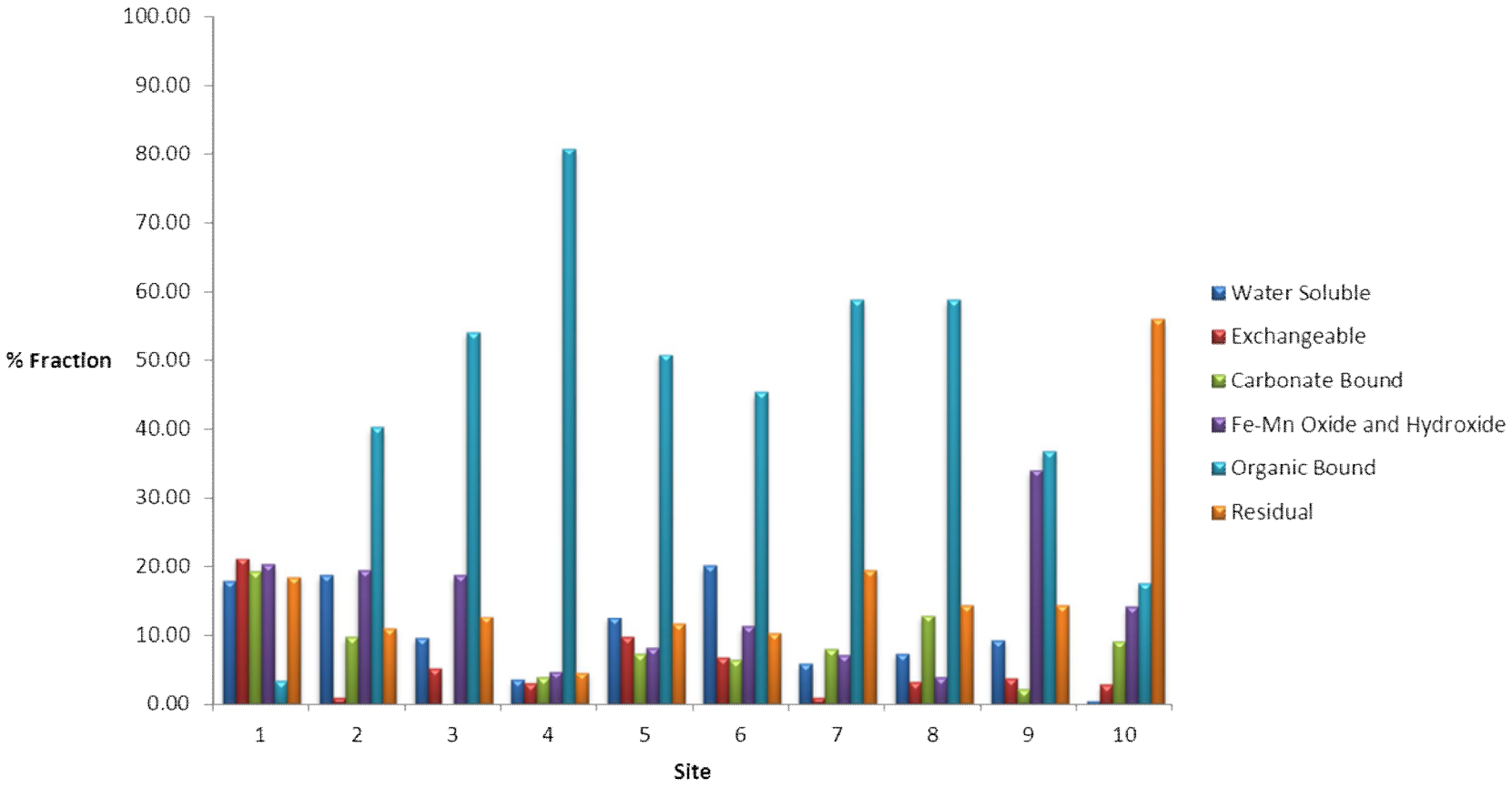


Fig. 4.43. Percentage Cu in each operationally fraction of atmospheric particulate dust (Warm and Wet Season).

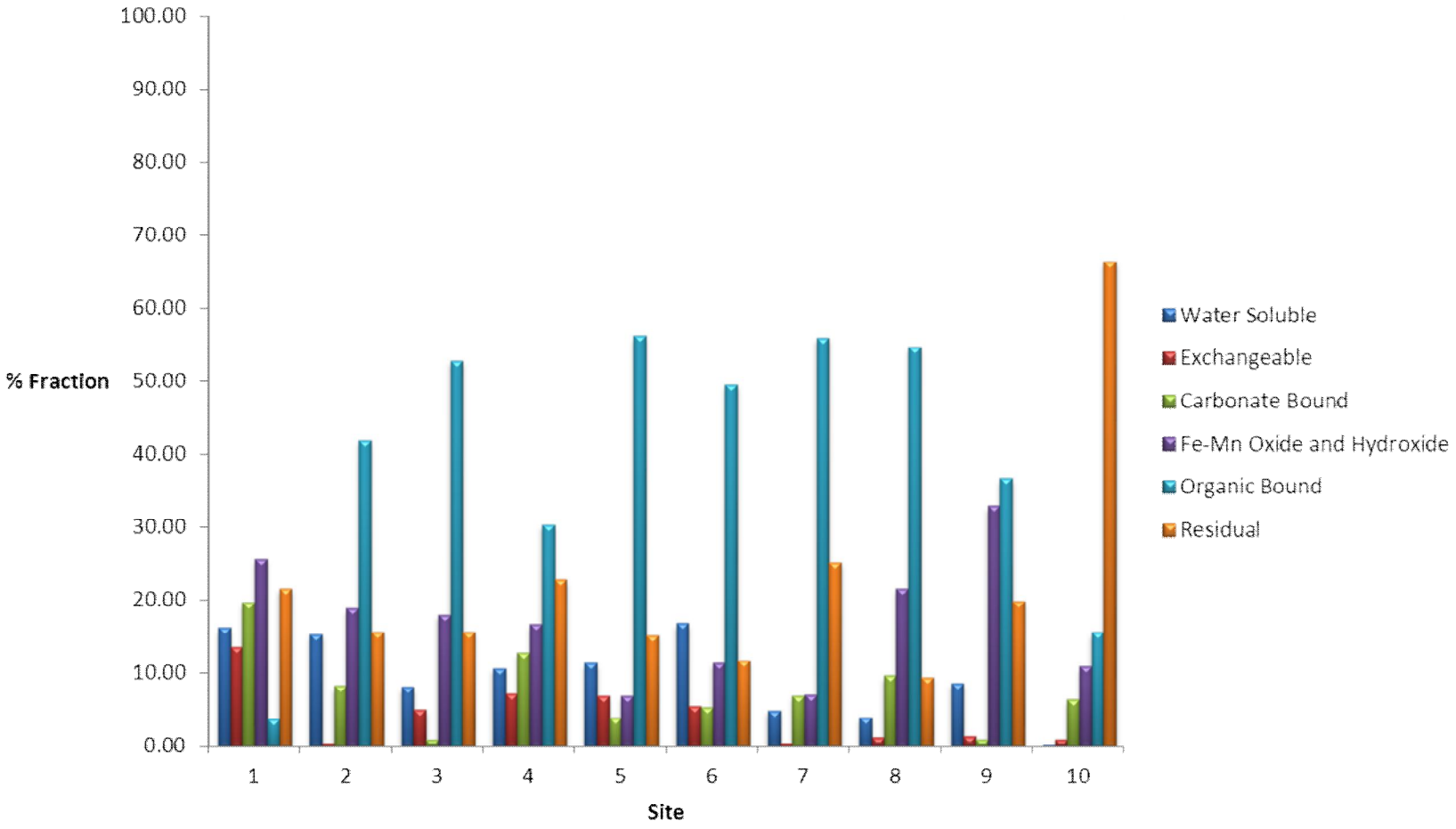


Fig. 4.44. Percentage Cu in each operationally fraction of atmospheric particulate dust (Warm and Dry Season).

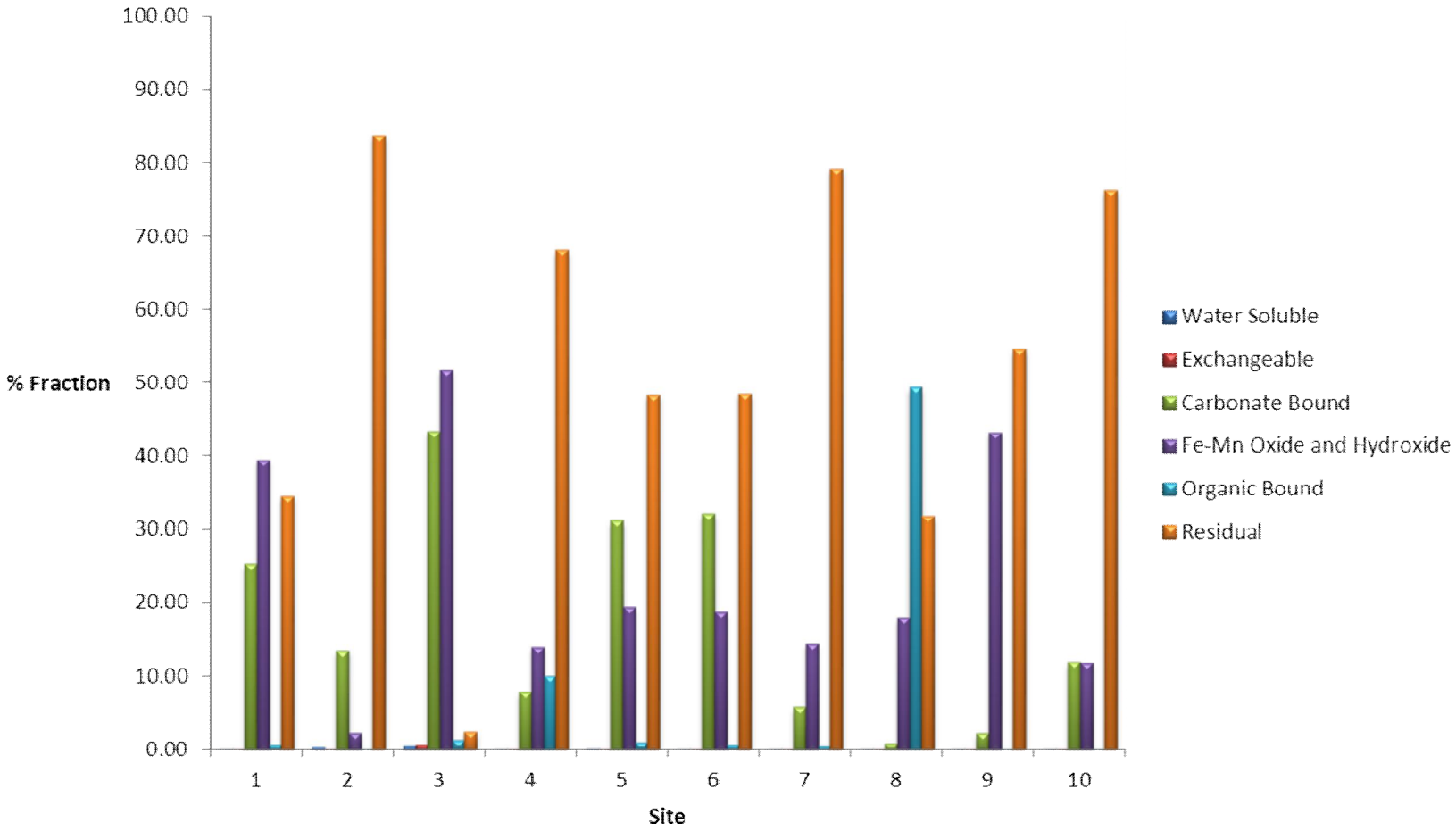


Fig. 4.45. Percentage Zn in each operationally fraction of atmospheric particulate dust (Cool and Dry Season).

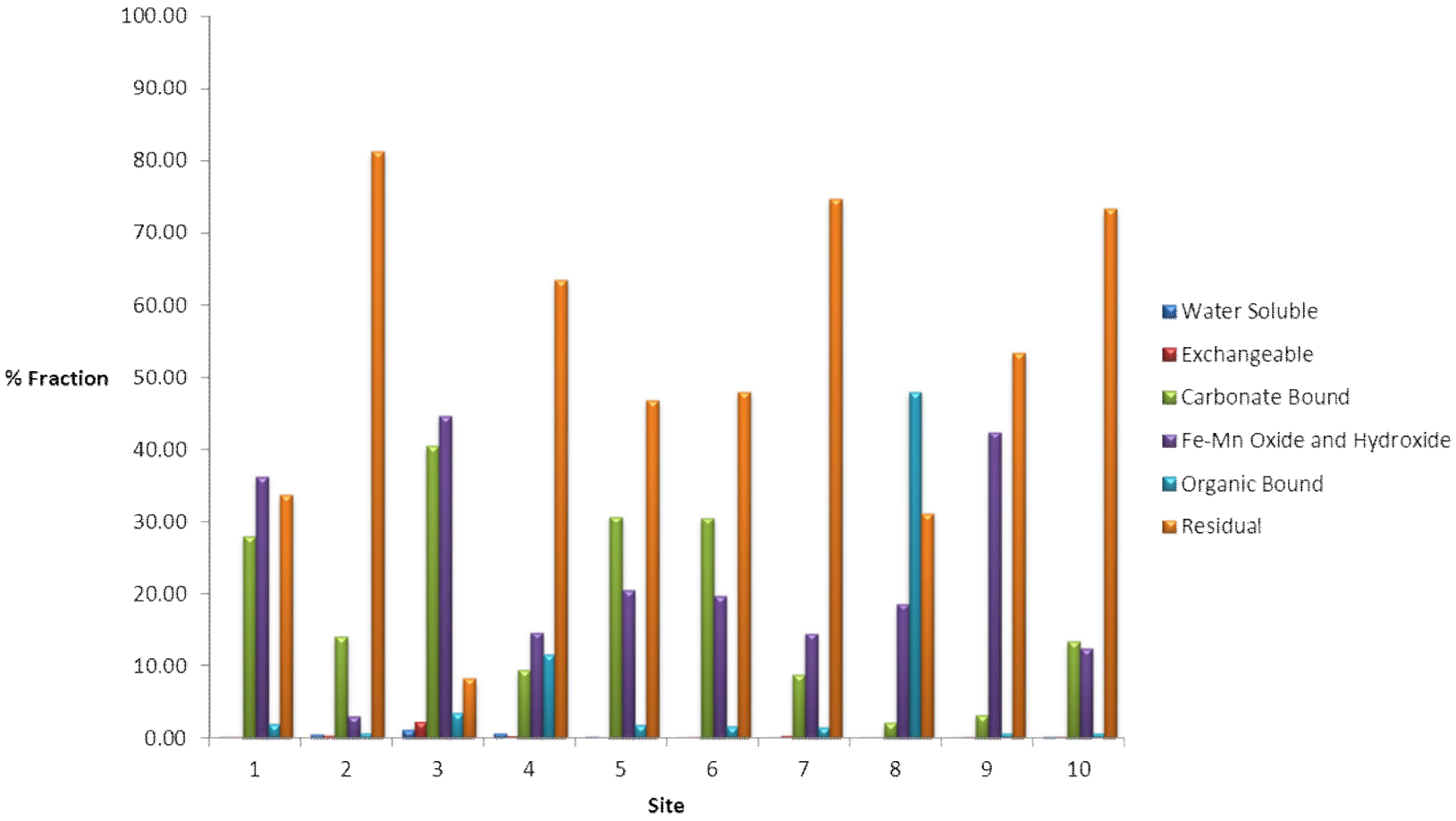


Fig. 4.46. Percentage Zn in each operationally fraction of atmospheric particulate dust (Hot and Dry Season).

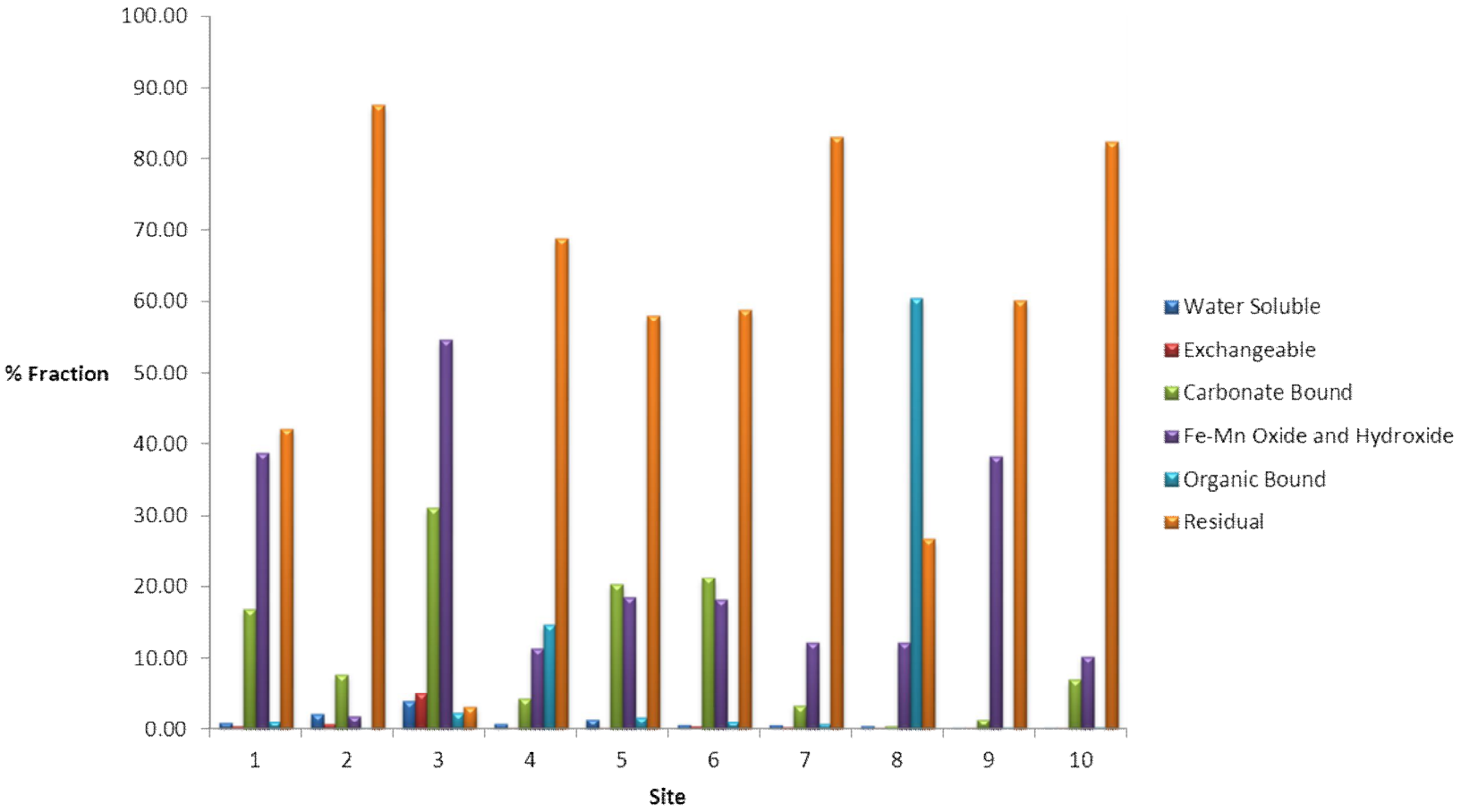


Fig. 4.47. Percentage Zn in each operationally fraction of atmospheric particulate dust (Warm and Wet Season).

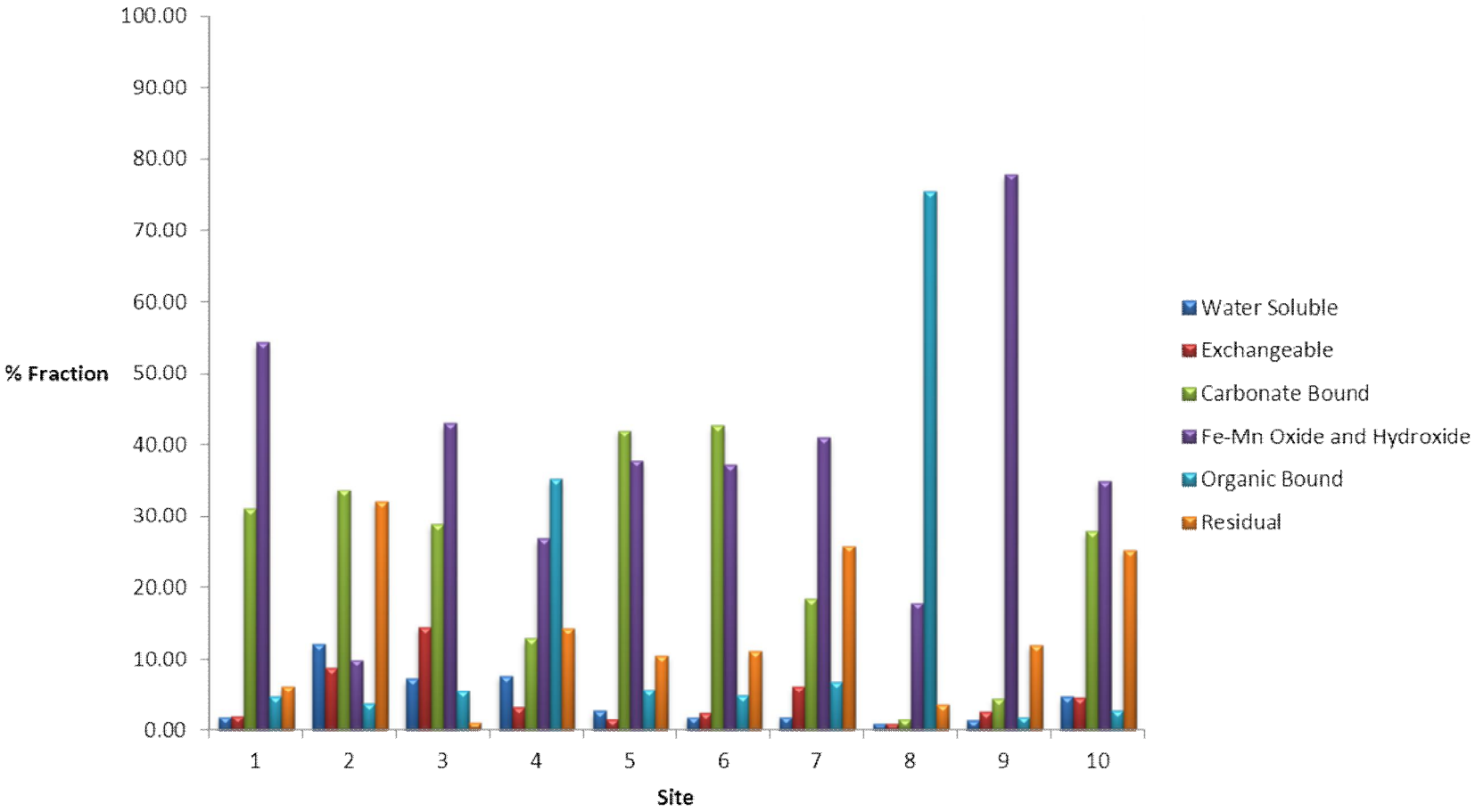


Fig. 4.48. Percentage Zn in each operationally fraction of atmospheric particulate dust (Warm and Dry Season).

Warm and dry season: FIV > FII > FV > FVI > FII > FI

4.7.2 Discussion

As observed from the results, the levels of Cd, Cr, Ni, Pb, Cu and Zn at all the sites in particulate dust were higher than those in soils with highest concentrations of Cd, Cr, Ni and Cu being in Warm and Wet Season, and Pb and Zn in Hot and Dry Season. Also, after the rainy season (Warm and Dry Season), there was a decrease in levels of metals across at all the sites. The reason was that particulate dust represents a more recent accumulation of pollutants and during rainy season (Warm and Wet Season) there was decrease in dust production and distance traveled by the particulate dust is reduced due to increase in humidity, thereby causing relatively low concentrations of metals. Chon *et al*. (1998) in a similar study in Seoul, Korea, reported similar trend for the same metals. Also, like Chon *et al*. (1995) and Chon *et al*. (1998), this study confirms that metal concentration in dusts is higher than soils.

Similarly, correlation analysis showed a strong relationship in the total metal content of soils and dusts. This implies that particulate dust is a principal source of soil contaminants. In this study, it has become increasingly evident that even in areas very far from the source, heavy metals may be supplied to soils in significant amounts owing to the atmospheric transport of pollutants. This corroborate with Leitâo (2005) that metal concentration in the road vicinity is not high once its initial amount in particulate dust around is low. However, extensive contamination found in dust reflects the airborne deposition of particulates originating from other sources than traffic emissions especially with negative correlations found for Cr, Ni, Cu and Zn and non significant positive correlation for Pb and Cd. Sources such as industrial emissions and electricity generating set could be responsible.

However, heavy metal speciation studies are important since slight changes in metal availability in the environment can cause these elements to be toxic to animals and plants (Banat *et al*., 2005). From the results presented above, Cd was found in its highest proportion in the form bound to Fe-Mn oxide (53.88%) at Site 3. The highest percentage of Cd in this fraction was relatively high and constitutes a large portion of non-residual Cd. Heavy metals enwrapped by Fe-Mn oxides or precipitated as hydroxide have been reported by Wang *et al*. (2010). Metals bound to Fe-Mn oxides would be released under reductive conditions (Singh *et al*., 1999) and, therefore, are unstable under anaerobic condition. Also, followed by Fe-Mn oxide in the non-residual fractions for Cd (47.04%) was the carbonate fraction, which is consistent with the findings of Massadeh *et al*. (2007). The high levels of Cd in the carbonate fraction in the present study may be probably a consequence of the more alkaline and calcareous nature (Chibbar, 1985) of the samples. At higher pH the substitution of Cd^{2+} for Ca^{2+} in calcite and precipitation of $CdCO_3$ is expected (Lindsay, 1979). Similar to this study, Feng *et al*. (2009) reported high percentage Cd in carbonate and Fe-MnO fractions.

In this study, little information on heavy metals in particulate settling dusts leads to comparison to street dust. Hence, the smaller percentage of Cd in the organic fraction as noted in the present study (< 20%) except for Site 10 is commonly found in street dusts (Harrison *et al*., 1981). The minor role for organic fraction in the fractionation of Cd in this study is consistent with the low adsorption constant of Cd to organic matter (Chlopecka *et al*., 1996) and with evidence that Cd does not appear to form strong organic complexes (Sposito *et al*., 1982; Keefer *et al*., 1984). Also, in the present study, the amount of Cd determined as sum of water soluble, exchangeable and carbonate fractions, was often more than 50% of the total at all the sites during Warm and Wet Season and represents the potential mobility of Cd to the environment. These

characteristics plus the known hazards to human health suggest that more frequent examination of the level of Cd in humans living around these roads in Kano Metropolis should be done.

As recorded in the results, the highest percentage of Cr (44.17 – 68.32% and 82.07 – 90.05%) in the sites across the seasons was found in the organic bound and residual fractions, respectively, indicating that Cr especially in Cool and Dry, and Hot and Dry Seasons show little risk to the environment. However, in Warm and Wet, and Warm and Dry Seasons, there was slight change in dominant fractions at Sites 5, 6 and 10, such that exchangeable and carbonate bound fractions dominate at the expense of organic and residual fractions in previous seasons. This could imply that there was change in environment conditions during this season favouring the availability of Cr at these sites in mobile phase. According to Wu *et al*. (2004), metals in this fraction are mainly fixed in the primary and secondary minerals and are chemically stable and biological inactive. The greater the percentage of metals present in this fraction, the smaller the risk of the metals because this portion of metals cannot be re-released to environment under normal conditions (Wang *et al*., 2010). Furthermore, the stable nature of the compound confirms the fact that the metal is bonded firmly within a mineral lattice restricting the bioavailability of this metal (Coetzee, 1993).

Ni is similar to Cr in that residual fractions were the major carriers of Ni in the particulate dust, followed by organic bound and Fe-Mn oxide fractions. However, in Warm and Wet Season, exchangeable fraction dominates Ni at Sites 1, 3, 4, 7 and 8. Also similar to Cr, source apportionment of Ni during this season, indicates anthropogenic sources of the metal. Similar trends in availability of Ni in residual and non-residual dust fractions have been reported by Sunderland and Tolosa (2000) and Banerjee (2003). Norrish (1975) has also indicated that during soil weathering, silicates commonly occlude Ni. Bruemer *et al*. (1988) and Banerjee (2003) suggested that the large proportion of Ni in residual fraction might be because Ni^{2+} has the highest field stabilization energy of the common divalent metals and thus has high potential to be enriched in clay minerals.

Fe-Mn oxide and organic bound were the next important fractions (2.44 – 65.20% and ND – 56.92%) containing Ni. Jenne (1968) has suggested that adsorption by Mn oxides controls Ni levels in soils. Using crystal field theory McKenzie (1979) concluded that substitution of Ni^{2+} for Mn in mixed valence, Mn oxides might be responsible for much of the adsorption. Furthermore, in Warm and Wet, and Warm and Dry Season, Ni was nearly equally distributed in water soluble, exchangeable and carbonate bound fractions. In the present study, it was observed that there was an increasing trend during rains and decreasing trend across the sites after rains in the percentage of Ni in the water soluble, exchangeable and carbonate bound fractions. This again depicts the effect of seasonal change on the availability of Ni in the dust samples, suggesting health risk especially during the rainy season.

For Pb, except at Sites 1 and 5 (across the season) and few exception at Site 3, 6 and 10 (Warm and Wet Season) and Sites 3 and 4 (Warm and Dry Season), all samples showed dominance of Pb in carbonate and exchangeable fractions. This implies anthropogenic source of Pb in the particulate dust samples. However, contrary to previous report in this study that traffic emission is the major source of Pb in roadside soil might not be the same for the particulate dust samples especially with non-significant correlation with traffic emissions. Hence other sources such as generating set emissions, which is a common phenomenon at the study sites due to consistent power outage could be responsible for the Pb in this fractions coupled with the nucleated city build-up that may possibly entrapped the particulate released during the emission process.

Inline with this study, Flores-Rodriguez *et al*. (1994) on the bioavailable and stable forms of heavy metals in atmospheric particulate dust showed that Fe-MnO and carbonate fractions of suspended solids were the most important fractions in terms of metal binding, irrespective of the heavy metal. This finding is in general agreement with the results of this study for Pb. Studies on the fractionation of atmospheric particulate dust have suggested that Pb has a high affinity for carbonates (Feng *et al*., 2009). As such, Pb is generally considered to be relatively mobile with the dust particles, primarily as a result of its small soluble component. High amount of Pb in the carbonate fractions is also reported in other studies on roadside soils (Massadeh *et al*., 2007). Howard and Sova (1993) noted, for example a larger part of Pb in the carbonate fraction in the most heavily contaminated roadside soil.

The percentage of Pb < 30% in the Fe-Mn oxide fraction is in broad agreement with the fractionation of Pb in soils (Ramos *et al*., 1994) and street dust (Fergusson and Ryan, 1984; Banerjee, 2003). The adsorption of Pb on the hydrous oxides of Fe and Mn is considered as a reasonably universal fixation mechanism (Banerjee, 2003).

The predominant form of Cu available in the entire fraction is organic fraction. The higher stability constant of Cu complexes with organic matter leads to higher organic fractions. Tessier *et al*. (1979) indicated that Cu exhibits the highest stability constants for most ligands among the heavy metals studied. Based on this, Ho (2000) suggested that the high affinity of organic ligands with heavy metals makes Cu in river sediments more stable, leading to the suppression of diffusion and dispersion of Cu, though dust samples were considered in this study, similar reasons could be responsible. However, it was suggested that only under strong oxidizing conditions would Cu be leached into the environment (Wang *et al*., 2010). In this fraction, the metal ion acts as the central ion, and the active organic matter groups act as the ligand or perhaps through the reaction of the sulphide ion and Cu. The organic fraction released in this step is hardly considered very mobile or available because the Cu is associated with stable high-molecular weight humic substances that decompose slowly (Singh *et al*., 1998). A high percentage (3.62 – 89.62%) of Cu was found in the oxidizable fraction, indicating that high organic matter and sulphide absorbed Cu and played a significant role in controlling the mobilization of this element. Cu is usually reported to dominate in the organic and residual fractions (Harrison *et al*., 1981; Hamilton *et al*., 1984; Ramos *et al*., 1994; Ma and Rao, 1997).

From the results, Zn fraction is considered to be occluded inside the crystalline structures and not readily available for plant absorption. The present findings are different with that of Shuman (1985), who reported that soil Zn was mainly associated with crystalline Fe-Mn oxide and with non-residual extractable fraction. Usero *et al*. (1998) and Mashal *et al*. (2009) using also the Tessier method found that Zn were bound to residual fraction. Maskall and Thornton (1998) indicate that in contaminated soils that Zn was mainly found in the residual fractions. The results for atmospheric particulate dust are similar, but with less association to Fe-Mn oxides and a higher percentage with the residual fraction.

4.8 Mobility Factor of Heavy Metals in Atmospheric Particulate Dust

Determination of heavy metal mobility is based on the relative amount of the metal in the first three fractions containing easily mobilizable phases. The mobility indices for Cd, Cr, Ni, Pb, Cu and Zn were expressed as the percentage mobility factor (MF) based on Equation 4.4. The results are summarized in Table 4.38. The percentage MF values range from 32.10 (Site 3) – 81.39 (Site 7), 31.52 (Site 3) – 84.73 (Site 7), 29.49 (Site 3) – 79.55 (Site 7), and 47.62 (Site 3) –

Table 4.38. Percentage mobility factor for heavy metal in atmospheric particulate dust across the seasons

Season	Site									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
						Cd				
A	37.04	38.98	32.10	52.92	61.52	57.81	81.39	44.13	61.80	45.52
B	31.53	33.69	35.52	48.30	58.61	61.09	84.73	41.00	56.60	52.24
C	34.34	37.65	29.49	52.12	59.00	61.21	79.55	42.53	58.72	51.65
D	47.92	49.25	47.62	61.74	75.70	69.83	92.75	58.54	71.59	55.84
						Cr				
A	47.57	3.04	14.01	29.70	57.85	43.46	9.60	39.93	1.22	45.23
B	28.74	1.41	11.02	6.31	30.59	11.44	5.09	4.58	0.72	15.04
C	22.38	1.24	6.44	9.79	35.05	11.44	2.43	4.26	0.39	11.28
D	23.88	7.10	31.59	14.08	56.58	10.10	15.22	6.77	2.79	10.79
						Ni				
A	51.12	41.89	55.15	56.62	32.26	33.94	31.09	32.47	56.41	23.69
B	6.26	5.90	6.80	9.80	2.72	3.11	10.09	4.91	10.18	2.70
C	6.09	5.54	7.26	9.01	2.62	2.69	8.73	5.14	9.26	2.13
D	50.90	44.67	55.08	56.38	33.47	39.40	64.17	46.92	51.96	24.20
						Pb				
A	26.00	41.55	37.81	43.55	49.10	43.76	54.96	47.87	66.95	57.07
B	40.67	56.13	50.67	75.61	41.73	45.07	63.32	66.57	74.45	61.39
C	37.71	53.47	50.56	76.44	43.27	53.84	65.63	57.77	74.27	67.69
D	31.70	44.42	38.92	68.18	33.52	36.20	51.46	56.63	68.70	52.52
						Cu				
A	49.30	23.80	13.75	30.42	21.89	27.43	11.97	14.51	10.71	7.36
B	47.12	18.16	12.22	4.30	17.47	21.44	5.55	10.50	12.83	6.51
C	44.21	16.82	12.98	4.03	16.90	20.90	5.32	6.92	11.71	4.34
D	58.13	29.32	14.74	10.13	29.49	33.14	14.68	23.22	14.95	12.40
						Zn				
A	34.87	54.42	50.58	23.67	46.19	46.98	26.38	3.12	8.40	37.01
B	25.39	13.90	44.55	7.92	31.37	32.22	5.87	0.92	2.17	11.81
C	28.33	14.99	43.82	10.32	31.00	30.82	9.24	2.33	3.58	13.79
D	17.97	10.48	39.93	5.10	21.78	22.05	4.05	0.82	1.47	7.11

Where;
A: Cool and Dry Season
B: Hot and Dry Season
C: Warm and Wet Season
D: Warm and Dry Season

75.70 (Site 5) for Cd, 3.04 (Site 2) – 57.85 (Site 5), 0.72 (Site 9) – 30.59 (Site 5), 0.39 (Site 9) – 35.05 (Site 5), and 2.79 (Site 9) – 56.58 (Site 5) for Cr, respectively for Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons.

Similarly for Pb, the percentage MF ranged from 32.26 (Site 5) – 56.41 (Site 9), 2.70 (Site 10) – 10.18 (Site 7), 2.13 (Site 10) – 9.01 (Site 4), and 24.20 (Site 10) – 64.17 (Site 7) for Ni, 26.00 (Site 1) – 66.95 (Site 9), 40.67 (Site 1) – 74.45 (Site 9), 37.71 (Site 1) – 76.44 (Site 4), and 31.70 (Site 1) – 68.70 (Site 9), 7.36 (Site 10) – 49.30 (Site 1), 4.30 (Site 4) – 47.12 (Site 1), 4.03 (Site 4) – 44.21 (Site 1), and 10.13 (Site 4) – 58.13 for Cu, and 3.12 (Site 8) – 54.42 (Site 2), 0.92 (Site 8) – 44.55 (Site 3), 2.33 (Site 8) – 43.82 (Site 3), and 0.82 (Site 8) – 39.93 (Site 3) for Zn in Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons, respectively. Also, the average profile of the MF for the metals across the seasons showed:

For Cd

Cool and Dry Season 7 > 9 > 5 > 6 > 4 > 10 > 8 > 2 > 1 > 3

Hot and Dry Season 7 > 6 > 5 > 9 > 10 > 4 > 8 > 3 > 2 > 1

Warm and Wet Season 7 > 6 > 5 > 9 > 4 > 10 > 8 > 2 > 1 > 3

Warm and Dry Season 7 > 5 > 9 > 6 > 4 > 8 > 10 > 2 > 1 > 3.

For Cr

Cool and Dry Season 5 > 1 > 10 > 6 > 8 > 4 > 3 > 7 > 2 > 9

Hot and Dry Season 5 > 1 > 10 > 6 > 3 > 4 > 7 > 8 > 2 > 9

Warm and Wet Season 5 > 1 > 6 > 10 > 4 > 3 > 8 > 7 > 2 > 9

Warm and Dry Season 5 > 3 > 1 > 7 > 4 > 10 > 6 > 2 > 8 > 9.

For Ni

Cool and Dry Season 4 > 9 > 3 > 1 > 2 > 6 > 8 > 5 > 7 > 10

Hot and Dry Season 9 > 7 > 4 > 3 > 1 > 2 > 8 > 6 > 5 > 10

Warm and Wet Season 9 > 4 > 7 > 3 > 1 > 2 > 8 > 6 > 5 > 10

Warm and Dry Season 7 > 4 > 3 > 9 > 1 > 8 > 2 > 6 > 5 > 10

For Pb

Cool and Dry Season 9 > 10 > 7 > 5 > 8 > 6 > 4 > 2 > 3 > 1

Hot and Dry Season 4 > 9 > 8 > 7 > 10 > 2 > 3 > 6 > 5 > 1

Warm and Wet Season 4 > 9 > 10 > 7 > 8 > 6 > 2 > 3 > 5 > 1

Warm and Dry Season 9 > 4 > 8 > 10 > 7 > 2 > 3 > 6 > 5 > 1

For Cu

Cool and Dry Season 1 > 4 > 6 > 2 > 5 > 8 > 3 > 7 > 9 > 10

Hot and Dry Season 1 > 6 > 2 > 5 > 9 > 3 > 8 > 10 > 7 > 4

Warm and Wet Season 1 > 6 > 5 > 2 > 3 > 9 > 8 > 7 > 10 > 4

Warm and Dry Season 1 > 6 > 5 > 2 > 8 > 9 > 3 > 7 > 10 > 4

For Zn

Cool and Dry Season 2 > 3 > 6 > 5 > 10 > 1 > 7 > 4 > 9 > 8

Hot and Dry Season 3 > 6 > 5 > 1 > 2 > 10 > 4 > 7 > 9 > 8

Warm and Wet Season 3 > 5 > 6 > 1 > 10 > 2 > 4 > 7 > 9 > 8

Warm and Dry Season 3 > 6 > 5 > 1 > 2 > 10 > 4 > 7 > 9 > 8

From the trends above, it is confirmed that Site 7 for Cd, Site 5 for Cr, Site 4, 7 and 9 for Ni, Site 4 and 9 for Pb, Site 1 for Cu, and Site 2 and 3 for Zn had the highest MF across the seasons. This is an indication that the level of water soluble, exchangeable and carbonate bound fractions for Cd, Cr, Ni, Pb, Cu and Zn in this study were relatively high, though less than 1 (minimum threshold for MF). Also as evident from the trends, Sites 1 and 3 (Cd), Site 9 (Cr), Site 10 (Ni), Site 1 (Pb), Sites 4 and 10 (Cu), and Site 8 (Zn) had the least MF value across the seasons, which could be an index of high stability (Ogunfowokan *et al*., 2009) of the metals in the samples.

Similarly, as could be seen from Table 4.38, in Cool and Dry, and Warm and Dry Seasons, the MF values for Cr, Ni and Zn, and Cu, respectively, were generally at the highest compared to other seasons, while Pb was generally at the highest in Hot and Dry, and Warm and Wet Seasons. This suggests that during the aforementioned seasons there was an increased mobility of the metals, representing the highest potential risk for the surrounding environment. Generally the mobility factors in all the seasons were less than 100 (< 1), indicating low pollution due to the metals.

Furthermore, from the results, Site 7 and Sites 4 and 9 showed the highest vulnerability to Cd and Pb exposure, respectively.

4.9 AIR QUALITY

4.9.1 Results

The raw data obtained from this study was analysed using comprehensive statistical software (SPSS Version 17). The average CO, H_2S, NO_2, SO_2, FL and NH_3 concentrations values observed at each site are summarized in Appendix XXX - XL. Seasonal variations of pollutants across the sites are shown in Figs 4.49 – 4.54. The results showed highest concentration for all pollutants between 3:00pm - 6:00pm in all the seasons. The t-test has been applied for comparing mean-values of pollutants obtained at different seasons per site. The p-value for CO at all sites (except sites 2, 7 and 9) was < 0.05, p-value for H_2S at all sites (except sites 1and 6) was < 0.05, for NO_2, p-value was < 0.05 at all sites except sites 2, 3, 6 and 10, p-value for SO_2 at all sites (except sites 4, 5, 8 and 9) was > 0.05, p-value for NH_3 at all sites was < 0.05, and for FL, p-value was > 0.05 at all sites except site 10. P-value less than 0.05 (<0.05) signifies 95% difference in their mean values across the seasons per site.

From the results for CO, seasonal average ranged from 5.42 – 7.04ppm for Site 1, 5.08 – 5.60ppm for Site 2, 4.92 – 7.21ppm for Site 3, 4.25 – 8.28ppm for Site 4, 6.50 – 14.33ppm for Site 5, 4.25 – 7.39ppm for Site 6, 5.42 – 8.17ppm for Site 7, 5.75 – 8.71ppm for Site 8, 6.33 –

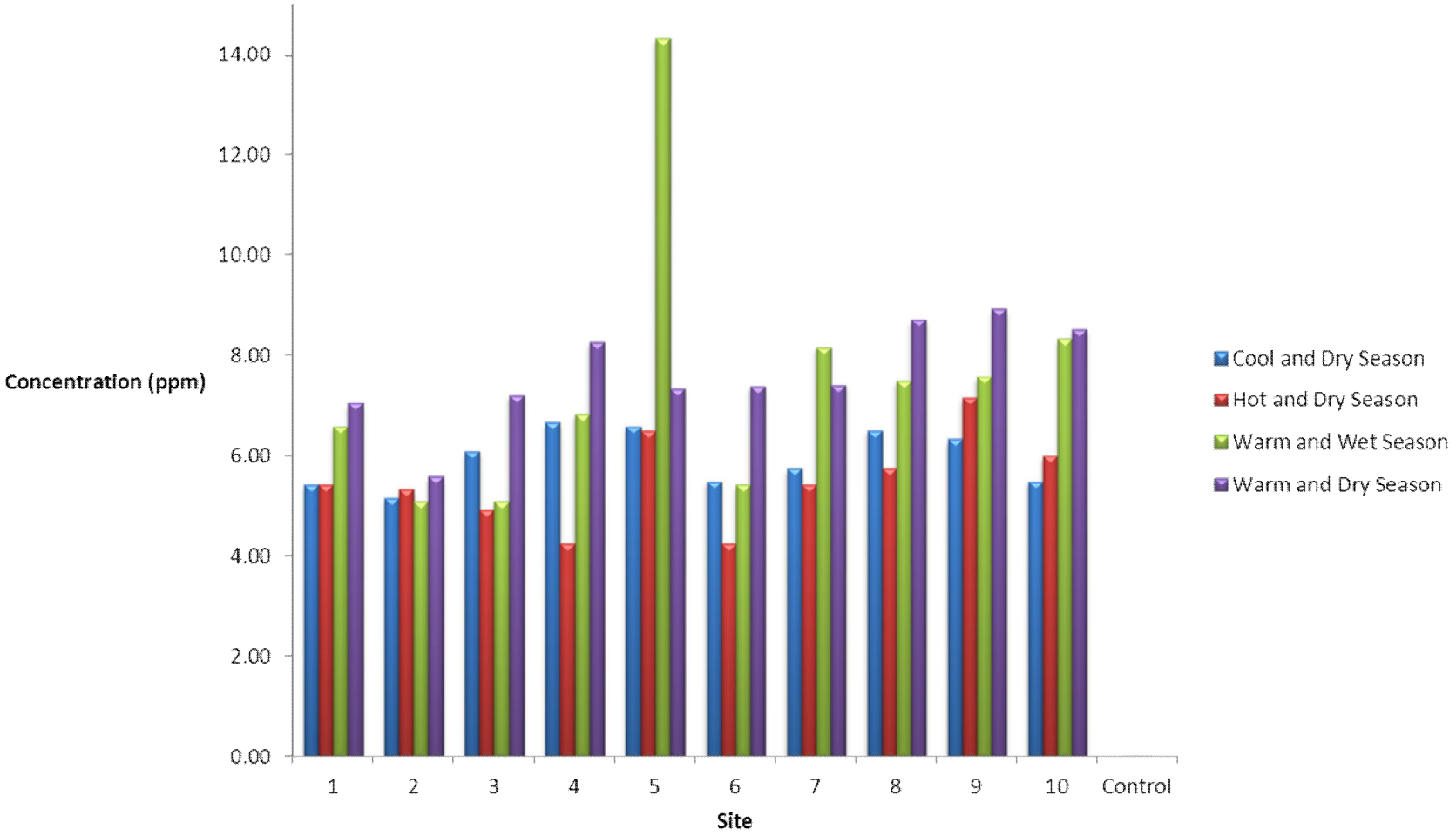


Fig. 4.49. Variation of CO across the sampling sites.

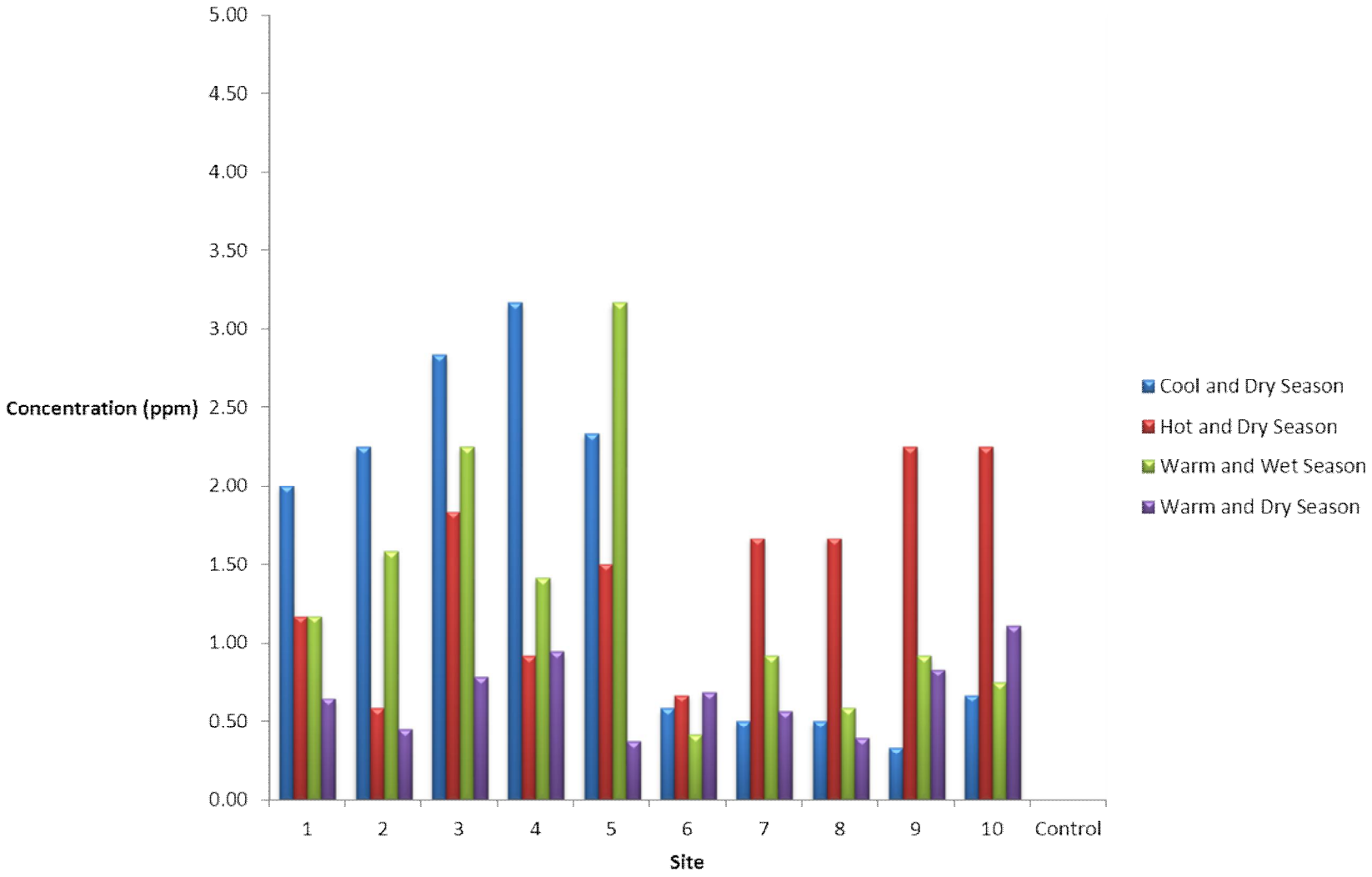


Fig. 4.50. Variation of H_2S across the sampling sites.

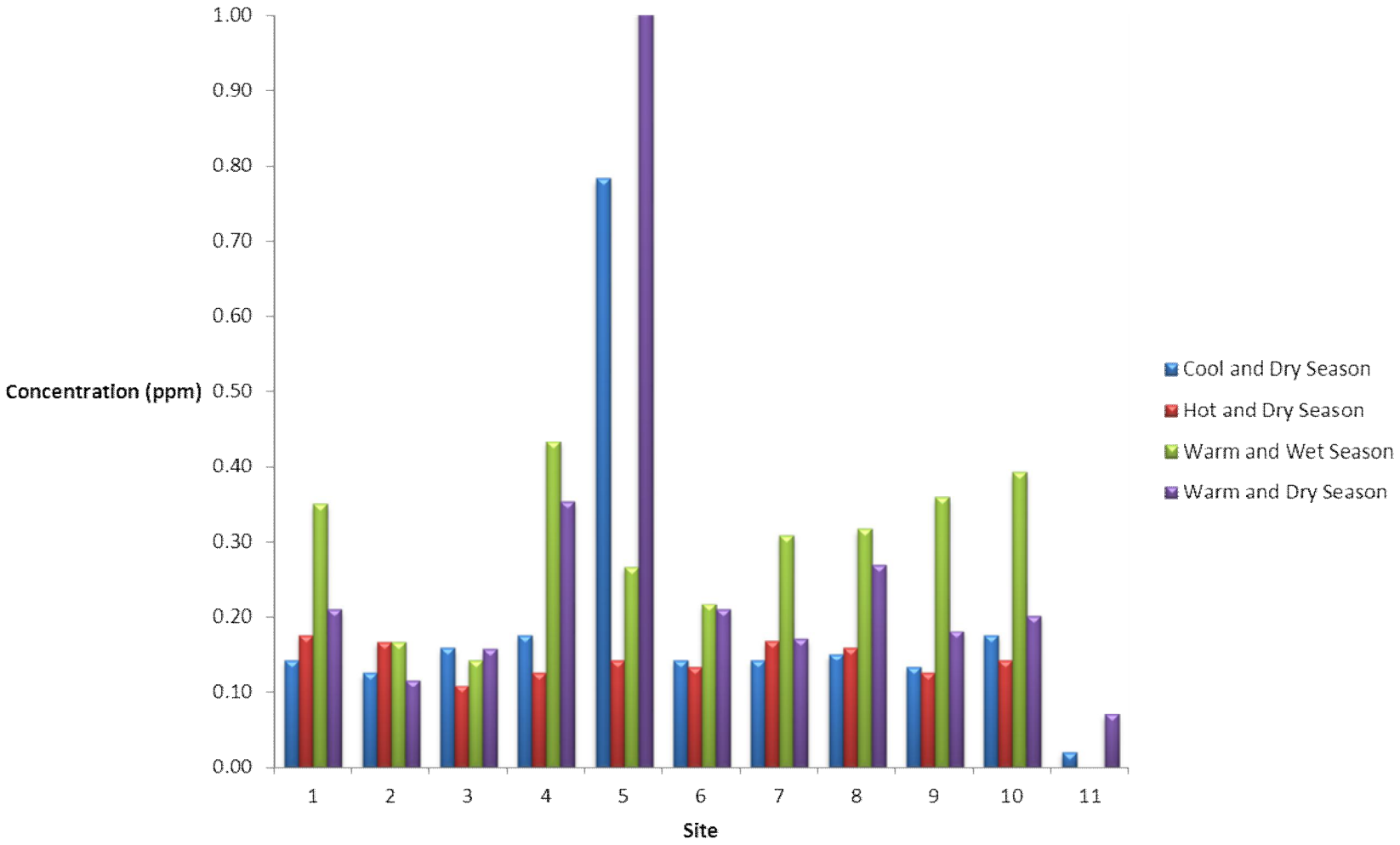


Fig. 4.51. Variation of NO_2 across the sampling sites.

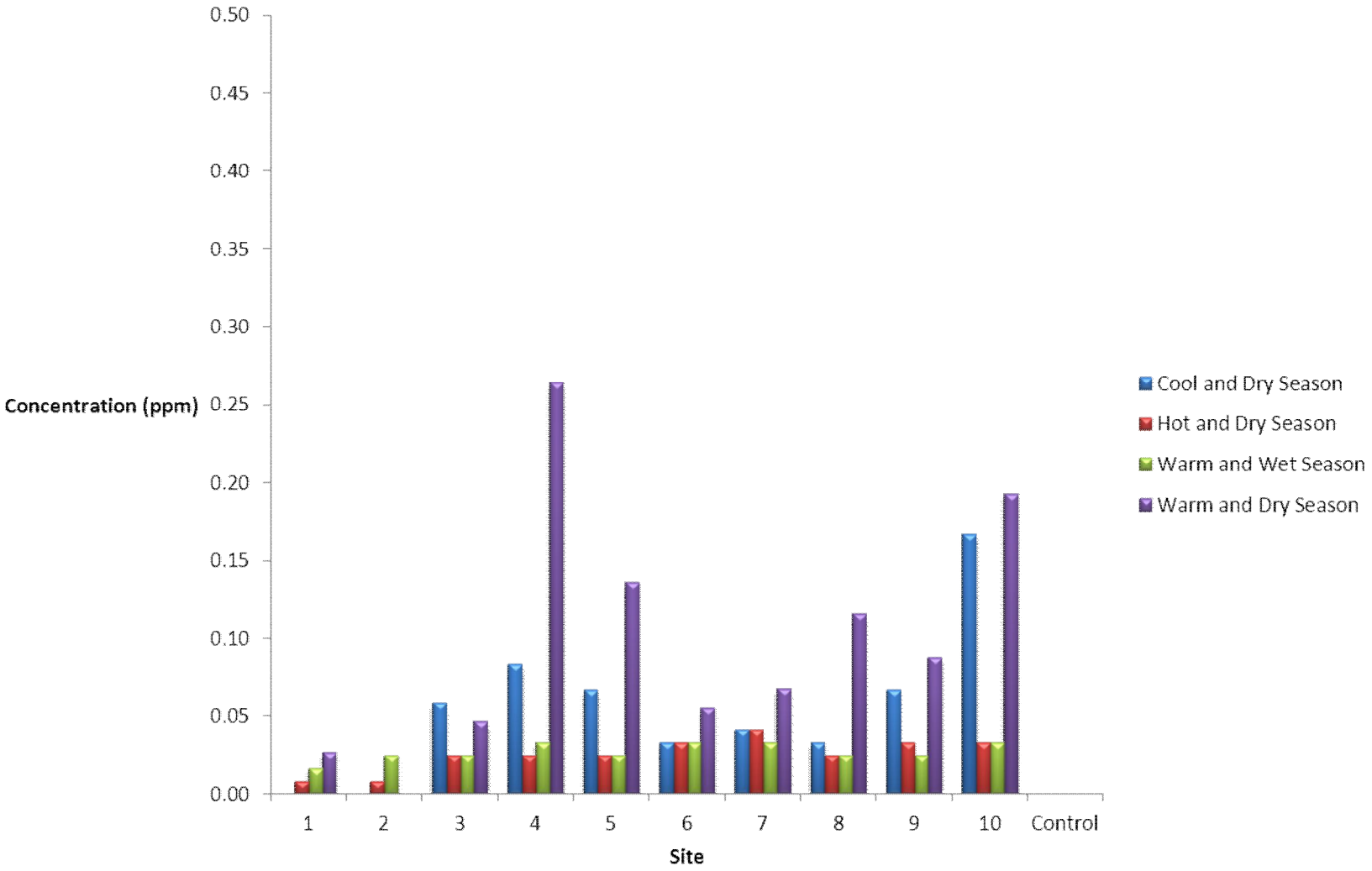


Fig. 4.52. Variation of SO_2 across the sampling sites.

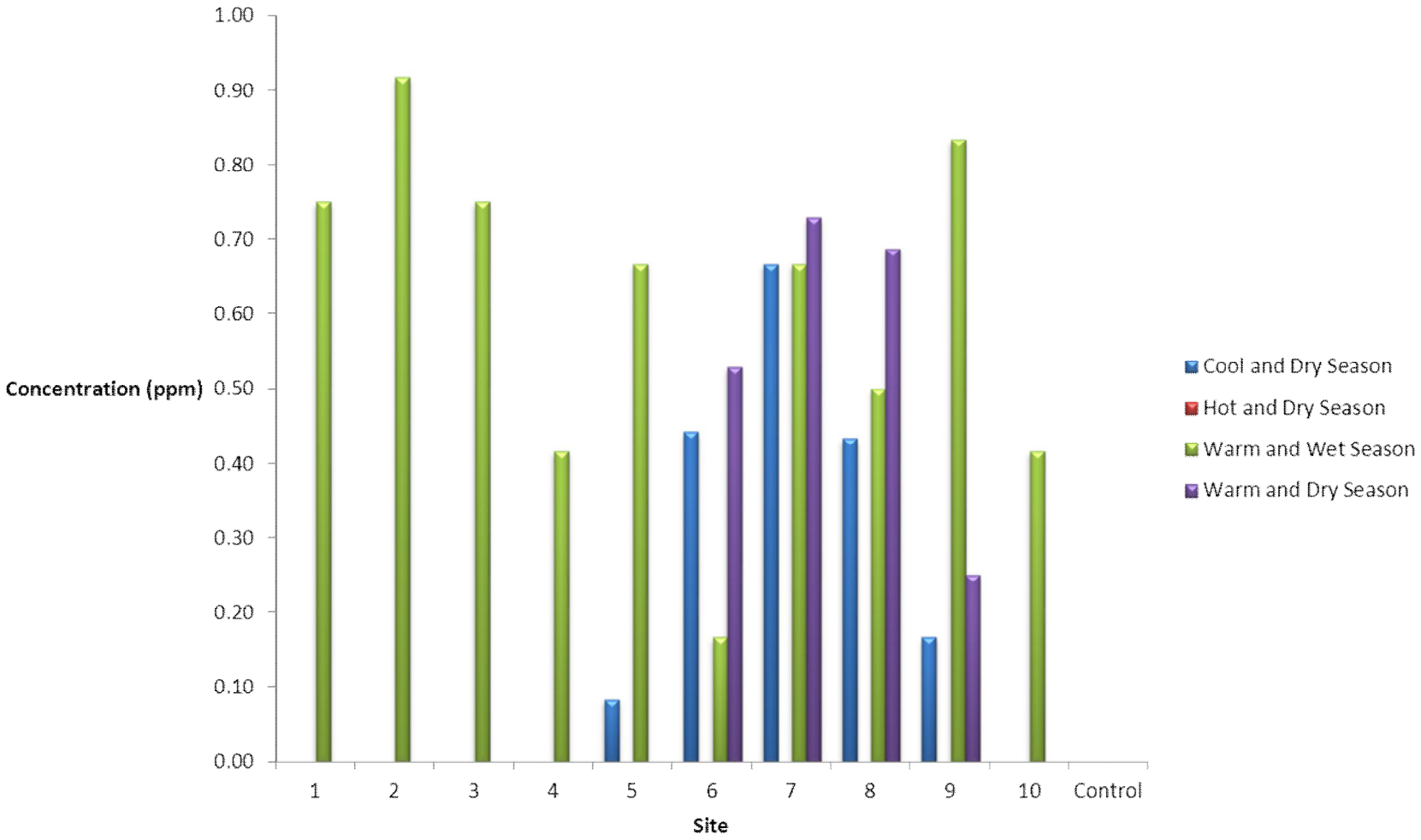


Fig. 4.53. Variation of Flammable gas (FL) across the sampling sites.

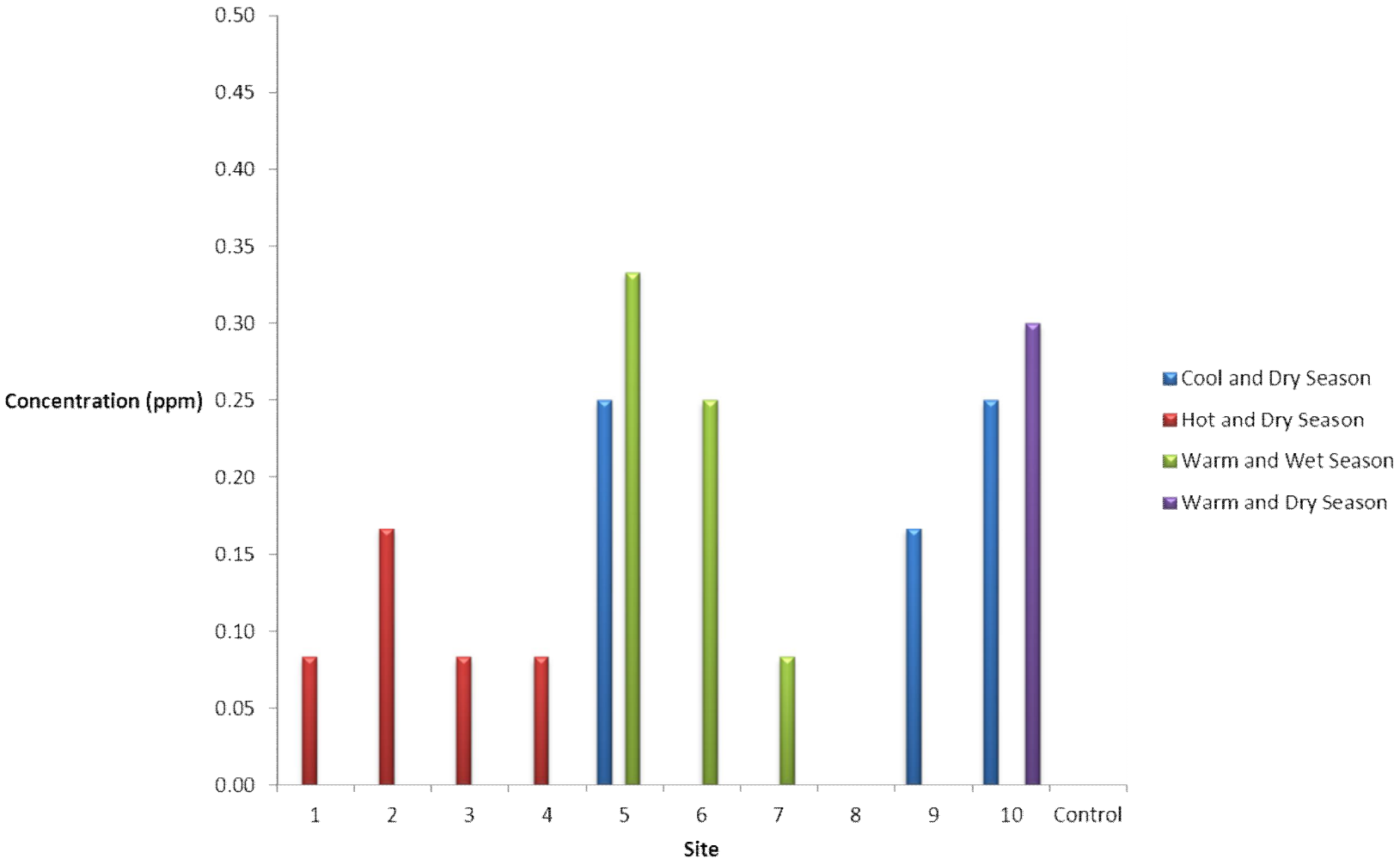


Fig. 4.54. Variation of NH_3 across the sampling sites.

8.93ppm for Site 9, 5.50 – 8.53ppm for Site 10, and 0.00 – 0.01ppm for control Site in the Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons, respectively. Highest concentration of CO at all sites (except sites 5 and 7) were observed during the Warm and Dry Season. The highest concentration of CO was at Site 5. Across the sites per season the profiles of CO were:

Cool and dry: 4 > 5 > 8 > 9 > 3 > 7 > 10 = 3 > 1 > 2
Hot and dry: 9 > 5 > 10 > 8 > 3 > 1 = 7 > 2 > 4 = 6
Warm and wet: 5 > 10 > 3 > 9 > 8 > 4 > 1 > 6 > 2 = 3
Warm and dry: 9 > 8 > 10 > 4 > 7 > 6 > 5 > 3 > 1 > 2

Seasonal average of H_2S showed the following ranges: 0.64 – 2.00, 0.45 -2.25, 0.78 – 2.83, 0.94 – 3.17, 0.37 – 3.17, 0.42 – 0.67, 0.50 – 1.67, 0.40 – 1.67, 0.33 – 2.25, and 0.67 – 2.25ppm for Sites 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 in Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons, respectively. No H_2S was detected at the control site. Similar to CO, highest level of H_2S was obtained at site 5. Average seasonal variation across the sites showed that highest concentrations were in Hot and Dry Season for Sites 6, 7, 8, 9 and 10, Cool and Dry Season for Sites 1, 2 and 3, and Warm and Wet Season for Site 5. The pattern of H_2S distribution across the sites in the four seasons was:

Cool and dry: 4 > 3 > 5 > 2 > 1 > 10 > 6 > 7 = 8 > 9
Hot and dry: 9 = 10 > 3 > 7 = 8 > 5 > 1 > 4 > 6 > 2
Warm and wet: 5 > 3 > 2 > 4 > 1 > 7 = 9 > 10 > 8 > 6
Warm and dry: 10 > 4 > 9 > 3 > 6 > 1 > 7 > 2 > 8 > 5

The results for NO_2 revealed seasonal average ranging between 0.14 – 0.35, 0.12 – 0.17, 0.11 – 0.16, 0.13 – 0.43, 0.14 – 1.09, 0.13 – 0.22, 0.14 – 0.31, 0.15 – 0.32, 0.13 – 0.36 and 0.14 – 0.39 for Sites 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 during Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons, respectively. Similar to H_2S, NO_2 was not detected at the Control Site. Highest levels of NO_2 were observed in Warm and Dry Season at Site 5. NO_2 distribution across the sites was found to have the following patterns:

Cool and dry: 5 > 4 > 10 > 3 > 8 > 1 = 6 = 7 > 2 = 9
Hot and dry: 1 > 2 = 7 > 8 > 5 = 10 > 4 = 6 = 9 > 3
Warm and wet: 4 > 10 > 9 > 1 > 8 > 7 > 5 > 6 > 2 > 3
Warm and dry: 5 > 4 > 8 > 1 = 6 > 10 > 9 > 2 = 7 > 3

However, compared to CO and H_2S, most of the sites had their highest NO_2 concentrations in the Warm and Wet Season.

For SO_2, seasonal average ranged between: ND – 0.03ppm for Site 1, ND – 0.03ppm for Site 2, 0.03 – 0.06ppm for Site 3, 0.03 – 0.26ppm for Site 4, 0.03 – 0.14ppm for Site 5, 0.03 – 0.06ppm for Site 6, 0.03 – 0.07ppm for Site 7, 0.03 – 0.12ppm for Site 8, 0.03 – 0.09ppm for Site 9, 0.03 – 0.19ppm for Site 10 during Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons, respectively. SO_2 was also not detected at the Control Site. Highest concentration of SO_2 at all sites was observed during the Warm and Dry Season. The highest concentration of SO_2 was at Site 4 during Warm and Wet Season. Distribution patterns of SO_2 across the sites were:

Cool and dry: 10 > 4 > 5 = 9 > 3 > 7 > 6 = 8 > 1 = 2
Hot and dry: 7 > 3 = 4 = 5 = 6 = 8 = 9 = 10 > 1 = 2
Warm and wet: 2 = 3 = 4 = 5 = 6 = 7 = 8 = 9 = 10 > 1
Warm and dry: 4 > 10 > 5 > 8 > 9 > 7 > 6 > 3 > 1 > 2

Seasonal average of FL showed the following ranges: ND – 0.75, ND – 0.92, ND – 0.75, ND – 0.42, ND – 0.67, ND – 0.53, ND – 0.73, ND – 0.69, ND – 0.83, and ND –

0.42ppm for Sites 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 during the Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons, respectively. No FL was detected at the Control Site. Highest level of FL was obtained at Site 2 in Warm and Wet Season. Average seasonal variation across the sites showed that highest concentrations were in Warm and Wet Season for Sites 1, 2, 3, 4, 5, 9 and 10, and Warm and Dry Season for Sites 6, 7 and 8. The pattern of FL distributions across the sites in the four seasons were:

Cool and dry: 7 > 6 > 8 > 9 > 5 > 1 > 2 > 3 > 4 > 10
Hot and dry: 1 = 2 = 3 = 4 = 5 = 6 = 7 = 8 = 9 = 10
Warm and wet: 2 > 9 > 1 = 3 > 5 = 7 > 8 > 4 = 10 > 6
Warm and dry: 7 > 8 > 6 > 9 > 1 > 2 > 3 > 4 > 5 > 10

The results for NH_3 revealed seasonal average ranging between: ND – 0.08, ND – 0.17, ND – 0.08, ND – 0.08, ND – 0.33, ND – 0.25, ND – 0.08, ND – 0.17 and ND – 0.25 for Sites 1, 2, 3, 4, 5, 6, 7, 9 and 10 during the Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons, respectively. NH_3 was not detected at Site 8 and Control Site. Highest concentration of NH_3 was observed in Warm and Wet Season at Site 5. Average seasonal variation across the sites showed that highest levels were in Cool and Dry Season for Sites 9 and 10, Hot and Dry Season for Sites 1, 2, 3, and 4, and Warm and Wet Season for Sites 5, 6 and 7. NH_3 distributions across the sites were found to have the following pattern:

Cool and dry: 5 > 10 > 9 > 1 = 2 = 3 = 4 = 6 = 7 = 8
Hot and dry: 2 > 1 = 3 = 4 > 5 = 6 = 7 = 8 = 9 = 10
Warm and wet: 5 > 6 > 7 > 1 = 2 = 3 = 4 = 8 = 9 = 10
Warm and dry: 1 = 2 = 3 = 4 = 5 = 6 = 7 = 8 = 9 = 10

The temperature and sound levels across the seasons are presented in Tables 4.50 and 4.51, respectively. The mean temperature for Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons ranged between 31.8 (Site 9) – 39.1^{0}C (Site 3), 33.1 (Site 7) – 36.6^{0}C (Site 1), 30.8 (Site 1) – 33.9^{0}C (Site 4), and 30.1 (Site 4) – 39.2^{0}C (Site 3), for Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons, respectively. A marked temperature difference was observed between the studied and control sites. This indicates that activities such as vehicular emission, with traffic could be responsible for the temperature difference. Highest temperature was obtained in Warm and Dry Season at all sites with few exceptions.

The mean sound levels across the seasons ranged between: 79.20 (Site 6) – 87.10dB (Site 9), 86.30 (Sites 3 and 10) – 89.90dB (Site 7), 83.70 (Site 7) – 89.60dB (Site 3), and 86.90 (Site 9) – 94.70dB (Site 5) for Cool and Dry, Hot and Dry, Warm and Wet, and Warm and Dry Seasons, respectively. For majority of the sites, highest sound levels were recorded in Warm and Dry Season, with the highest at Site 5.

The degree of association between pollutant and metrological data, and traffic volume was investigated with bivariate Pearson correlation across the seasons (Tables 4. 52 – 4.55). Some of the variables were either positive or negative significantly correlated at 0.01 and 0.05 p-levels. For Cool and Dry season, CO had strong correlation with H_2S and SO_2, H_2S with NO_2. Significant ($p < 0.05$) negative correlation was observed between CO: sound, and H_2S: NO_2 and temperature. During Hot and Dry Season, significant positive correlation was found between CO: H_2S, NO_2 and SO_2, H_2S: NO_2 and SO_2, and NO_2: SO_2. Strong association ($p < 0.05$) between pollutants were observed in Warm and Wet Season, CO: H_2S, NO_2, SO_2 and NH_3, H_2S: NH_3, NO_2: SO_2, and SO_2: FL. In Warm and dry Season, significant positive correlation ($p < 0.01$) was

Table 4.50. Average temperature (^{0}C) of sampling sites across the seasons

Site	Season			
	Cool and Dry	Hot and Dry	Warm and Wet	Warm and Dry
1	36.2	36.6	30.8	36.5
2	38.4	35.8	31.6	38.8
3	39.1	35.7	32.9	39.2
4	37.1	33.3	33.9	30.1
5	38.5	35.4	32.5	39.5
6	37.1	34.8	33.6	35.6
7	38.4	33.1	32.7	35.2
8	37.8	33.8	32.5	33.5
9	31.8	33.4	32.2	33.3
10	33.9	33.8	31.1	33.0
Control	30.0	31.5	30.5	30.3

Table 4.51. Mean Sound level (dB) along sampling sites across the seasons

Site	Season			
	Cool and Dry	Hot and Dry	Warm and Wet	Warm and Dry
1	85.00	86.00	86.80	92.70
2	83.40	89.80	84.40	92.00
3	80.90	86.30	89.60	92.70
4	83.50	87.40	85.20	91.70
5	80.10	86.80	85.90	94.70
6	79.20	86.50	85.60	90.00
7	78.40	89.90	83.70	89.30
8	85.30	86.70	84.90	90.10
9	87.10	87.90	87.80	86.90

10	82.40	86.30	85.40	88.60

Table 4.52. Correlation among air quality parameters and traffic volume (Cool and Dry season)

Parameter	CO	H_2S	NO_2	SO_2	FL	NH_3	Temperature	Sound Level	Traffic
CO	1.000								
H_2S	0.214*	1.000							
NO_2	0.080	0.304**	1.000						
SO_2	0.192*	-0.048	0.004	1.000					
FL	-0.042	-0.220*	-0.083	-0.056	1.000				
NH_3	-0.104	-0.002	0.148	0.051	-.029	1.000			
Temperature	0.110	-0.698*	-0.625	.a	.a	.a	1.000		
Sound Level	-0.696*	0.082	0.293	.a	.a	.a	-0.589	1.000	
Traffic	0.270	0.050	0.370	.a	.a	.a	-0.052	-0.401	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

a. Cannot be computed because at least one of the variables is constant.

Table 4.53. Correlation among air quality parameters and traffic volume (Hot and Dry Season)

Parameter	CO	H_2S	NO_2	SO_2	FL	NH_3	Temperature	Sound Level	Traffic

CO	1.000								
H_2S	0.594**	1.000							
NO_2	0.451**	0.262**	1.000						
SO_2	0.637**	0.486**	0.295**	1.000					
FL	.[a]	.[a]	.[a]	.[a]	.[a]				
NH_3	-0.035	-0.033	0.078	0.103	.[a]	1.000			
Temperature	-0.142	-0.217	-0.586	.[a]	.[a]	.[a]	1.000		
Sound Level	-0.537	-0.163	0.408	.[a]	.[a]	.[a]	-0.295	1.000	
Traffic	-0.526	-0.158	0.329	.[a]	.[a]	.[a]	0.124	-0.195	1.000

***. Correlation is significant at the 0.01 level (2-tailed).*

a. Cannot be computed because at least one of the variables is constant.

Table 4.54. Correlation among air quality parameters and traffic volume (Warm and Wet Season)

Parameter	CO	H_2S	NO_2	SO_2	FL	NH_3	Temperature	Sound Level	Traffic
CO	1.000								
H_2S	0.594**	1.000							
NO_2	0.400**	0.028	1.000						
SO_2	0.491**	0.176	0.618**	1.000					
FL	-0.055	-0.025	0.146	0.312**	1.000				
NH_3	0.473**	0.422**	-0.032	0.060	-0.197*	1.000			

Temperature	-0.155	0.129	-0.004	.[a]	0.042	.[a]	1.000		
Sound Level	-0.256	-0.437	0.461	.[a]	-0.274	.[a]	-0.018	1.000	
Traffic	0.068	0.017	0.123	.[a]	0.355	.[a]	0.197	-0.170	1.000

***. Correlation is significant at the 0.01 level (2-tailed).*

a. Cannot be computed because at least one of the variables is constant.

**. Correlation is significant at the 0.05 level (2-tailed).*

Table 4.55. Correlation among air quality parameters and traffic volume (Warm and Dry Season)

Parameter	CO	H_2S	NO_2	SO_2	FL	NH_3	Temperature	Sound Level	Traffic
CO	1.000								
H_2S	0.378[**]	1.000							
NO_2	0.129	0.050	1.000						
SO_2	0.338[**]	0.182[*]	0.156	1.000					
FL	0.266[**]	0.056	-0.095	-0.017	1.000				
NH_3	-0.008	0.206[*]	-0.035	0.031	0.035	1.000			
Temperature	-0.260	-0.498	-0.407	-0.148	.[a]	.[a]	1.000		
Sound Level	-0.533	-0.812[**]	-0.639[*]	-0.322	.[a]	.[a]	0.615	1.000	
Traffic	0.155	0.428	0.397	0.502	.[a]	.[a]	0.104	-0.086	1.000

***. Correlation is significant at the 0.01 level (2-tailed).*

**. Correlation is significant at the 0.05 level (2-tailed).*

a. Cannot be computed because at least one of the variables is constant.

found between CO: H_2S, SO_2 and FL, and significant correlation ($p < 0.05$) between H_2S: SO_2 and NH_3.

According to Sharma *et al*. (2009), the significant positive correlation indicates that the emission sources are somewhat similar. However, from the correlation tables, if the changes in the emission and temperature were considered in parallel, it could be argued that the considerable variation in the pollution levels observed for all pollutants were mainly due to changes in the emission patterns and not in temperature. Mild relationship between traffic and gaseous pollutants could be due to the fact that vehicles produced after 1989 were all equipped with a catalyst which emit 8 to 12 times less CO and 3 to 6 times less NO_2, depending on the catalyst type used in (Samaras *et al*., 1997) comparison to the conventional technology vehicles (Kalabokas *et al*., 1999). Also, coupled with this is possibility of emission generated through stationary source of the pollutants e. g. generating set running on either diesel or petrol due to consistent power outage. This could be the basic reason why the increase in traffic volume is not associated with a corresponding increase in atmospheric levels of the studied pollutants.

4.9.2 Discussion

From the results obtained, the concentrations of pollutants were maximal in the afternoon and minimal during the morning period. This was similar to report by Ragini *et al*. (2009), where higher concentrations of SO_2 and NO_2 were maximal in the afternoon and minimal during the morning period. However, the variations of these parameters may be attributed to the dynamics of the atmospheric boundary layer and associated convective turbulence which extensively mixed and redistributed pollutants to a greater vertical extent. After the sunset, mixed layer deforms and with advancing night, the boundary layer becomes increasingly stratified finally forming a nocturnal inversion and a shallow stable boundary layer near the surface and residual layer aloft. With night proceeding, the nocturnal inversion gains height and inhibits vertical transport of aerosols and gases (Coyle *et al*., 2002).

As observed from the bar graph (Fig. 4.49), except at Sites 5 and 6, in Warm and Wet Season, highest concentrations of CO was recorded in Warm and Dry Season at all Sites, with the highest at Site 9. This could be attributed to seasonal change and sources of pollution at these sites which could be stationary sources and burning of refuse especially at Site 9. The atmospheric CO along the corridors of the roads when compared with values reported in literature was found to be higher than 1.6 – 3.8ppm, an average range of atmospheric concentration of urban air pollutants in Anthens, Greece (Kalabokas *et al*., 1999). Also, the values reported in this study were higher than range of 0.7 – 1.9ppm in Jahara, Kuwait (Ettouney *et al*., 2010). However, the values in this study were lower than range of 233 – 317ppm reported in three cities of Nigeria: Lagos, Ibadan and Ado - Ekiti (Koku and Osuntogun, 2007). Comparing the values of CO at the ten sites, the highest value was seen at Site 5 due to traffic congestion, since this site is located at a local market serving as last bus-stop for most intra-city buses and taxes, and the road leads to Kantin Kwari (an International Market) thereby experiencing flux of traffic especially during the afternoon-evening hours.

In terms of air quality index (AQI), the CO variation across the seasons revealed that in Cool and Dry, and Hot and Dry Seasons, air quality was moderate at all sites except at Sites 4, 5 and 8. Also, in Warm and Wet and Warm and Dry Seasons, air quality at Sites 2, 3 and 6 was moderate while other sites were poor. Generally, conditions of the air

quality during afternoon – evening hours indicates poor air quality. This suggests that residences along these sites were exposed to CO, that reduces the oxygen carrying capacity of blood, which in turn impairs oxygen release into tissue and adversely affects sensitive organs such as the brain and heart (Bascom *et al*., 1996). CO results from incomplete combustion of diesel or gasoline in traffic engines, non-transportation fuel combustion, bush burning and some indoor sources such as leaking gas stove (Han and Naeher, 2006).

Similarly, across the seasons H_2S was found to be highest at Sites 1, 2, 3 and 4 during Cool and Dry Season, Site 5 in Warm and Wet Season, Site 6 in Warm and Dry Season and Sites 7, 8, 9 an10 in Hot and Dry Season. Seasonal and source variation could be responsible for variations in the sites. H_2S is emitted during combustion of coal and gases emitted during the decay of organic matter. This could be the source of bad odour at this sites as observed during sampling. Also, decay of food stuff, waste and refuse generated within these sites left for a long time could be responsible for high H_2S emission. The H_2S level in this study is higher than the range 0.167 – 0.265 ppm reported for Abeokuta Metropolis, Nigeria (Oguntoke and Yusuf, 2008).

Highest levels of NO_2 were obtained at all sites during Warm and Wet Season except at Site 5 with highest level during Warm and Dry Season. This is an indication that at Site 5, there was an increase in emission due to automobile. This corroborate with high correlation coefficient (0.397) between traffic and NO_2 in Warm and Dry Season. Also, when the levels of NO_2 were compared with values reported in literature, seasonal mean of NO_2were found lower than 35 – 108ppm reported in Anthens, Greece (Kalabokas *et al*., 1999), and fall within 0.20 – 0.521ppm reported for Calabar Metropolis, Nigeria (Okafor *et al*., 2009) but quite high when compared with the limits set by FEPA (1991) for NO_2 which is 0.06ppm. Also, in comparison with AQI at all studied sites, AQI is very poor. This is most likely due to high traffic density and stationary fuel combustion process emissions from running of generators (Etiuma *et al*., 2006) which is very common within the metropolis due to erratic power supply. Generally, from the results of NO_2, it can be deduced that the distribution pattern of NO_2 showed an increase during Warm and Wet Season across the sites, which could be due to air/wind velocity during this period.

Across all the sites, highest levels of SO_2 were recorded in Warm and Dry Season with exception at Site 2. High positive correlation (0.502) between traffic volume and SO_2 during this season could be responsible. Furthermore, the concentration of SO_2 is lower than ranges of 3.21 – 5.18ppm, 7.4 – 15.5ppm, and 16 – 64ppm reported by Ayodele and Abubakar (2010), Ettouney *et al*. (2010), and Kalabokas *et al*. (1999), respectively. At some sites the emission values were within 0.14ppm (average of 24hrs) limit of USEPA (2001) ambient air quality standards, while at Sites 4 and 10, SO_2 was above the USEPA limit. The reasons for high value at Sites 4 and 10 may be attributed to the several processes such as refuse dumpsite located along these sites. Comparing data with AQI levels, the air quality for SO_2 was in the range of moderate to very poor at Sites 3 – 10, while at Sites 1 and 2, AQI for SO_2 was in the range of very good to good.

The average seasonal value of NH_3 in the atmosphere at the sites ranged between 0.00 – 0.92ppm. This range is lower than 0.861 – 4.300 reported for Calabar metropolis, Nigeria (Okafor *et al*., 2009). NH_3 sources in the atmosphere are animal waste, ammonification of humus, followed by emissions from soils, loss of NH_3 based fertilizer from soil and industrial emission (Okafor *et al*., 2009). Low concentrations of NH_3 from this study may be due to unavailability of some of these sources. Similar to NH_3, Flame

gases (FL) are relatively very low at the sites, which could indicate fewer hazards due to this pollutant.

CHAPTER FIVE
CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The results from the study generally revealed the presence of metals in roadside soils of Kano metropolis with possible source as activities carried out along and on the roads. The heavy metal concentration of roadside samples from Kano Metropolis varied to a great extent with the sampling sites and metal type. The concentration of different metals studied was in the following decreasing order across the seasons: Zn > Pb > Ni > Cu > Cr > Cd. Metal contamination in the roadside soils in the study area was higher compared to the control area for all metals investigated. This indicates that activities along the roads deposit metals along the side soils. The dependence of metal concentrations on traffic volume showed that correlation were found to be generally poor for all the metals except for CdB, CrB and CuB (during Cool and Dry Season), and Pb. This may be due to the fact that other sources such as waste disposal could be responsible for soil heavy metal burden. Ecological risk study showed that Zn followed by Cd then Pb tend to pose potential risk in that order.

On average the percentage of heavy metals retained by each fraction in the roadside soil and dust was different according to metal type. The metals Cr, Ni and Zn were retained predominantly by the residual fraction, while Cd was highest in the Fe-Mn oxide fraction, Pb in the carbonate bound fraction, and Cu in the organic fraction. It was also found that concentrations in the water soluble and exchangeable fractions were generally low for most of the studied sites. Considering the proportion of metals bound to the water soluble, exchangeable and the carbonate bound fractions, the comparative mobility of metals was in the order: Ni > Cd > Pb > Cr > Cu > Zn. Highest MF for all studied metals was obtained in 150µm samples with exception of Ni, Pb and Cu where highest percentage MF was obtained in 1400µm samples and 355µm for Zn. As potential changes of redox state and pH may remobilize the metals bound to carbonate, Fe-Mn oxide and organic matter, and may release and flush them through drain networks into streams (Lee *et al*., 2005). This could indicate other sources than fine particulate emission from vehicles responsible. With regards toxicity, it appears that Cd, Cr, Ni, Pb and Cu pollution along the roadside are of concern.

The results showed that traffic emissions in Kano metropolis include pollutants like CO, H_2S, NO_2 and SO_2 as well as traces of FL and NH_3. The concentrations of the CO, H_2S, NO_2 and SO_2 observed with few exceptions at some sites were above the AQI stipulated by USEPA especially during the afternoon periods. This implies that traffic emission within Kano metropolis is not within the safe limits. Hence, the results revealed that transport-related pollution in Kano metropolis is significant with possibly severe health consequences. Also, the presence of another striking feature in average concentration of pollutants at all the sites across the seasons was noted. One can clearly discern a decrease in concentration during Hot and Dry Season. In most of the sites, decrease in concentration of pollutants decreases during this season.

In general, this study revealed pollutants such as metals in soils and dust, and gaseous pollutants in air that directly or indirectly threaten the environment and life of inhabitants of Kano metropolis, and that vehicular emission and other activities carried out along the roads remains the dominant sources of these pollutants.

5.2 RECOMMENDATIONS

Improvement to the study would be to consider more elaborate traffic flow and queuing, to include meteorological factors such wind factors and to study the relation of tailpipe emissions to air pollution especially due to primary pollutants (CO, NO_2, and SO_2) and metals.

These suggestions and suggestive enhancements required better understanding of traffic behaviour, emission trend and dispersion process. This is to help the city planners to plan the residential colonies, so as to cause minimum exposure to the residents.

(i) To facilitate this, as developing country, it is wise to carefully plan infrastructural investment plans and to adopt increasingly severe rules for vehicles movement, traffic management and traffic air – soil – water quality assessment.

(ii) Also, to facilitate these actions, it is urgent that data that are relevant to cities within the country be developed.

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Appendix I

Mean Cd levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (cool and dry season)

Fraction	SITE										
	1	2	3	4	5	6	7	8	9	10	Control
I[a]	0.01	ND	ND	ND	0.70	0.70	0.50	1.40	0.50	0.50	0.00
I[b]	ND	0.60	ND	ND	1.30	0.90	0.90	1.20	1.20	0.90	0.01
I[c]	0.02	0.80	ND	0.10	2.00	1.50	0.90	1.82	1.20	1.20	0.02
II[a]	ND	ND	0.01	ND	0.70	0.10	0.75	0.80	0.60	0.50	0.00
II[b]	ND	ND	0.10	0.10	1.20	0.50	2.00	0.90	1.00	1.20	0.00
II[c]	ND	ND	0.10	1.92	1.40	1.50	2.20	2.10	1.00	1.85	0.00
III[a]	0.20	0.01	0.60	1.20	1.30	0.10	0.90	0.10	0.83	1.10	0.01
III[b]	0.70	0.90	0.60	2.50	1.50	0.10	0.90	0.50	0.90	0.90	0.01
III[c]	1.32	0.80	0.71	2.50	1.50	1.20	1.50	0.90	1.75	1.50	0.02
IV[a]	0.52	0.60	0.50	1.12	0.50	0.00	0.10	1.90	0.75	0.50	0.02
IV[b]	0.86	0.70	0.80	2.00	0.50	0.10	0.10	1.90	0.80	0.50	0.02
IV[c]	0.90	0.75	0.80	2.00	1.20	0.10	0.10	1.95	1.25	0.75	0.03
V[a]	ND	0.52	0.10	1.00	0.10	0.90	0.01	1.40	0.50	0.70	0.01
V[b]	0.30	0.70	0.50	1.50	0.50	1.40	0.01	1.62	0.50	1.80	0.01
V[c]	0.40	0.75	0.50	1.70	0.60	1.40	0.10	1.75	0.80	3.50	0.01
VI[a]	0.40	0.10	ND	ND	0.10	0.50	0.75	1.50	0.10	1.05	0.02
VI[b]	0.90	1.20	ND	0.70	1.10	0.50	0.75	2.00	0.10	1.00	0.02
VI[c]	1.10	1.40	ND	0.70	1.10	1.50	0.50	2.50	0.60	1.05	0.03

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix II

Mean Cd levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (hot and dry season)

Fraction	SITE										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	0.01	ND	ND	ND	0.72	0.72	0.60	1.59	0.75	0.75	ND
I^b	ND	0.69	ND	ND	1.59	1.03	1.03	1.38	1.38	1.19	0.02
I^c	0.01	1.09	ND	0.07	2.45	1.93	0.98	2.34	1.68	1.61	0.03
II^a	ND	0.15	0.01	ND	0.86	0.06	0.74	0.91	0.65	0.59	0.04
II^b	ND	ND	0.06	0.06	1.34	0.61	2.29	1.01	1.22	1.34	0.05
II^c	ND	ND	0.07	2.48	1.79	1.69	2.50	2.13	1.37	2.36	0.07
III^a	0.12	0.01	0.79	1.43	1.49	0.06	0.97	0.06	0.92	1.23	0.01
III^b	0.89	1.01	0.83	2.92	1.69	0.06	0.86	0.46	1.01	1.01	0.01
III^c	1.75	1.05	0.82	3.06	2.21	1.50	1.70	1.65	2.23	1.84	0.02
IV^a	0.76	0.80	0.60	1.71	0.60	0.00	0.21	2.17	0.74	0.74	0.01
IV^b	0.83	0.73	1.10	1.98	0.76	0.06	0.06	2.23	0.79	0.76	0.02
IV^c	1.13	0.86	1.23	2.06	1.34	0.07	0.07	2.43	1.58	0.89	0.03
V^a	ND	0.89	0.06	1.02	0.06	1.11	0.01	1.70	0.59	0.70	0.01
V^b	0.48	0.72	0.30	1.35	0.30	1.29	0.01	1.87	0.90	2.13	0.01
V^c	0.59	0.81	0.65	1.92	0.88	1.56	0.07	2.16	0.85	4.26	0.01
VI^a	0.54	0.06	ND	ND	0.06	0.60	0.75	1.65	0.06	1.38	0.02
VI^b	1.03	1.22	0.16	0.44	1.16	0.63	0.94	2.50	0.53	1.41	0.02
VI^c	1.30	1.68	ND	1.02	1.82	2.10	1.05	3.15	0.84	1.80	0.03

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix III

Mean Cd levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (warm and wet season)

Fraction	SITE										
	1	2	3	4	5	6	7	8	9	10	Control
I[a]	0.01	ND	ND	ND	0.63	0.63	0.45	1.26	0.45	0.45	ND
I[b]	ND	0.54	ND	ND	1.17	0.81	0.81	1.08	1.08	0.81	0.01
I[c]	0.02	0.72	ND	0.09	1.80	1.35	0.81	1.64	1.08	1.08	0.02
II[a]	ND	ND	0.01	ND	0.63	0.09	0.68	0.72	0.54	0.45	ND
II[b]	ND	ND	0.09	0.09	1.08	0.45	1.80	0.81	0.90	1.08	0.01
II[c]	ND	ND	0.09	1.73	1.26	1.35	1.98	1.89	0.90	1.67	0.01
III[a]	0.15	0.01	0.45	0.90	0.98	0.08	0.68	0.08	0.62	0.83	ND
III[b]	0.53	0.68	0.45	1.88	1.13	0.08	0.68	0.38	0.68	0.68	0.10
III[c]	0.99	0.60	0.53	1.88	1.13	0.90	1.13	0.68	1.31	1.13	0.16
IV[a]	0.39	0.45	0.38	0.84	0.38	ND	0.08	1.43	0.56	0.38	ND
IV[b]	0.65	0.53	0.60	1.50	0.38	0.08	0.08	1.43	0.60	0.38	0.10
IV[c]	0.68	0.56	0.60	1.50	0.90	0.08	0.08	1.46	0.94	0.56	0.16
V[a]	ND	0.43	0.08	0.82	0.08	0.74	0.01	1.15	0.41	0.57	0.10
V[b]	0.25	0.57	0.41	1.23	0.41	1.15	0.01	1.33	0.41	1.48	0.10
V[c]	0.33	0.62	0.41	1.39	0.49	1.15	0.08	1.44	0.66	2.87	0.14
VI[a]	0.33	0.08	ND	ND	0.08	0.41	0.62	1.23	0.08	0.86	0.10
VI[b]	0.74	0.98	ND	0.57	0.90	0.41	0.62	1.64	0.08	0.82	0.20
VI[c]	0.90	1.15	ND	0.57	0.90	1.23	0.41	2.05	0.49	0.86	0.33

[a, b, c] **Grain size 1400µm, 355µm and 150µm respectively.**

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix IV

Mean Cd levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (warm and dry season)

Fraction	SITE										
	1	2	3	4	5	6	7	8	9	10	Control
I[a]	ND	ND	ND	ND	0.50	0.50	0.50	1.25	0.75	0.75	0.00
I[b]	ND	0.50	ND	ND	1.25	0.75	0.75	1.00	1.00	1.00	0.01
I[c]	ND	0.75	ND	ND	1.50	1.25	0.50	1.53	1.20	1.10	0.02
II[a]	ND	0.25	ND	ND	0.75	ND	0.50	0.75	0.50	0.50	0.04
II[b]	ND	ND	ND	ND	1.00	0.50	1.75	0.75	1.00	1.00	0.40
II[c]	ND	ND	ND	1.75	1.25	1.00	1.50	1.05	1.03	1.65	0.56
III[a]	ND	ND	0.75	1.25	1.25	ND	0.75	ND	0.75	1.00	0.01
III[b]	0.75	0.75	0.75	2.25	1.25	ND	0.50	0.25	0.75	0.75	0.05
III[c]	1.25	0.75	0.50	2.00	1.75	1.00	1.00	1.53	1.53	1.20	0.08
IV[a]	0.75	0.75	0.50	1.75	0.50	ND	0.25	1.75	0.50	0.75	0.01
IV[b]	0.50	0.50	1.00	1.25	0.75	ND	ND	1.75	0.50	0.75	0.04
IV[c]	0.75	0.50	1.00	1.00	0.75	ND	ND	1.60	1.05	0.55	0.06
V[a]	ND	1.00	ND	0.75	ND	1.00	ND	1.50	0.50	0.50	0.18
V[b]	0.50	0.50	0.00	0.75	ND	0.75	ND	1.50	1.00	1.75	0.31
V[c]	0.50	0.50	0.50	1.25	0.75	1.00	ND	1.58	0.50	3.05	0.43
VI[a]	0.50	ND	ND	ND	ND	0.50	0.50	1.25	ND	1.25	0.15
VI[b]	0.75	0.75	0.25	ND	0.75	0.50	0.75	2.00	0.75	1.25	0.10
VI[c]	0.75	1.00	0.00	0.75	1.50	1.50	1.00	2.00	0.60	1.53	0.17

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix V

Mean Cr levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (cool and dry season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I[a]	ND	0.10	0.30	0.10	1.32	0.11	ND	ND	ND	ND	ND
I[b]	ND	0.10	0.50	0.56	3.12	0.10	1.00	ND	ND	0.51	ND
I[c]	ND	0.40	6.33	1.21	4.01	0.10	1.10	ND	0.56	0.40	ND
II[a]	ND	0.10	ND	0.21	0.26	1.61	1.10	ND	0.20	ND	ND
II[b]	ND	0.40	ND	1.11	1.12	0.00	1.10	1.20	0.20	0.90	ND
II[c]	1.10	0.60	0.14	1.00	7.16	0.62	1.10	4.22	0.40	0.90	ND
III[a]	1.10	ND	ND	ND	1.00	4.10	ND	5.61	ND	5.21	ND
III[b]	6.20	0.10	ND	1.21	1.00	6.21	ND	5.90	ND	7.15	ND
III[c]	7.32	0.10	0.26	2.12	1.62	6.50	1.21	7.29	0.60	10.62	ND
IV[a]	ND	20.90	0.10	6.21	0.13	6.21	1.50	5.10	1.21	5.98	ND
IV[b]	ND	21.40	0.10	6.48	0.17	6.50	8.10	6.00	1.01	6.56	ND
IV[c]	ND	4.50	0.10	7.56	2.10	6.50	5.60	6.56	1.01	8.06	ND
V[a]	ND	1.00	0.52	4.61	2.00	2.30	4.10	4.10	2.56	5.60	ND
V[b]	ND	1.20	5.54	5.00	2.00	5.21	7.20	5.06	5.61	6.00	ND
V[c]	ND	1.50	5.54	5.10	2.10	5.32	7.61	15.78	6.50	6.00	ND
VI[a]	1.40	0.50	12.10	2.14	6.21	4.11	5.00	6.56	30.30	6.08	ND
VI[b]	10.10	0.90	10.15	12.10	7.01	4.62	6.10	10.45	21.21	6.10	ND
VI[c]	10.10	32.43	13.10	12.21	7.56	7.11	6.78	69.41	90.14	9.54	ND

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix VI

Mean Cr levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (hot and dry season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	ND	0.06	0.18	0.06	0.79	0.07	ND	ND	ND	ND	ND
I^b	ND	0.06	0.31	0.35	3.51	0.06	0.63	ND	ND	0.32	ND
I^c	ND	0.28	8.28	4.35	6.66	0.07	0.77	ND	0.39	0.28	ND
II^a	ND	0.06	ND	0.12	0.15	0.95	0.65	ND	0.12	ND	ND
II^b	ND	0.24	ND	0.68	0.68	ND	0.67	0.73	0.12	0.55	ND
II^c	0.74	0.78	0.09	0.68	9.05	0.42	0.74	2.85	0.27	0.61	ND
III^a	0.64	ND	ND	ND	0.59	5.76	ND	6.35	ND	6.56	ND
III^b	7.04	0.06	ND	0.74	0.62	7.05	ND	7.32	ND	7.78	ND
III^c	8.55	0.07	0.18	5.01	1.10	8.16	0.82	12.61	0.41	11.81	ND
IV^a	ND	24.63	0.06	3.69	0.08	6.97	0.89	3.03	0.72	3.56	ND
IV^b	ND	25.41	0.06	7.00	0.10	7.78	9.21	3.66	0.62	4.00	0.01
IV^c	ND	4.47	0.07	8.95	5.38	6.17	7.43	4.49	0.69	5.52	0.02
V^a	ND	0.91	0.63	6.35	1.17	1.35	11.32	5.47	4.72	6.64	ND
V^b	ND	1.04	6.62	6.45	1.20	6.28	7.47	6.04	7.12	7.53	ND
V^c	ND	1.32	10.26	7.38	1.37	5.08	11.93	20.98	7.64	9.56	ND
VI^a	1.82	0.62	13.71	1.28	6.73	5.92	6.15	7.09	36.33	6.80	ND
VI^b	13.03	2.14	12.75	13.97	7.83	6.33	7.25	13.25	23.26	7.88	ND
VI^c	14.25	45.98	38.75	16.95	9.84	9.35	8.95	95.84	119.97	11.35	ND

$^{a, b, c}$ Grain size 1400µm, 355µm and 150µm respectively.

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix VII

Mean Cr levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (warm and wet season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I[a]	ND	0.09	0.27	0.09	1.19	0.10	ND	ND	ND	ND	ND
I[b]	ND	0.09	0.45	0.50	2.81	0.09	0.90	ND	ND	0.46	ND
I[c]	ND	0.36	5.70	1.09	3.61	0.09	0.99	ND	0.50	0.36	ND
II[a]	ND	0.09	ND	0.19	0.23	1.45	0.99	ND	0.18	ND	ND
II[b]	ND	0.36	ND	1.00	1.01	0.00	0.99	1.08	0.18	0.81	ND
II[c]	0.99	0.54	0.13	0.90	6.44	0.56	0.99	3.80	0.36	0.81	ND
III[a]	0.83	ND	ND	0.00	0.75	3.08	ND	4.21	ND	3.91	ND
III[b]	4.65	0.08	ND	0.91	0.75	4.66	ND	4.43	ND	5.36	ND
III[c]	5.49	0.08	0.20	1.59	1.22	4.88	0.91	5.47	0.45	7.97	ND
IV[a]	0.00	15.68	0.08	4.66	0.10	4.66	1.13	3.83	0.91	4.49	ND
IV[b]	ND	16.05	0.08	4.86	0.13	4.88	6.08	4.50	0.76	4.92	ND
IV[c]	ND	3.38	0.08	5.67	1.58	4.88	4.20	4.92	0.76	6.05	ND
V[a]	ND	0.82	0.43	3.78	1.64	1.89	3.36	3.36	2.10	4.59	ND
V[b]	ND	0.98	4.54	4.10	1.64	4.27	5.90	4.15	4.60	4.92	ND
V[c]	ND	1.23	4.54	4.18	1.72	4.36	6.24	12.94	5.33	4.92	ND
VI[a]	1.15	0.41	9.92	1.75	5.09	3.37	4.10	5.38	24.85	4.99	ND
VI[b]	8.28	0.74	8.32	9.92	5.75	3.79	5.00	8.57	17.39	5.00	ND
VI[c]	8.28	26.59	10.74	10.01	6.20	5.83	5.56	56.92	73.91	7.82	ND

[a, b, c] **Grain size 1400µm, 355µm and 150µm respectively.**

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix VIII

Mean Cr levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (warm and dry season)

Fraction	SITE										
	1	2	3	4	5	6	7	8	9	10	Control
I[a]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
I[b]	ND	ND	ND	ND	2.50	ND	ND	ND	ND	ND	ND
I[c]	ND	ND	5.50	5.00	5.50	ND	ND	ND	ND	ND	ND
II[a]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
II[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
II[c]	ND	0.55	ND	ND	6.25	ND	ND	ND	ND	ND	ND
III[a]	ND	ND	ND	ND	ND	5.75	ND	5.25	ND	6.00	ND
III[b]	5.25	ND	ND	ND	ND	5.25	ND	6.00	ND	5.50	ND
III[c]	5.25	ND	ND	5.25	ND	5.50	ND	11.25	ND	6.75	ND
IV[a]	ND	20.50	ND	ND	ND	5.50	ND	ND	ND	ND	ND
IV[b]	ND	20.25	ND	5.00	ND	6.25	7.00	ND	ND	ND	ND
IV[c]	ND	2.03	ND	5.50	5.75	2.50	5.25	ND	ND	ND	ND
V[a]	ND	0.55	0.55	6.25	ND	ND	15.25	5.25	5.50	5.75	ND
V[b]	ND	0.53	5.50	5.75	ND	5.25	5.25	5.00	6.25	6.55	ND
V[c]	ND	0.53	10.25	6.25	ND	2.50	10.75	16.50	5.25	8.70	ND
VI[a]	1.63	0.53	10.75	ND	5.00	5.75	5.25	5.25	30.25	5.25	ND
VI[b]	10.75	2.53	10.25	10.25	5.53	5.50	5.50	10.75	16.00	6.50	ND
VI[c]	10.25	33.25	42.25	12.00	6.50	6.25	6.00	67.50	81.25	6.68	ND

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix IX

Mean Ni levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (cool and dry season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I[a]	5.23	0.90	6.12	7.25	5.00	1.90	7.00	5.50	1.21	40.20	ND
I[b]	53.10	2.61	6.26	7.50	6.14	6.00	4.12	36.10	10.50	8.40	ND
I[c]	53.60	10.50	10.98	10.50	5.50	6.00	58.12	36.00	10.80	8.40	ND
II[a]	53.00	1.12	1.20	6.21	4.14	5.10	1.40	4.21	7.21	5.00	ND
II[b]	55.00	2.00	5.20	7.50	5.00	5.25	5.00	3.00	8.00	5.25	ND
II[c]	55.60	6.21	11.00	7.50	5.50	6.50	36.10	35.50	10.75	5.25	ND
III[a]	56.20	5.80	5.76	2.52	5.50	5.00	10.10	5.50	10.00	5.00	ND
III[b]	56.20	6.00	10.80	5.50	5.50	5.00	28.20	11.00	7.15	5.50	ND
III[c]	56.20	6.00	11.20	11.00	10.90	5.00	51.20	30.15	50.15	12.15	ND
IV[a]	6.20	10.21	5.50	10.15	6.00	6.10	6.00	10.15	15.21	7.80	ND
IV[b]	6.50	17.00	5.85	10.50	10.00	10.00	6.10	50.40	15.21	12.40	ND
IV[c]	60.15	20.10	6.10	10.50	10.50	10.50	6.10	50.60	56.15	10.00	ND
V[a]	56.00	4.21	10.50	6.21	1.21	ND	7.90	0.50	ND	3.10	ND
V[b]	56.00	4.50	10.50	5.20	5.46	ND	20.10	10.00	ND	10.00	ND
V[c]	56.10	4.90	11.00	8.00	10.50	5.25	38.40	30.15	1.21	45.00	ND
VI[a]	48.15	5.10	6.50	2.61	10.10	10.10	10.20	20.10	4.15	10.00	ND
VI[b]	52.95	5.21	8.20	3.00	15.20	15.20	30.00	40.15	2.10	10.50	ND
VI[c]	50.10	5.21	10.50	3.22	22.50	15.20	30.61	45.60	6.40	12.00	ND

[a, b, c] **Grain size 1400µm, 355µm and 150µm respectively.**

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO

V Bound to Organic Matter
VI Residual Fraction

Appendix X

Mean Ni levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (hot and dry season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	6.44	0.54	7.12	7.95	6.15	1.14	7.35	6.60	0.73	48.27	ND
I^b	66.00	1.63	7.19	8.28	7.28	7.19	2.58	44.59	12.97	9.63	ND
I^c	74.27	14.53	15.04	14.53	7.53	8.05	79.53	49.88	14.74	9.56	ND
II^a	62.54	0.66	0.71	6.91	2.44	3.01	0.83	2.48	7.50	2.95	ND
II^b	67.10	1.22	6.37	7.93	3.05	6.41	6.41	1.83	8.54	3.20	ND
II^c	74.99	7.74	14.68	8.61	7.26	8.27	48.16	47.76	10.97	3.54	ND
III^a	65.20	6.61	6.73	1.47	6.44	4.53	14.83	6.29	12.14	6.00	ND
III^b	68.85	6.92	12.95	6.77	9.69	6.30	39.18	13.07	4.40	6.77	ND
III^c	75.96	7.82	14.59	14.62	14.38	10.71	65.59	41.07	70.14	15.40	ND
IV^a	7.26	15.15	6.40	12.44	9.67	6.75	6.84	12.14	15.15	7.91	ND
IV^b	7.32	19.83	6.77	12.66	12.51	12.35	6.92	55.30	18.73	13.82	ND
IV^c	80.76	27.64	7.95	14.21	17.64	14.21	18.22	65.66	76.48	13.87	ND
V^a	65.52	5.83	12.14	7.29	4.07	0.00	8.13	0.29	0.00	5.03	ND
V^b	65.10	5.85	12.45	4.62	6.43	3.15	24.21	12.30	0.00	12.30	ND
V^c	72.54	6.60	17.06	8.78	13.49	10.08	47.87	42.51	0.79	58.66	ND
VI^a	56.34	6.36	7.50	1.57	9.36	18.21	12.27	27.21	5.64	12.45	ND
VI^b	66.06	6.85	8.41	3.44	22.16	22.16	37.66	44.00	4.44	13.28	ND
VI^c	72.35	7.50	11.03	5.93	30.10	28.32	49.60	56.42	11.66	19.25	ND

$^{a, b, c}$ Grain size 1400µm, 355µm and 150µm respectively.
I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO

V Bound to Organic Matter
VI Residual Fraction

Appendix XI

Mean Ni levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (warm and wet season)

Fraction	Site										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**Control**
I[a]	4.71	0.81	5.51	6.53	4.50	1.71	6.30	4.95	1.09	36.18	ND
I[b]	47.79	2.35	5.63	6.75	5.53	5.40	3.71	32.49	9.45	7.56	ND
I[c]	48.24	9.45	9.88	9.45	4.95	5.40	52.31	32.40	9.72	7.56	ND
II[a]	47.70	1.01	1.08	5.59	3.73	4.59	1.26	3.79	6.49	4.50	ND
II[b]	49.50	1.80	4.68	6.75	4.50	4.73	4.50	2.70	7.20	4.73	ND
II[c]	50.04	5.59	9.90	6.75	4.95	5.85	32.49	31.95	9.68	4.73	ND
III[a]	42.15	4.35	4.32	1.89	4.13	3.75	7.58	4.13	7.50	3.75	ND
III[b]	42.15	4.50	8.10	4.13	4.13	3.75	21.15	8.25	5.36	4.13	ND
III[c]	42.15	4.50	8.40	8.25	8.18	3.75	38.40	22.61	37.61	9.11	ND
IV[a]	4.65	7.66	4.13	7.61	4.50	4.58	4.50	7.61	11.41	5.85	ND
IV[b]	4.88	12.75	4.39	7.88	7.50	7.50	4.58	37.80	11.41	9.30	ND
IV[c]	45.11	15.08	4.58	7.88	7.88	7.88	4.58	37.95	42.11	7.50	ND
V[a]	45.92	3.45	8.61	5.09	0.99	ND	6.48	0.41	ND	2.54	ND
V[b]	45.92	3.69	8.61	4.26	4.48	ND	16.48	8.20	ND	8.20	ND
V[c]	46.00	4.02	9.02	6.56	8.61	4.31	31.49	24.72	0.99	36.90	ND
VI[a]	39.48	4.18	5.33	2.14	8.28	8.28	8.36	16.48	3.40	8.20	ND
VI[b]	43.42	4.27	6.72	2.46	12.46	12.46	24.60	32.92	1.72	8.61	ND
VI[c]	41.08	4.27	8.61	2.64	18.45	12.46	25.10	37.39	5.25	9.84	ND

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.
I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO

V Bound to Organic Matter
VI Residual Fraction

Appendix XII

Mean Ni levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (warm and dry season)

Fraction	SITE										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	5.50	ND	5.75	6.00	5.25	ND	5.25	5.50	ND	40.25	ND
I^b	52.50	ND	5.25	5.75	5.50	5.50	ND	35.25	10.25	7.00	ND
I^c	52.50	10.25	10.50	10.25	5.25	5.50	55.50	35.25	10.25	5.25	ND
II^a	53.00	ND	ND	5.50	ND	ND	ND	ND	5.50	ND	ND
II^b	55.00	ND	5.25	5.50	ND	5.25	5.50	ND	6.00	ND	ND
II^c	55.50	5.25	10.75	5.25	5.25	5.75	35.25	35.25	5.50	ND	ND
III^a	55.25	5.50	5.75	ND	5.50	2.75	15.25	5.25	10.75	5.25	ND
III^b	55.75	5.25	10.25	5.50	10.25	5.25	35.50	10.25	ND	5.50	ND
III^c	55.50	5.50	10.25	10.50	10.25	10.75	45.25	30.25	53.00	10.50	ND
IV^a	6.00	15.25	5.25	10.25	10.25	5.25	5.50	10.25	10.25	5.50	ND
IV^b	5.50	15.50	5.25	10.25	10.50	10.25	5.25	40.25	15.50	10.25	ND
IV^c	57.75	20.25	5.50	10.25	15.25	10.25	20.50	45.25	55.50	10.25	ND
V^a	56.00	5.75	10.25	6.25	5.75	ND	6.00	ND	ND	5.50	ND
V^b	52.50	5.25	10.25	2.50	5.25	5.25	20.25	10.50	ND	10.50	ND
V^c	55.50	5.25	15.25	5.50	10.25	10.25	35.25	35.25	ND	45.25	ND
VI^a	45.75	5.50	6.00	ND	5.50	20.25	10.25	25.25	5.25	10.75	ND
VI^b	52.75	5.75	5.25	2.50	20.25	20.25	30.25	30.25	5.00	10.75	ND
VI^c	53.25	5.50	5.25	5.25	20.50	25.25	40.25	35.00	10.25	15.50	ND

$^{a, b, c}$ Grain size 1400µm, 355µm and 150µm respectively.
I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter

VI Residual Fraction

Appendix XIII

Mean Pb levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (cool and dry season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	1.21	ND	0.31	1.50	10.26	ND	0.10	5.25	2.61	20.50	0.10
I^b	2.00	1.04	0.50	2.61	20.00	0.21	0.10	6.00	4.00	21.00	0.20
I^c	5.21	2.00	1.16	10.15	20.15	11.21	0.62	10.16	26.56	21.00	0.30
II^a	5.63	0.20	0.98	5.10	2.61	1.00	0.21	4.00	21.61	15.00	0.10
II^b	6.23	0.50	6.24	15.26	16.70	1.21	0.11	4.00	20.15	15.00	0.20
II^c	7.10	1.78	6.57	26.15	20.16	1.00	1.26	4.25	30.13	21.80	0.28
III^a	4.50	2.15	5.12	6.14	16.26	2.61	15.00	6.20	20.00	16.20	0.20
III^b	10.21	5.00	20.52	16.20	42.12	0.11	80.21	10.79	20.00	19.10	0.20
III^c	14.50	50.23	47.15	83.21	279.00	26.15	60.21	50.11	21.00	30.15	0.31
IV^a	3.07	0.85	20.15	0.94	5.00	10.00	20.11	20.11	6.15	21.50	5.10
IV^b	4.12	0.86	0.00	5.50	20.12	10.26	10.21	20.21	20.75	36.10	6.00
IV^c	5.50	20.15	26.13	5.50	106.15	30.15	30.12	20.89	20.77	45.00	9.60
V^a	1.20	5.70	1.22	5.00	15.16	12.14	80.55	5.20	10.15	2.10	6.00
V^b	0.90	10.20	5.60	7.71	10.11	9.90	6.00	10.11	10.22	5.00	6.00
V^c	2.00	11.10	5.67	21.56	450.61	20.00	10.22	9.50	11.56	5.00	8.40
VI^a	40.12	2.71	2.26	2.22	31.22	6.00	10.15	7.00	4.11	11.20	7.21
VI^b	38.40	4.21	20.22	5.61	6.14	6.21	11.00	5.20	5.25	10.00	7.00
VI^c	59.15	36.14	56.56	30.21	20.11	20.15	15.21	20.11	6.15	22.10	11.55

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.

I Water
II Exchangeable
III Bound to Carbonate

IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix XIV

Mean Pb levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (hot and dry season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	0.73	ND	0.19	0.90	12.31	ND	0.06	6.15	1.57	24.60	1.40
I^b	1.25	0.65	0.31	1.63	25.16	0.13	0.06	7.19	2.50	25.94	1.00
I^c	6.97	1.40	0.81	13.93	27.93	15.37	0.43	14.29	36.09	28.53	1.50
II^a	6.57	0.12	0.58	6.11	4.49	0.59	0.12	5.46	24.70	18.29	1.70
II^b	7.00	0.31	6.86	18.31	19.03	0.74	0.07	5.34	24.19	17.84	2.00
II^c	7.83	1.86	7.98	31.32	26.77	1.35	1.36	6.41	43.79	28.22	2.80
III^a	2.63	1.26	3.00	6.81	15.51	1.53	14.77	6.84	24.13	24.25	1.90
III^b	6.28	3.08	24.77	18.57	53.73	0.07	92.38	16.01	24.60	36.50	2.00
III^c	19.89	66.12	62.32	114.72	379.95	51.78	116.25	81.50	27.54	68.27	3.12
IV^a	1.83	0.83	24.04	0.56	6.40	12.20	17.92	15.39	6.78	25.29	4.42
IV^b	5.87	0.84	12.35	6.56	27.68	12.21	24.22	42.52	24.55	43.07	5.45
IV^c	6.85	30.59	34.85	7.54	142.93	37.61	48.20	55.24	27.76	58.23	8.72
V^a	0.70	6.55	0.71	6.00	14.86	12.95	53.26	6.55	11.93	1.23	4.56
V^b	0.54	12.27	3.36	7.63	18.07	11.79	6.90	27.22	12.28	5.70	5.00
V^c	1.30	13.55	3.69	27.18	572.07	26.00	16.72	31.85	16.78	6.50	7.00
VI^a	48.22	1.63	5.11	1.33	37.78	6.75	12.24	7.80	5.62	12.87	6.26
VI^b	61.97	2.63	27.95	6.63	6.81	7.01	16.25	12.94	6.09	12.03	6.50
VI^c	90.58	53.47	78.44	38.82	24.58	24.43	31.82	24.23	8.51	29.30	10.73

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.
I Water
II Exchangeable
III Bound to Carbonate

IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix XV

Mean Pb levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (warm and wet season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	1.09	ND	0.28	1.35	9.23	ND	0.09	4.73	2.35	18.45	0.10
I^b	1.80	0.94	0.45	2.35	18.00	0.19	0.09	5.40	3.60	18.90	0.20
I^c	4.69	1.80	1.04	9.14	18.14	10.09	0.56	9.14	23.90	18.90	0.30
II^a	5.07	0.18	0.88	4.59	2.35	0.90	0.19	3.60	19.45	13.50	0.00
II^b	5.61	0.45	5.62	13.73	15.03	1.09	0.10	3.60	18.14	13.50	0.10
II^c	6.39	1.60	5.91	23.54	18.14	0.90	1.13	3.83	27.12	19.62	0.14
III^a	3.38	1.61	3.84	4.61	12.20	1.96	11.25	4.65	15.00	12.15	0.00
III^b	7.66	3.75	15.39	12.15	31.59	0.08	60.16	8.09	15.00	14.33	0.10
III^c	10.88	37.67	35.36	62.41	209.25	19.61	45.16	37.58	15.75	22.61	0.16
IV^a	2.30	0.64	15.11	0.71	3.75	7.50	15.08	15.08	4.61	16.13	0.30
IV^b	3.09	0.65	0.00	4.13	15.09	7.70	7.66	15.16	15.56	27.08	0.56
IV^c	4.13	15.11	19.60	4.13	79.61	22.61	22.59	15.67	15.58	33.75	0.90
V^a	0.98	4.67	1.00	4.10	12.43	9.95	66.05	4.26	8.32	1.72	0.50
V^b	0.74	8.36	4.59	6.32	8.29	8.12	4.92	8.29	8.38	4.10	1.10
V^c	1.64	9.10	4.65	17.68	369.50	16.40	8.38	7.79	9.48	4.10	1.54
VI^a	32.90	2.22	1.85	1.82	25.60	4.92	8.32	5.74	3.37	9.18	0.50
VI^b	31.49	3.45	16.58	4.60	5.03	5.09	9.02	4.26	4.31	8.20	0.89
VI^c	48.50	29.63	46.38	24.77	16.49	16.52	12.47	16.49	5.04	18.12	1.47

$^{a, b, c}$ Grain size 1400µm, 355µm and 150µm respectively.
I Water
II Exchangeable
III Bound to Carbonate

IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix XVI

Mean Pb levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (warm and dry season)

Fraction	SITE										
	1	2	3	4	5	6	7	8	9	10	Control
I[a]	ND	ND	ND	ND	10.25	ND	ND	5.00	ND	20.50	ND
I[b]	ND	ND	ND	ND	20.25	ND	ND	5.50	ND	20.50	0.10
I[c]	4.75	ND	ND	9.75	19.75	10.75	ND	10.25	25.00	19.75	0.15
II[a]	5.50	ND	ND	5.25	5.00	ND	ND	5.25	20.25	16.00	ND
II[b]	5.25	ND	5.00	14.75	14.50	ND	ND	4.75	19.50	14.25	0.50
II[c]	4.50	0.98	5.25	20.25	19.50	1.00	0.75	5.25	34.75	20.00	0.70
III[a]	ND	ND	ND	5.50	10.25	ND	10.25	5.50	21.25	25.25	2.80
III[b]	ND	ND	19.75	14.00	45.25	ND	70.00	15.25	20.00	40.25	2.50
III[c]	14.75	47.00	44.50	85.50	279.75	50.00	110.75	69.75	19.50	70.25	3.90
IV[a]	ND	0.55	20.25	ND	5.75	10.50	10.00	5.75	5.25	21.00	5.30
IV[b]	5.50	0.53	20.25	5.25	25.25	9.75	29.50	49.50	19.50	34.50	6.00
IV[c]	4.50	24.50	24.75	5.50	102.50	24.75	40.25	59.75	19.75	40.00	9.60
V[a]	ND	5.50	ND	5.25	10.25	10.00	10.50	6.00	10.25	ND	1.70
V[b]	ND	10.25	ND	5.00	20.00	9.75	5.50	35.25	10.25	4.50	2.34
V[c]	ND	9.75	ND	20.25	429.50	20.00	15.50	39.50	14.25	5.00	3.28
VI[a]	40.25	ND	6.25	ND	31.75	5.25	10.25	6.00	5.25	10.25	9.10
VI[b]	60.75	ND	24.50	5.00	4.75	5.00	15.00	15.50	4.50	9.25	8.10
VI[c]	70.25	40.25	55.50	25.25	15.00	14.75	30.25	14.50	6.00	19.75	13.37

[a, b, c] **Grain size 1400µm, 355µm and 150µm respectively.**
I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO

V Bound to Organic Matter
VI Residual Fraction

Appendix XVII

Mean Cu levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (cool and dry season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	0.20	0.20	ND	4.00	ND	ND	0.50	0.72	0.15	0.10	ND
I^b	1.25	0.15	2.10	4.00	ND	ND	1.00	0.90	2.00	0.10	ND
I^c	3.00	5.50	2.50	4.25	5.00	9.00	4.60	1.56	2.00	0.10	ND
II^a	0.00	0.10	ND	0.56	ND	0.10	0.50	ND	0.10	0.00	ND
II^b	0.58	0.10	ND	1.00	1.25	0.10	0.50	ND	0.50	0.10	ND
II^c	3.21	0.25	1.20	3.25	3.56	2.75	0.72	0.62	0.70	0.50	ND
III^a	0.10	0.00	ND	1.00	0.50	1.50	2.00	0.15	0.00	0.10	ND
III^b	0.50	0.10	ND	1.50	0.50	1.75	5.00	0.15	0.50	0.00	ND
III^c	3.52	3.10	ND	5.00	3.15	3.12	6.88	3.00	0.50	2.00	ND
IV^a	1.50	0.25	1.50	0.50	ND	0.15	0.75	ND	4.25	1.00	ND
IV^b	5.78	0.92	1.57	2.56	0.22	ND	1.20	ND	5.00	1.00	ND
IV^c	4.21	7.10	6.00	7.00	4.00	6.25	7.00	1.00	9.10	3.50	ND
V^a	4.00	0.00	1.12	3.00	0.00	1.56	9.00	2.56	1.00	0.62	ND
V^b	1.10	0.92	7.10	15.20	0.00	2.00	10.00	15.10	6.00	1.00	ND
V^c	0.70	15.20	18.00	127.00	26.15	26.15	60.15	16.20	10.20	4.50	ND
VI^a	4.10	4.00	1.00	2.00	ND	ND	4.00	0.15	2.56	1.00	ND
VI^b	4.10	5.00	5.25	5.25	2.71	2.71	5.00	3.15	5.00	1.00	ND
VI^c	5.00	5.21	5.28	9.00	7.51	7.51	25.15	5.00	5.00	18.15	ND

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.
I Water
II Exchangeable

III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix XVIII

Mean Cu levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (hot and dry season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	0.12	0.12	ND	4.20	ND	ND	0.30	0.88	0.09	0.06	ND
I^b	0.78	0.09	2.23	5.00	ND	2.83	1.23	0.56	2.19	0.06	ND
I^c	4.20	7.70	3.52	5.78	6.30	12.08	6.37	1.44	3.17	0.07	ND
II^a	ND	0.06	ND	0.33	ND	0.06	0.30	ND	0.06	ND	ND
II^b	0.35	0.06	1.19	1.53	0.76	0.06	0.61	ND	0.31	0.06	ND
II^c	3.52	0.17	2.18	3.90	3.75	3.88	0.49	0.42	0.47	0.34	ND
III^a	0.06	ND	0.00	0.59	0.29	0.88	2.78	0.09	ND	0.06	ND
III^b	0.31	0.06	0.00	1.25	1.85	1.08	5.83	0.09	0.31	ND	ND
III^c	5.11	4.13	0.36	6.97	2.14	3.82	9.10	3.57	0.34	2.38	ND
IV^a	3.29	0.15	0.89	0.61	ND	0.09	0.77	ND	4.92	0.60	ND
IV^b	3.53	0.56	4.31	3.41	0.74	ND	1.04	3.20	6.41	0.61	ND
IV^c	6.65	9.49	7.88	9.08	3.80	8.22	9.25	8.05	12.23	4.09	ND
V^a	4.12	ND	0.95	2.94	6.29	0.91	10.22	1.50	0.59	0.36	ND
V^b	0.66	0.55	8.01	18.05	16.52	1.20	12.90	15.81	7.05	0.60	ND
V^c	0.94	21.09	23.24	165.59	31.30	35.69	74.54	20.44	13.62	5.87	ND
VI^a	4.86	4.52	1.22	2.99	ND	ND	4.22	0.39	2.74	0.60	ND
VI^b	4.91	6.09	5.78	6.09	3.27	1.69	8.28	9.94	5.78	0.95	ND
VI^c	5.60	7.85	6.85	12.43	8.42	8.41	33.53	3.50	7.35	25.13	ND

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.
I Water
II Exchangeable

III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix XIX

Mean Cu levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (warm and wet season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	0.18	0.18	ND	3.60	ND	ND	0.45	0.65	0.14	0.09	ND
I^b	1.13	0.14	1.89	3.60	ND	ND	0.90	0.81	1.80	0.09	ND
I^c	2.70	4.95	2.25	3.83	4.50	8.10	4.14	1.40	1.80	0.09	ND
II^a	ND	0.09	ND	0.50	ND	0.09	0.45	ND	0.09	ND	ND
II^b	0.52	0.09	ND	0.90	1.13	0.09	0.45	ND	0.45	0.09	ND
II^c	2.89	0.23	1.08	2.93	3.20	2.48	0.65	0.56	0.63	0.45	ND
III^a	0.08	ND	ND	0.75	0.38	1.13	1.50	0.11	ND	0.08	ND
III^b	0.38	0.08	ND	1.13	0.38	1.31	3.75	0.11	0.38	ND	ND
III^c	2.64	2.33	ND	3.75	2.36	2.34	5.16	2.25	0.38	1.50	ND
IV^a	1.13	0.19	1.13	0.38	ND	0.11	0.56	ND	3.19	0.75	ND
IV^b	4.34	0.69	1.18	1.92	0.17	ND	0.90	ND	3.75	0.75	ND
IV^c	3.16	5.33	4.50	5.25	3.00	4.69	5.25	0.75	6.83	2.63	ND
V^a	3.28	ND	0.92	2.46	ND	1.28	7.38	2.10	0.82	0.51	ND
V^b	0.90	0.75	5.82	12.46	ND	1.64	8.20	12.38	4.92	0.82	ND
V^c	0.57	12.46	14.76	104.14	21.44	21.44	49.32	13.28	8.36	3.69	ND
VI^a	3.36	3.28	0.82	1.64	ND	ND	3.28	0.12	2.10	0.82	ND
VI^b	3.36	4.10	4.31	4.31	2.22	2.22	4.10	2.58	4.10	0.82	ND
VI^c	4.10	4.27	4.33	7.38	6.16	6.16	20.62	4.10	4.10	14.88	ND

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.
I Water
II Exchangeable

III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix XX

Mean Cu levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (warm and dry season)

Fraction	SITE										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**Control**
I[a]	ND	ND	ND	3.00	ND	ND	ND	0.75	ND	ND	ND
I[b]	ND	ND	1.48	4.00	ND	4.53	0.98	ND	1.50	ND	ND
I[c]	3.00	5.50	2.53	4.00	4.00	8.25	4.50	0.50	2.53	ND	ND
II[a]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
II[b]	ND	ND	1.95	1.50	ND	ND	0.50	ND	ND	ND	ND
II[c]	2.00	ND	2.03	2.53	2.00	3.00	ND	ND	ND	ND	ND
III[a]	ND	ND	ND	ND	ND	ND	2.75	ND	ND	ND	ND
III[b]	ND	ND	ND	0.53	2.50	ND	4.48	ND	ND	ND	ND
III[c]	4.00	2.98	0.53	5.25	ND	2.50	6.50	2.25	ND	1.50	ND
IV[a]	4.03	ND	ND	0.53	ND	ND	0.55	ND	4.03	ND	ND
IV[b]	ND	ND	5.50	3.03	1.00	ND	0.50	5.25	5.50	ND	ND
IV[c]	5.50	6.75	5.50	6.25	1.55	5.75	6.50	10.75	8.75	2.48	ND
V[a]	3.05	ND	0.50	2.03	10.75	ND	8.48	ND	ND	ND	ND
V[b]	ND	ND	6.25	14.88	27.53	ND	11.50	11.25	5.75	ND	ND
V[c]	0.75	17.25	17.75	127.75	22.00	28.75	54.53	15.25	10.75	4.53	ND
VI[a]	4.00	3.53	1.03	2.98	ND	ND	3.03	0.50	2.00	ND	ND
VI[b]	3.75	4.75	4.00	4.50	2.53	ND	8.25	12.75	4.25	0.53	ND
VI[c]	3.00	6.00	4.50	8.75	4.53	4.50	22.75	ND	5.50	17.75	ND

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.
I Water
II Exchangeable
III Bound to Carbonate

IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix XXI

Mean Zn levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (cool and dry season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	ND	0.65	10.00	1.00	ND	0.50	0.10	ND	0.10	ND	ND
I^b	0.51	2.00	10.00	1.52	3.00	4.12	0.70	1.00	0.10	ND	0.10
I^c	2.10	34.50	10.00	10.15	15.15	4.90	3.70	17.10	2.11	0.10	0.15
II^a	ND	ND	1.50	1.00	0.50	0.00	ND	0.10	ND	0.10	4.21
II^b	ND	2.15	1.00	1.00	0.50	1.21	ND	0.50	2.22	0.10	5.00
II^c	1.00	10.00	12.56	2.15	0.50	3.11	2.15	0.50	1.25	1.50	7.00
III^a	97.00	30.15	214.60	216.20	300.00	200.16	70.00	10.10	60.25	340.00	3.01
III^b	130.56	142.50	294.00	274.15	350.70	446.00	120.15	72.22	75.10	368.00	5.00
III^c	482.15	1300.00	850.10	700.10	2430.10	2120.00	270.20	160.00	260.22	721.21	7.80
IV^a	480.00	400.20	30.12	250.00	781.50	880.00	862.11	3190.00	220.00	421.22	6.12
IV^b	1200.14	402.00	570.15	1380.10	2200.10	1040.50	880.00	3570.11	6079.21	620.00	6.50
IV^c	1412.50	402.00	1900.00	2350.00	2815.00	2310.00	1270.11	6500.21	9800.00	1346.00	10.40
V^a	12.42	0.50	0.20	4.00	42.60	3.52	1.22	15.21	2.00	0.00	6.15
V^b	10.00	1.32	13.90	60.15	90.15	10.20	10.21	300.20	2.00	2.15	6.50
V^c	15.10	13.40	32.14	1210.00	100.20	50.00	29.00	12922.00	20.12	12.80	9.10
VI^a	7400.00	4400.00	4216.00	7000.00	3815.00	2800.00	3520.00	5500.00	240.12	4400.25	7.84
VI^b	9095.00	6480.12	6542.12	8300.00	4900.10	5300.12	4435.10	11400.00	9321.00	6090.00	8.10
VI^c	1400.00	17200.14	100.21	13000.00	8000.00	6800.00	7912.00	13100.00	14010.00	9900.11	13.37

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.
I Water
II Exchangeable

III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix XXII

Mean Zn levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (hot and dry season)

Fraction	Site										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	0.75	1.89	6.30	1.20	0.30	1.80	0.66	1.95	0.66	0.90	4.00
I^b	1.55	3.13	14.22	16.42	3.44	5.08	1.69	6.72	2.25	1.09	4.50
I^c	3.22	40.78	21.18	43.51	13.23	7.46	3.99	18.80	10.40	11.27	6.75
II^a	0.87	0.30	3.23	8.11	1.62	2.66	2.66	3.16	8.70	0.50	3.00
II^b	0.90	14.27	9.61	8.39	6.25	7.91	7.17	10.83	9.74	0.82	3.60
II^c	3.38	29.19	42.06	18.33	7.26	10.37	13.10	18.73	19.74	10.97	5.04
III^a	121.53	69.26	185.94	190.68	252.87	178.96	115.98	35.60	60.55	222.15	3.50
III^b	168.39	157.44	314.42	277.00	346.83	408.51	193.36	140.36	141.67	287.05	3.89
III^c	486.13	1025.78	764.05	663.58	1823.49	1613.98	362.75	299.37	304.28	609.93	6.07
IV^a	344.36	294.94	102.71	230.12	550.97	621.92	605.48	1956.51	182.81	288.71	7.20
IV^b	800.25	296.61	448.29	926.19	1451.71	774.55	655.90	2269.11	3772.37	419.53	7.90
IV^c	1080.07	377.26	1442.44	1763.19	2081.20	1782.88	1022.44	4624.41	6796.57	972.87	12.64
V^a	18.82	24.42	32.73	47.24	72.74	39.35	12.27	30.98	20.04	10.68	2.00
V^b	21.60	24.34	44.49	83.19	105.39	53.07	49.03	245.67	37.35	23.94	2.10
V^c	39.88	62.82	79.39	999.70	133.54	100.10	73.61	8513.86	69.79	34.48	2.94
VI^a	4587.29	2785.65	2707.65	4353.90	2349.90	1732.35	2418.15	3345.30	184.42	2667.60	11.00
VI^b	5872.34	4229.61	4302.11	5349.38	3141.78	3426.48	3251.63	7242.34	5881.88	3836.72	10.00
VI^c	1212.58	12355.10	321.80	9285.85	5777.28	5276.25	6386.63	9373.53	10349.33	6972.25	16.50

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO

V Bound to Organic Matter
VI Residual Fraction

Appendix XXIII

Mean Zn levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (warm and wet season)

Fraction	Site										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**Control**
I[a]	ND	0.59	9.00	0.90	ND	0.45	0.09	ND	0.09	ND	1.00
I[b]	0.46	1.80	9.00	1.37	2.70	3.71	0.63	0.90	0.09	ND	0.12
I[c]	1.89	31.05	9.00	9.14	13.64	4.41	3.33	15.39	1.90	0.09	0.18
II[a]	ND	ND	1.35	0.90	0.45	0.00	0.00	0.09	0.00	0.09	3.20
II[b]	ND	1.94	0.90	0.90	0.45	1.09	0.00	0.45	2.00	0.09	3.60
II[c]	0.90	9.00	11.30	1.94	0.45	2.80	1.94	0.45	1.13	1.35	5.04
III[a]	72.75	22.61	160.95	162.15	225.00	150.12	52.50	7.58	45.19	255.00	2.80
III[b]	97.92	106.88	220.50	205.61	263.03	334.50	90.11	54.17	56.33	276.00	3.00
III[c]	361.61	975.00	637.58	525.08	1822.58	1590.00	202.65	120.00	195.17	540.91	4.68
IV[a]	360.00	300.15	22.59	187.50	586.13	660.00	646.58	2392.50	165.00	315.92	1.20
IV[b]	900.11	301.50	427.61	1035.08	1650.08	780.38	660.00	2677.58	4559.41	465.00	1.80
IV[c]	1059.38	301.50	1425.00	1762.50	2111.25	1732.50	952.58	4875.16	7350.00	1009.50	2.88
V[a]	10.18	0.41	0.16	3.28	34.93	2.89	1.00	12.47	1.64	ND	5.00
V[b]	8.20	1.08	11.40	49.32	73.92	8.36	8.37	246.16	1.64	1.76	5.00
V[c]	12.38	10.99	26.35	992.20	82.16	41.00	23.78	10596.04	16.50	10.50	7.00
VI[a]	6068.00	3608.00	3457.12	5740.00	3128.30	2296.00	2886.40	4510.00	196.90	3608.21	6.80
VI[b]	7457.90	5313.70	5364.54	6806.00	4018.08	4346.10	3636.78	9348.00	7643.22	4993.80	7.45
VI[c]	1148.00	14104.11	82.17	10660.00	6560.00	5576.00	6487.84	10742.00	11488.20	8118.09	12.29

[a, b, c] Grain size 1400µm, 355µm and 150µm respectively.
I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix XXIV

Mean Zn levels ($mgkg^{-1}$) in different chemical fractions of roadside soils in Kano Metropolis (Warm and Dry Season)

Fraction	SITE										
	1	2	3	4	5	6	7	8	9	10	Control
I^a	ND	0.50	10.00	ND	ND	ND	ND	ND	ND	ND	2.00
I^b	ND	ND	6.75	0.50	2.75	3.00	ND	ND	ND	ND	2.20
I^c	1.50	33.75	6.50	9.75	15.00	4.75	3.00	16.75	ND	ND	3.30
II^a	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.60
II^b	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.24
II^c	ND	ND	11.25	0.50	0.50	2.48	ND	ND	ND	ND	4.54
III^a	99.75	ND	226.75	245.75	319.50	207.50	74.75	9.25	66.75	329.00	3.30
III^b	127.75	139.25	272.00	249.75	369.25	450.00	202.75	70.00	73.75	364.25	3.00
III^c	467.50	1450.00	832.50	675.00	2275.00	2050.00	254.25	145.50	249.00	660.00	4.68
IV^a	460.25	382.50	29.75	225.00	775.00	879.25	860.25	3125.00	208.25	479.25	8.50
IV^b	1169.75	420.25	525.00	1375.00	1950.00	1025.00	870.00	3569.75	6077.50	617.50	9.00
IV^c	1369.50	400.00	1875.00	2325.00	2775.00	2300.00	1275.00	6432.50	9757.50	1332.50	14.40
V^a	10.80	ND	0.50	40.75	45.25	2.50	ND	11.25	1.25	ND	3.00
V^b	ND	0.75	14.75	56.50	74.25	6.75	9.00	285.25	3.25	ND	4.00
V^c	2.00	11.00	29.75	1225.00	78.75	43.75	24.50	12857.50	16.75	ND	5.60
VI^a	7387.50	4375.00	4300.00	6225.00	3725.00	2772.50	3572.50	5465.00	231.75	4429.75	16.20
VI^b	9082.50	6475.00	7875.00	8325.00	4400.00	5319.75	4425.00	11457.50	9357.50	6064.75	16.50
VI^c	14225.00	17302.50	93.75	12225.00	7822.50	6725.00	7825.00	13057.50	14040.00	9817.50	27.23

[a, b, c] **Grain size 1400µm, 355µm and 150µm respectively.**

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix XXV

Cd levels ($mgkg^{-1}$) in different chemical fractions of atmospheric dust particulate along roads in Kano Metropolis

Fraction	Season	SITE									
		1	2	3	4	5	6	7	8	9	10
I	Cool and Dry Season	0.01	1.09	ND	0.07	2.45	1.93	0.98	2.34	1.68	1.61
	Hot and Dry Season	0.05	1.86	ND	0.23	4.66	3.50	2.10	4.24	2.80	2.80
	Warm and Wet Season	0.03	2.50	ND	0.16	5.64	4.43	2.25	5.39	3.86	3.70
	Warm and Dry Season	0.02	0.89	ND	0.11	2.23	1.67	1.00	2.03	1.34	1.34
II	Cool and Dry Season	0.01	ND	0.07	2.48	1.79	1.69	2.50	2.13	1.37	2.36
	Hot and Dry Season	ND	ND	0.21	4.03	2.94	3.15	4.62	4.41	2.10	3.89
	Warm and Wet Season	0.02	ND	0.15	5.55	4.01	3.78	5.59	4.76	3.06	5.29
	Warm and Dry Season	ND	ND	0.11	2.07	1.51	1.62	2.38	2.27	1.08	2.00
III	Cool and Dry Season	1.75	1.05	0.82	3.06	2.21	1.50	1.70	1.65	2.23	1.84
	Hot and Dry Season	2.94	1.78	1.58	5.58	3.35	2.68	3.35	2.01	3.90	3.35
	Warm and Wet Season	4.07	2.46	1.92	7.13	5.15	3.49	3.96	3.84	5.19	4.28
	Warm and Dry Season	1.19	0.72	0.64	2.25	1.35	1.08	1.35	0.81	1.58	1.35
IV	Cool and Dry Season	1.13	0.86	1.23	2.06	1.34	0.07	0.07	2.43	1.58	0.89
	Hot and Dry Season	3.06	2.55	2.72	6.80	4.08	0.34	0.34	6.63	4.25	2.55
	Warm and Wet Season	3.88	2.94	4.23	7.05	4.58	0.23	0.23	8.34	5.40	3.05
	Warm and Dry Season	0.47	0.39	0.42	1.05	0.63	0.05	0.05	1.02	0.66	0.39
V	Cool and Dry Season	0.59	0.81	0.65	1.92	0.88	1.56	0.07	2.16	0.85	4.26
	Hot and Dry Season	0.43	0.80	0.54	1.82	0.64	1.50	0.11	1.87	0.86	3.75
	Warm and Wet Season	0.64	0.89	0.72	2.11	0.97	1.72	0.07	2.38	0.93	4.68
	Warm and Dry Season	0.32	0.60	0.40	1.37	0.48	1.13	0.08	1.41	0.64	2.81
VI	Cool and Dry Season	1.30	1.68	ND	1.02	1.82	2.10	1.05	3.15	0.84	1.80
	Hot and Dry Season	3.01	3.83	ND	1.91	3.01	4.10	1.37	6.83	1.64	2.87
	Warm and Wet Season	3.37	4.37	ND	2.64	4.73	5.46	2.73	8.19	2.18	4.69
	Warm and Dry Season	0.52	0.66	ND	0.33	0.52	0.71	0.24	1.18	0.28	0.50

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO

V Bound to Organic Matter
VI Residual Fraction

Appendix XXVI

Cr levels ($mgkg^{-1}$) in different chemical fractions of atmospheric dust particulate along roads in Kano Metropolis

Fraction	Season	SITE									
		1	2	3	4	5	6	7	8	9	10
I	Cool and Dry Season	0.01	0.28	8.28	4.35	6.66	0.07	0.77	ND	0.39	0.28
	Hot and Dry Season	ND	0.29	4.62	0.88	2.93	0.07	0.80	ND	0.41	0.29
	Warm and Wet Season	0.01	0.20	6.05	3.17	4.86	0.05	0.56	ND	0.29	0.20
	Warm and Dry Season	ND	0.37	5.81	1.11	3.68	0.09	1.01	ND	0.51	0.37
II	Cool and Dry Season	0.74	0.78	0.09	0.68	9.05	0.42	0.74	2.85	0.27	0.61
	Hot and Dry Season	0.79	0.43	0.10	0.72	5.16	0.45	0.79	3.04	0.29	0.65
	Warm and Wet Season	0.61	0.64	0.08	0.55	7.42	0.34	0.61	2.34	0.22	0.50
	Warm and Dry Season	1.01	0.55	0.13	0.92	6.56	0.57	1.01	3.87	0.37	0.82
III	Cool and Dry Season	8.55	0.07	0.18	5.01	1.10	8.16	0.82	12.61	0.41	11.81
	Hot and Dry Season	4.83	0.07	0.17	1.40	1.07	4.29	0.80	4.81	0.40	7.01
	Warm and Wet Season	4.79	0.04	0.10	2.81	0.62	4.57	0.46	7.06	0.23	6.61
	Warm and Dry Season	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02
IV	Cool and Dry Season	ND	2.03	ND	5.50	5.75	2.50	5.25	ND	ND	0.00
	Hot and Dry Season	ND	4.82	0.11	8.09	2.25	6.96	5.99	7.02	1.08	8.62
	Warm and Wet Season	ND	4.78	0.07	9.57	5.75	6.60	7.95	4.81	0.74	5.91
	Warm and Dry Season	ND	2.77	0.06	4.66	1.29	4.01	3.45	4.04	0.62	4.97
V	Cool and Dry Season	ND	0.53	10.25	6.25	0.00	2.50	10.75	16.50	5.25	8.70
	Hot and Dry Season	ND	5.77	21.32	19.63	8.08	20.48	29.29	60.74	25.02	23.09
	Warm and Wet Season	0.07	5.07	39.50	28.40	5.25	19.56	45.93	80.76	29.40	36.78
	Warm and Dry Season	ND	1.80	6.63	6.11	2.51	6.37	9.11	18.89	7.78	7.18
VI	Cool and Dry Season	10.25	33.25	42.25	12.00	6.50	6.25	6.00	6.75	81.25	6.68
	Hot and Dry Season	13.94	44.77	18.08	16.86	10.44	9.82	9.36	95.82	124.44	13.17
	Warm and Wet Season	18.66	60.23	50.76	22.20	12.89	12.25	11.72	125.55	157.16	14.87
	Warm and Dry Season	6.45	20.72	8.37	7.80	4.83	4.54	4.33	44.34	57.58	6.09

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO

V Bound to Organic Matter
VI Residual Fraction

Appendix XXVII

Ni levels ($mgkg^{-1}$) in different chemical fractions of atmospheric dust particulate along roads in Kano Metropolis

Fraction	Season	SITE									
		1	2	3	4	5	6	7	8	9	10
I	Cool and Dry Season	10.25	14.53	15.04	14.53	7.53	8.05	5.25	5.50	10.25	9.56
	Hot and Dry Season	4.82	0.95	0.99	0.95	0.50	0.54	5.23	3.24	0.97	0.76
	Warm and Wet Season	6.61	1.29	1.34	1.29	0.67	0.72	7.08	4.44	1.31	0.85
	Warm and Dry Season	34.71	6.80	7.11	6.80	3.56	3.88	37.63	23.31	6.99	5.44
II	Cool and Dry Season	5.50	7.74	14.68	8.61	7.26	8.27	5.25	5.75	5.25	3.54
	Hot and Dry Season	4.61	0.52	0.91	0.62	0.46	0.54	3.00	2.95	0.89	0.44
	Warm and Wet Season	6.15	0.63	1.20	0.71	0.60	0.68	3.95	3.92	0.90	0.29
	Warm and Dry Season	65.05	7.27	12.87	8.78	6.44	7.61	42.24	41.54	12.58	6.14
III	Cool and Dry Season	53.00	7.82	14.59	14.62	14.38	10.71	10.25	10.75	10.50	15.40
	Hot and Dry Season	5.28	0.56	1.05	1.03	1.02	0.47	4.81	2.83	4.71	1.14
	Warm and Wet Season	7.06	0.73	1.36	1.36	1.34	1.00	6.10	3.82	6.52	1.43
	Warm and Dry Season	29.89	3.19	5.96	5.85	5.80	2.66	27.23	16.04	26.68	6.46
IV	Cool and Dry Season	55.50	27.64	7.95	14.21	17.64	14.21	15.25	10.25	7.65	13.87
	Hot and Dry Season	45.11	15.08	4.58	7.88	7.88	7.88	4.58	37.95	42.11	7.50
	Warm and Wet Season	61.38	21.01	6.04	10.80	13.41	10.80	13.85	49.90	58.12	10.54
	Warm and Dry Season	40.15	13.42	4.07	7.01	7.01	7.01	4.07	33.78	37.48	6.68
V	Cool and Dry Season	0.00	6.60	17.06	8.78	13.49	10.08	10.25	10.25	0.79	58.66
	Hot and Dry Season	61.23	5.35	12.01	8.73	11.46	5.73	41.91	32.91	1.32	49.12
	Warm and Wet Season	79.21	7.20	18.63	9.58	14.73	11.00	52.28	46.42	0.86	64.06
	Warm and Dry Season	52.44	4.58	10.28	7.48	9.82	4.91	35.90	28.18	1.13	42.07
VI	Cool and Dry Season	10.25	7.50	11.03	5.93	30.10	28.32	20.50	25.25	11.66	19.25
	Hot and Dry Season	114.14	11.87	23.92	7.34	51.26	34.63	69.74	103.89	14.58	27.34
	Warm and Wet Season	164.87	17.09	25.13	13.51	68.60	64.53	113.04	128.58	26.56	43.87
	Warm and Dry Season	32.45	3.38	6.80	2.09	14.58	9.85	19.83	29.54	4.15	7.77

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO

V Bound to Organic Matter
VI Residual Fraction

Appendix XXVIII

Pb levels ($mgkg^{-1}$) in different chemical fractions of atmospheric dust particulate along roads in Kano Metropolis

Fraction	Season	SITE									
		1	2	3	4	5	6	7	8	9	10
I	Cool and Dry Season	6.97	1.40	0.81	13.93	27.93	15.37	0.43	14.29	36.09	28.53
	Hot and Dry Season	7.29	2.80	1.62	14.21	28.21	15.69	0.87	14.22	37.18	29.40
	Warm and Wet Season	9.69	1.95	1.13	19.36	38.82	21.37	0.60	19.86	50.17	39.65
	Warm and Dry Season	4.61	1.77	1.03	8.98	17.83	9.92	0.55	8.99	23.50	18.58
II	Cool and Dry Season	7.83	1.86	7.98	31.32	26.77	1.35	1.36	6.41	43.79	28.22
	Hot and Dry Season	9.30	2.33	8.61	34.26	26.41	1.31	1.65	5.57	39.47	28.56
	Warm and Wet Season	10.18	2.42	10.37	40.72	34.80	1.76	1.76	8.34	56.93	36.68
	Warm and Dry Season	5.33	1.34	4.93	19.61	15.12	0.75	0.95	3.19	22.60	16.35
III	Cool and Dry Season	19.89	66.12	62.32	11.47	38.00	51.78	116.25	81.50	27.54	68.27
	Hot and Dry Season	20.30	70.32	66.01	116.49	390.60	36.61	84.29	70.15	29.40	42.21
	Warm and Wet Season	28.04	93.22	87.87	161.76	535.73	73.01	163.92	114.92	38.83	96.26
	Warm and Dry Season	9.46	32.78	30.77	54.29	182.05	17.06	39.29	32.70	13.70	19.67
IV	Cool and Dry Season	6.85	30.59	34.85	7.54	14.29	37.61	48.20	55.24	27.76	58.23
	Hot and Dry Season	4.87	17.85	23.15	4.87	94.05	26.71	26.69	18.51	18.40	39.87
	Warm and Wet Season	6.10	27.22	31.02	6.71	127.20	33.47	42.90	49.16	24.70	51.82
	Warm and Dry Season	3.91	14.34	18.59	3.91	75.53	21.45	21.43	14.86	14.78	32.02
V	Cool and Dry Season	1.30	13.55	3.69	27.18	57.21	26.00	16.72	31.85	16.78	6.50
	Hot and Dry Season	2.27	12.61	6.44	24.49	511.89	22.72	11.61	10.79	13.13	5.68
	Warm and Wet Season	1.48	15.45	4.20	30.98	652.16	29.64	19.06	36.31	19.13	7.41
	Warm and Dry Season	1.50	8.34	4.26	16.19	338.46	15.02	7.68	7.14	8.68	3.76
VI	Cool and Dry Season	90.58	53.47	78.44	38.82	24.58	24.43	31.82	24.23	8.51	29.30
	Hot and Dry Season	46.67	28.51	44.63	23.84	15.87	15.90	12.00	15.87	4.85	17.44
	Warm and Wet Season	71.56	42.24	61.97	30.67	19.42	19.30	25.14	19.14	6.72	23.14
	Warm and Dry Season	36.38	22.23	34.78	18.58	12.37	12.39	9.35	12.37	3.78	13.59

I Water
II Exchangeable
III Bound to Carbonate

IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix XXIX

Cu levels ($mgkg^{-1}$) in different chemical fractions of atmospheric dust particulate along roads in Kano Metropolis

Fraction	Season	SITE									
		1	2	3	4	5	6	7	8	9	10
I	Cool and Dry Season	4.20	7.70	3.52	5.78	6.30	12.08	6.37	1.44	3.17	0.07
	Hot and Dry Season	3.15	5.78	2.63	4.46	5.25	9.45	4.83	1.64	2.10	0.11
	Warm and Wet Season	4.28	7.85	3.59	5.89	6.43	12.32	6.50	1.47	3.23	0.07
	Warm and Dry Season	2.43	4.46	2.03	3.45	4.05	7.30	3.73	1.26	1.62	0.08
II	Cool and Dry Season	3.52	0.17	2.18	3.90	3.75	3.88	0.49	0.42	0.47	0.34
	Hot and Dry Season	3.27	0.26	1.22	3.32	3.63	2.81	0.73	0.63	0.71	0.51
	Warm and Wet Season	3.58	0.17	2.22	3.97	3.82	3.95	0.49	0.43	0.48	0.34
	Warm and Dry Season	2.86	0.22	1.07	2.90	3.17	2.45	0.64	0.55	0.62	0.45
III	Cool and Dry Season	5.11	4.13	0.36	6.97	2.14	3.82	9.10	3.57	0.34	2.38
	Hot and Dry Season	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02
	Warm and Wet Season	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02
	Warm and Dry Season	2.61	2.30	0.00	3.71	2.34	2.32	5.11	2.23	0.37	1.49
IV	Cool and Dry Season	6.65	9.49	7.88	9.08	3.80	8.22	9.25	8.05	12.23	4.09
	Hot and Dry Season	3.46	5.83	4.93	5.75	3.28	5.13	5.75	0.82	7.47	2.87
	Warm and Wet Season	5.47	7.80	6.48	7.46	3.13	6.76	7.60	6.62	10.05	3.36
	Warm and Dry Season	2.75	4.64	3.92	4.57	2.61	4.08	4.57	0.65	5.95	2.29
V	Cool and Dry Season	0.94	21.09	23.24	16.56	31.30	35.69	74.54	20.44	13.62	5.87
	Hot and Dry Season	1.01	21.89	25.92	182.88	37.66	37.66	86.62	23.33	14.69	6.48
	Warm and Wet Season	1.38	30.80	33.93	241.76	45.69	52.10	108.83	29.85	19.88	8.56
	Warm and Dry Season	0.44	9.59	11.35	80.11	16.49	16.49	37.94	10.22	6.43	2.84
VI	Cool and Dry Season	5.60	7.85	6.85	12.43	8.42	8.41	33.53	3.50	7.35	25.13
	Hot and Dry Season	3.89	4.05	4.11	7.00	5.84	5.84	19.57	3.89	3.89	14.12
	Warm and Wet Season	4.36	6.11	5.33	9.68	6.56	6.55	26.12	2.73	5.73	19.58
	Warm and Dry Season	2.50	2.61	2.64	4.51	3.76	3.76	12.59	2.50	2.50	9.09

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO

V Bound to Organic Matter
VI Residual Fraction

Appendix XXX

Zn levels ($mgkg^{-1}$) in different chemical fractions of atmospheric dust particulate along roads in Kano Metropolis

Fraction	Season	SITE									
		1	2	3	4	5	6	7	8	9	10
I	Cool and Dry Season	2.87	36.34	18.87	38.77	11.79	6.64	3.56	16.75	9.27	10.04
	Hot and Dry Season	2.60	42.64	12.36	12.55	18.73	6.06	4.57	21.14	2.61	0.12
	Warm and Wet Season	3.98	50.44	26.19	53.82	16.37	9.22	4.94	23.25	12.87	13.94
	Warm and Dry Season	1.68	27.67	8.02	8.14	12.15	3.93	2.97	13.72	1.69	0.08
II	Cool and Dry Season	3.04	26.28	37.86	16.50	6.53	9.33	11.79	16.86	17.77	9.87
	Hot and Dry Season	1.20	12.02	15.10	2.58	0.60	3.74	2.58	0.60	1.50	1.80
	Warm and Wet Season	4.05	35.03	50.47	21.99	8.71	12.44	15.71	22.48	23.69	13.16
	Warm and Dry Season	0.81	8.10	10.17	1.74	0.41	2.52	1.74	0.41	1.01	1.22
III	Cool and Dry Season	48.13	101.55	75.64	65.69	180.53	159.78	35.91	29.64	30.12	60.38
	Hot and Dry Season	583.88	1574.30	1029.47	847.82	2942.85	2567.32	327.21	193.76	315.13	873.39
	Warm and Wet Season	583.36	1230.94	916.86	796.29	2188.19	1936.78	435.30	359.24	365.14	731.92
	Warm and Dry Season	35.80	96.53	63.12	51.98	180.43	157.41	20.06	11.88	19.32	53.55
IV	Cool and Dry Season	84.25	29.43	112.51	137.53	162.33	139.06	79.75	360.70	530.13	75.88
	Hot and Dry Season	913.89	260.09	1229.30	1520.45	1821.31	1494.57	821.76	4205.64	6340.60	870.86
	Warm and Wet Season	756.05	264.08	1009.71	1234.23	1456.84	1248.02	715.71	3237.09	4757.60	681.01
	Warm and Dry Season	82.63	23.52	111.15	137.48	164.68	135.14	74.30	380.26	573.30	78.74
V	Cool and Dry Season	7.18	11.31	14.29	179.95	24.04	18.02	13.25	1532.50	12.56	6.21
	Hot and Dry Season	13.59	12.06	28.93	1089.00	90.18	45.00	26.10	11629.80	18.11	11.52
	Warm and Wet Season	39.08	61.57	77.80	979.71	130.87	98.10	72.14	8343.59	68.39	33.79
	Warm and Dry Season	2.23	1.98	4.74	178.60	14.79	7.38	4.28	1907.29	2.97	1.89
VI	Cool and Dry Season	9.49	96.74	2.52	72.71	45.24	41.31	50.01	73.39	81.04	54.59
	Hot and Dry Season	799.40	9821.28	57.22	7423.00	4568.00	3882.80	4517.75	7480.10	7999.71	5652.96
	Warm and Wet Season	700.87	7141.25	186.00	5367.22	3339.26	3049.67	3691.47	5417.90	5981.91	4029.96
	Warm and Dry Season	89.89	1104.35	6.43	834.68	513.65	436.60	508.00	841.10	899.53	635.65

I Water
II Exchangeable
III Bound to Carbonate
IV Bound to Fe-MnO
V Bound to Organic Matter
VI Residual Fraction

Appendix XXXI

Mean atmospheric concentrations (ppm) of air pollutants across the seasons at Site 1

	Season	Period												SA
		7:00am	8:00am	9:00am	10:00am	11:00am	12:00pm	1:00pm	2:00pm	3:00pm	4:00pm	5:00pm	6:00pm	
CO	**Cool and Dry Season**	5.00	5.00	6.00	5.00	5.00	6.00	6.00	5.00	5.00	6.00	5.00	6.00	5.42
	Hot and Dry Season	6.00	5.00	6.00	6.00	5.00	5.00	5.00	6.00	6.00	6.00	5.00	4.00	5.42
	Warm and Wet Season	5.00	5.00	5.00	6.00	7.00	6.00	7.00	6.00	7.00	9.00	8.00	8.00	6.58
	Warm and Dry Season	5.50	5.50	5.50	5.50	7.00	7.50	10.00	10.50	8.50	6.50	6.00	6.50	7.04
H_2S	**Cool and Dry Season**	ND	0.00	0.00	0.00	0.00	1.00	2.00	1.00	3.00	6.00	5.00	6.00	2.00
	Hot and Dry Season	1.00	1.00	1.00	1.00	1.00	1.00	1.00	2.00	1.00	1.00	2.00	1.00	1.17
	Warm and Wet Season	1.00	1.00	1.00	1.00	2.00	1.00	2.00	2.00	1.00	1.00	1.00	0.00	1.17
	Warm and Dry Season	0.00	0.00	0.00	0.20	0.25	1.10	0.90	1.00	1.00	1.00	1.10	1.15	0.64
NO_2	**Cool and Dry Season**	0.10	0.10	0.10	0.10	0.10	0.20	0.10	0.20	0.20	0.20	0.20	0.10	0.14
	Hot and Dry Season	0.10	0.10	0.10	0.10	0.10	0.20	0.30	0.10	0.20	0.20	0.40	0.20	0.18
	Warm and Wet Season	0.20	0.30	0.40	0.20	0.30	0.40	0.20	0.40	0.50	0.40	0.50	0.40	0.35
	Warm and Dry Season	0.11	0.11	0.11	0.21	0.20	0.31	0.41	0.22	0.31	0.21	0.20	0.11	0.21
SO_2	**Cool and Dry Season**	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.01

	Warm and Wet Season	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.02
	Warm and Dry Season	ND	ND	0.00	0.00	0.00	0.11	0.11	0.10	0.00	0.00	0.00	0.00	0.03
FL	**Cool and Dry Season**	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	ND	ND	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	3.00	1.00	0.75
	Warm and Dry Season	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NH_3	**Cool and Dry Season**	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.08
	Warm and Wet Season	ND	ND	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

SA: Seasonal Average

Appendix XXXII

Mean atmospheric concentrations (ppm) of air pollutants across the seasons at Site 2

	Season	**Period**												**SA**
		7:00am	**8:00am**	**9:00am**	**10:00am**	**11:00am**	**12:00pm**	**1:00pm**	**2:00pm**	**3:00pm**	**4:00pm**	**5:00pm**	**6:00pm**	
CO	**Cool and Dry Season**	4.00	6.00	6.00	4.00	4.00	6.00	6.00	5.00	6.00	6.00	4.00	5.00	5.17
	Hot and Dry Season	5.00	5.00	4.00	6.00	5.00	4.00	6.00	6.00	7.00	5.00	5.00	6.00	5.33
	Warm and Wet Season	6.00	5.00	5.00	6.00	5.00	5.00	4.00	6.00	5.00	3.00	4.00	7.00	5.08
	Warm and Dry Season	4.15	6.20	5.10	6.15	5.10	3.90	7.20	6.05	8.05	6.10	4.05	5.15	5.60
H_2S	**Cool and Dry Season**	0.00	0.00	0.00	1.00	1.00	2.00	3.00	1.00	4.00	6.00	4.00	5.00	2.25

	Hot and Dry Season	0.00	0.00	0.00	1.00	0.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00	0.58
	Warm and Wet Season	1.00	1.00	1.00	2.00	1.00	1.00	2.00	2.00	2.00	2.00	3.00	1.00	1.58
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	1.10	1.10	1.05	1.10	0.00	1.00	0.45
NO_2	**Cool and Dry Season**	0.10	0.10	0.10	0.10	0.10	0.20	0.10	0.10	0.20	0.10	0.10	0.20	0.13
	Hot and Dry Season	0.10	0.10	0.10	0.10	0.20	0.10	0.20	0.30	0.20	0.20	0.20	0.20	0.17
	Warm and Wet Season	0.10	0.10	0.10	0.20	0.10	0.20	0.30	0.20	0.10	0.20	0.30	0.10	0.17
	Warm and Dry Season	0.10	0.11	0.11	0.10	0.11	0.12	0.10	0.11	0.11	0.10	0.11	0.21	0.12
SO_2	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.01
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.03
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FL	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	1.00	1.00	1.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	2.00	1.00	0.92
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NH_3	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	1.00	0.17
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

SA: Seasonal Average

Appendix XXXIII

	Season	Period												SA
		7:00am	8:00am	9:00am	10:00am	11:00am	12:00pm	1:00pm	2:00pm	3:00pm	4:00pm	5:00pm	6:00pm	
CO	Cool and Dry Season	7.00	6.00	6.00	6.00	6.00	7.00	6.00	6.00	6.00	6.00	5.00	6.00	6.08
	Hot and Dry Season	4.00	5.00	3.00	5.00	4.00	5.00	5.00	5.00	6.00	8.00	5.00	4.00	4.92
	Warm and Wet Season	3.00	5.00	5.00	5.00	5.00	6.00	4.00	5.00	5.00	8.00	4.00	6.00	5.08
	Warm and Dry Season	7.50	5.50	6.05	6.00	5.40	8.50	10.50	9.00	10.00	6.10	5.45	6.50	7.21
H_2S	Cool and Dry Season	1.00	1.00	1.00	2.00	2.00	3.00	4.00	2.00	1.00	6.00	5.00	6.00	2.83
	Hot and Dry Season	2.00	1.00	2.00	2.00	1.00	1.00	3.00	2.00	1.00	2.00	3.00	2.00	1.83
	Warm and Wet Season	2.00	2.00	3.00	3.00	2.00	2.00	2.00	3.00	3.00	3.00	1.00	1.00	2.25
	Warm and Dry Season	1.05	1.05	1.05	1.10	0.31	0.85	1.15	0.55	1.10	1.15	0.00	0.00	0.78
NO_2	Cool and Dry Season	0.20	0.10	0.10	0.20	0.10	0.20	0.20	0.10	0.10	0.30	0.20	0.10	0.16
	Hot and Dry Season	0.10	0.10	0.10	0.10	0.10	0.20	0.10	0.00	0.20	0.10	0.10	0.10	0.11
	Warm and Wet Season	0.20	0.30	0.10	0.10	0.10	0.10	0.20	0.10	0.10	0.10	0.20	0.10	0.14
	Warm and Dry Season	0.21	0.12	0.11	0.11	0.10	0.10	0.11	0.23	0.13	0.31	0.24	0.11	0.16
SO_2	Cool and Dry Season	0.10	0.10	0.10	0.10	0.10	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.06
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.03
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.03
	Warm and Dry Season	0.10	0.11	0.11	0.12	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.05

FL	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	0.75
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NH_3	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.08
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Mean atmospheric concentrations (ppm) of air pollutants across the seasons at Site 3
SA: Seasonal Average

Appendix XXXIV

Mean atmospheric concentrations (ppm) of air pollutants across the seasons at Site 4

	Season	**Period**												**SA**
		7:00am	**8:00am**	**9:00am**	**10:00am**	**11:00am**	**12:00pm**	**1:00pm**	**2:00pm**	**3:00pm**	**4:00pm**	**5:00pm**	**6:00pm**	
CO	**Cool and Dry Season**	6.00	7.00	6.00	6.00	6.00	7.00	7.00	6.00	7.00	5.00	8.00	9.00	6.67
	Hot and Dry Season	5.00	2.00	2.00	4.00	5.00	2.00	5.00	5.00	5.00	5.00	5.00	6.00	4.25
	Warm and Wet Season	3.00	4.00	3.00	5.00	6.00	6.00	6.00	6.00	5.00	11.00	15.00	12.00	6.83
	Warm and Dry Season	7.10	6.50	6.25	7.20	10.25	10.50	11.35	11.30	7.20	5.10	7.10	9.50	8.28
H_2S	**Cool and Dry Season**	0.00	0.00	0.00	1.00	3.00	2.00	4.00	3.00	3.00	5.00	8.00	9.00	3.17
	Hot and Dry Season	1.00	1.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00	2.00	0.00	1.00	0.92
	Warm and Wet	1.00	1.00	1.00	1.00	0.00	1.00	3.00	1.00	1.00	5.00	1.00	1.00	1.42

	Season												
	Warm and Dry Season	1.05	0.00	1.10	0.61	1.05	0.90	0.85	0.95	1.00	1.80	1.00	1.00	0.94
NO_2	Cool and Dry Season	0.10	0.10	0.10	0.10	0.20	0.30	0.10	0.20	0.10	0.30	0.30	0.20	0.18
	Hot and Dry Season	0.10	0.00	0.10	0.20	0.00	0.10	0.20	0.10	0.20	0.20	0.10	0.20	0.13
	Warm and Wet Season	0.20	0.20	0.20	0.10	0.10	0.00	0.20	0.30	0.40	1.00	1.30	1.20	0.43
	Warm and Dry Season	0.21	0.21	0.22	0.41	0.21	0.40	0.42	0.72	0.61	0.31	0.30	0.22	0.35
SO_2	Cool and Dry Season	0.10	0.10	0.10	0.00	0.00	0.10	0.10	0.10	0.10	0.00	0.10	0.20	0.08
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.03
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.10	0.03
	Warm and Dry Season	0.11	0.12	0.11	0.20	0.32	0.55	0.75	0.80	0.21	0.00	0.00	0.00	0.26
FL	Cool and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	0.00	0.00	0.00	1.00	1.00	0.00	0.00	1.00	1.00	0.00	0.00	1.00	0.42
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NH_3	Cool and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.08
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

SA: Seasonal Average

Appendix XXXV

Mean atmospheric concentrations (ppm) of air pollutants across the seasons at Site 5

	Season	Period												SA
		7:00am	8:00am	9:00am	10:00am	11:00am	12:00pm	1:00pm	2:00pm	3:00pm	4:00pm	5:00pm	6:00pm	
CO	**Cool and Dry Season**	7.00	7.00	6.00	6.00	5.00	7.00	6.00	7.00	7.00	5.00	7.00	9.00	6.58
	Hot and Dry Season	5.00	5.00	4.00	4.00	5.00	5.00	6.00	7.00	5.00	10.00	12.00	10.00	6.50
	Warm and Wet Season	6.00	5.00	5.00	7.00	8.00	7.00	7.00	10.00	12.00	35.00	37.00	33.00	14.33
	Warm and Dry Season	6.10	7.05	6.15	4.10	5.05	6.05	10.10	11.15	9.90	5.05	7.90	9.50	7.34
H_2S	**Cool and Dry Season**	1.00	0.00	1.00	1.00	0.00	1.00	1.00	1.00	1.00	5.00	7.00	9.00	2.33
	Hot and Dry Season	0.00	0.00	0.00	0.00	1.00	1.00	2.00	1.00	1.00	4.00	3.00	5.00	1.50
	Warm and Wet Season	1.00	1.00	1.00	3.00	2.00	2.00	4.00	2.00	2.00	8.00	6.00	6.00	3.17
	Warm and Dry Season	0.00	0.00	0.00	0.20	0.35	0.44	0.51	1.05	0.90	1.00	0.00	0.00	0.37
NO_2	**Cool and Dry Season**	0.20	0.20	0.20	0.20	0.10	0.30	1.20	1.00	1.00	3.00	1.00	1.00	0.78
	Hot and Dry Season	0.10	0.20	0.10	0.10	0.10	0.10	0.10	0.20	0.20	0.10	0.20	0.20	0.14
	Warm and Wet Season	0.10	0.10	0.20	0.10	0.20	0.30	0.20	0.40	0.50	0.20	0.60	0.30	0.27
	Warm and Dry Season	0.11	0.11	0.12	0.54	0.61	1.05	2.05	1.20	2.05	3.05	1.05	1.15	1.09
SO_2	**Cool and Dry Season**	0.10	0.10	0.10	0.00	0.00	0.20	0.10	0.10	0.10	0.00	0.00	0.00	0.07
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.03
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.03
	Warm and Dry Season	0.11	0.11	0.11	0.21	0.22	0.12	0.22	0.10	0.11	0.00	0.11	0.21	0.14
FL	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.08
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	0.00	0.00	0.00	1.00	1.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00	0.67
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NH_3	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	1.00	0.00	0.25
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	1.00	1.00	1.00	0.33
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

SA: Seasonal Average

Appendix XXXVI

Mean atmospheric concentrations (ppm) of air pollutants across the seasons at Site 6

	Season	Period												SA
		7:00am	8:00am	9:00am	10:00am	11:00am	12:00pm	1:00pm	2:00pm	3:00pm	4:00pm	5:00pm	6:00pm	
CO	**Cool and Dry Season**	5.00	6.00	4.00	6.00	4.00	5.00	6.00	6.00	5.00	6.00	6.00	7.00	5.50
	Hot and Dry Season	3.00	2.00	2.00	2.00	3.00	3.00	4.00	3.00	2.00	10.00	9.00	8.00	4.25
	Warm and Wet Season	4.00	5.00	5.00	3.00	4.00	5.00	4.00	6.00	6.00	8.00	7.00	8.00	5.42
	Warm and Dry Season	5.05	6.00	4.10	5.90	7.50	9.10	10.90	11.70	9.10	6.10	6.15	7.05	7.39
H_2S	**Cool and Dry Season**	0.00	1.00	0.00	1.00	1.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	0.58
	Hot and Dry Season	0.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.67
	Warm and Wet Season	1.00	1.00	1.00	0.00	0.00	1.00	0.00	1.00	0.00	0.00	0.00	0.00	0.42
	Warm and Dry Season	0.00	0.95	0.00	0.95	0.98	0.40	0.85	0.10	1.00	1.00	1.00	1.00	0.69
NO_2	**Cool and Dry Season**	0.10	0.20	0.10	0.10	0.10	0.20	0.10	0.20	0.20	0.10	0.10	0.20	0.14
	Hot and Dry Season	0.10	0.10	0.10	0.20	0.10	0.20	0.10	0.10	0.10	0.20	0.20	0.10	0.13
	Warm and Wet Season	0.20	0.10	0.10	0.10	0.10	0.40	0.10	0.10	0.10	0.30	0.50	0.50	0.22
	Warm and Dry Season	0.11	0.21	0.11	0.21	0.30	0.21	0.41	0.21	0.31	0.11	0.11	0.21	0.21
SO_2	**Cool and Dry Season**	0.00	0.00	0.00	0.10	0.00	0.10	0.00	0.00	0.00	0.00	0.10	0.10	0.03
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.10	0.03
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.10	0.10	0.10	0.03
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.11	0.22	0.00	0.11	0.11	0.06
FL	**Cool and Dry Season**	1.00	1.00	1.00	0.00	0.00	0.00	1.00	1.00	0.10	0.00	0.10	0.10	0.44
	Hot and Dry	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	Season													
	Warm and Wet Season	0.00	0.00	0.00	0.00	1.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.17
	Warm and Dry Season	0.95	1.00	1.00	1.00	1.05	0.00	0.00	1.05	0.10	0.00	0.10	0.10	0.53
NH_3	Cool and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	1.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.25
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

SA: Seasonal Average

Appendix XXXVII

	Season	Period												SA
		7:00am	8:00am	9:00am	10:00am	11:00am	12:00pm	1:00pm	2:00pm	3:00pm	4:00pm	5:00pm	6:00pm	
CO	Cool and Dry Season	5.00	4.00	5.00	5.00	6.00	6.00	5.00	4.00	6.00	8.00	8.00	7.00	5.75
	Hot and Dry Season	3.00	3.00	3.00	3.00	3.00	3.00	4.00	3.00	3.00	14.00	11.00	12.00	5.42
	Warm and Wet Season	6.00	7.00	7.00	6.00	6.00	7.00	7.00	6.00	7.00	12.00	13.00	14.00	8.17
	Warm and Dry Season	5.05	4.50	5.50	6.50	7.50	6.50	10.25	11.15	6.00	10.60	8.20	7.25	7.42
H_2S	Cool and Dry Season	0.00	0.00	1.00	0.00	0.00	0.00	1.00	0.00	1.00	1.00	1.00	1.00	0.50
	Hot and Dry Season	0.00	0.00	0.00	0.00	2.00	2.00	3.00	1.00	3.00	3.00	2.00	4.00	1.67
	Warm and Wet Season	1.00	1.00	1.00	1.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.92
	Warm and Dry Season	0.00	0.00	1.10	0.11	0.20	0.41	0.63	0.55	0.13	1.00	1.25	1.40	0.57
NO_2	Cool and Dry	0.10	0.20	0.10	0.20	0.10	0.10	0.20	0.20	0.10	0.10	0.10	0.20	0.14

	Season													
	Hot and Dry Season	0.10	0.00	0.11	0.20	0.10	0.10	0.20	0.10	0.10	0.30	0.30	0.40	0.17
	Warm and Wet Season	0.10	0.30	0.10	0.30	0.10	0.20	0.30	0.10	0.40	0.60	0.70	0.50	0.31
	Warm and Dry Season	0.11	0.22	0.13	0.17	0.20	0.21	0.12	0.20	0.21	0.13	0.13	0.21	0.17
SO_2	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.00	0.00	0.10	0.10	0.10	0.04
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.10	0.10	0.04
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.10	0.10	0.10	0.03
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.10	0.16	0.10	0.10	0.10	0.12	0.13	0.07
FL	**Cool and Dry Season**	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00	1.00	0.67
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	1.00	1.00	0.00	1.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	0.67
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	1.10	1.05	1.45	1.85	1.05	1.10	1.15	0.73
NH_3	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.08
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Mean atmospheric concentrations (ppm) of air pollutants across the seasons at Site 7
SA: Seasonal Average

Appendix XXXVIII

Mean atmospheric concentrations (ppm) of air pollutants across the seasons at Site 8

	Season	Period												SA
		7:00am	8:00am	9:00am	10:00am	11:00am	12:00pm	1:00pm	2:00pm	3:00pm	4:00pm	5:00pm	6:00pm	
CO	**Cool and Dry Season**	5.00	6.00	5.00	6.00	6.00	5.00	5.00	5.00	6.00	9.00	10.00	10.00	6.50
	Hot and Dry Season	4.00	3.00	1.00	4.00	7.00	3.00	5.00	6.00	7.00	10.00	9.00	10.00	5.75
	Warm and Wet Season	7.00	7.00	7.00	8.00	2.00	10.00	8.00	4.00	8.00	9.00	10.00	10.00	7.50
	Warm and Dry Season	5.00	7.00	5.00	6.50	8.05	10.20	10.80	12.20	10.25	9.25	9.90	10.35	8.71
H_2S	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	1.00	1.00	1.00	0.00	1.00	1.00	1.00	0.50
	Hot and Dry Season	0.00	0.00	0.00	0.00	2.00	1.00	2.00	2.00	3.00	4.00	4.00	2.00	1.67
	Warm and Wet Season	1.00	1.00	1.00	0.00	0.00	1.00	0.00	0.00	0.00	1.00	1.00	1.00	0.58
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.95	0.00	0.90	0.90	1.00	1.00	0.40
NO_2	**Cool and Dry Season**	0.10	0.10	0.10	0.10	0.20	0.10	0.20	0.20	0.10	0.20	0.20	0.20	0.15
	Hot and Dry Season	0.10	0.10	0.10	0.10	0.10	0.20	0.10	0.20	0.20	0.30	0.30	0.10	0.16
	Warm and Wet Season	0.10	0.10	0.10	0.10	0.30	0.20	0.10	0.10	0.60	0.60	0.70	0.80	0.32
	Warm and Dry Season	0.10	0.10	0.11	0.31	0.45	0.45	0.35	0.20	0.35	0.35	0.20	0.25	0.27
SO_2	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.00	0.10	0.10	0.10	0.03
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.03
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.03
	Warm and Dry Season	0.00	0.00	0.00	0.35	0.13	0.13	0.11	0.11	0.23	0.11	0.11	0.11	0.12
FL	**Cool and Dry Season**	1.00	1.00	0.00	0.10	0.10	1.00	0.00	0.00	1.00	1.00	0.00	0.00	0.43
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	0.00	0.00	0.00	0.00	1.00	1.00	0.00	0.00	1.00	1.00	1.00	1.00	0.50
	Warm and Dry Season	1.10	1.15	0.00	0.41	0.52	0.50	1.20	1.40	0.92	1.05	0.00	0.00	0.69
NH_3	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

SA: Seasonal Average

Appendix XXXIX

Mean atmospheric concentrations (ppm) of air pollutants across the seasons at Site 9

	Season	Period												SA
		7:00am	8:00am	9:00am	10:00am	11:00am	12:00pm	1:00pm	2:00pm	3:00pm	4:00pm	5:00pm	6:00pm	
CO	**Cool and Dry Season**	5.00	5.00	5.00	6.00	4.00	5.00	5.00	5.00	6.00	9.00	10.00	11.00	6.33
	Hot and Dry Season	5.00	4.00	4.00	5.00	6.00	6.00	7.00	7.00	8.00	13.00	10.00	11.00	7.17
	Warm and Wet Season	8.00	7.00	6.00	7.00	3.00	2.00	3.00	6.00	8.00	14.00	15.00	12.00	7.58
	Warm and Dry Season	5.30	5.00	5.20	8.15	10.25	9.25	11.10	10.25	12.15	9.20	10.10	11.25	8.93
H_2S	**Cool and Dry Season**	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	1.00	0.00	0.33
	Hot and Dry Season	1.00	1.00	1.00	2.00	3.00	2.00	3.00	2.00	2.00	3.00	5.00	2.00	2.25
	Warm and Wet Season	1.00	1.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00	1.00	1.00	1.00	0.92
	Warm and Dry Season	1.05	0.00	0.00	1.10	1.20	1.15	1.10	1.10	1.20	1.05	1.00	0.00	0.83
NO_2	**Cool and Dry Season**	0.10	0.10	0.10	0.10	0.20	0.10	0.20	0.10	0.10	0.10	0.20	0.20	0.13
	Hot and Dry Season	0.10	0.10	0.10	0.10	0.10	0.10	0.20	0.20	0.10	0.20	0.10	0.10	0.13
	Warm and Wet Season	0.20	0.20	0.20	0.10	0.10	0.10	0.50	0.30	0.10	0.80	0.80	0.90	0.36
	Warm and Dry Season	0.11	0.11	0.10	0.31	0.21	0.25	0.15	0.25	0.11	0.13	0.24	0.20	0.18
SO_2	**Cool and Dry Season**	0.00	0.10	0.00	0.00	0.00	0.00	0.10	0.20	0.10	0.10	0.10	0.10	0.07
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.10	0.10	0.10	0.03
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.03
	Warm and Dry Season	0.00	0.10	0.00	0.00	0.10	0.13	0.13	0.14	0.14	0.11	0.10	0.10	0.09
FL	**Cool and Dry Season**	0.00	1.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.17
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	1.00	1.00	1.00	1.00	0.00	1.00	1.00	0.00	1.00	1.00	1.00	1.00	0.83
	Warm and Dry Season	0.00	1.00	0.00	0.00	0.00	0.00	1.00	0.00	1.00	0.00	0.00	0.00	0.25
NH_3	**Cool and Dry Season**	0.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.17
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

SA: Seasonal Average

Appendix XL

Mean atmospheric concentrations (ppm) of air pollutants across the seasons at Site 10

	Season	Period												SA
		7:00am	8:00am	9:00am	10:00am	11:00am	12:00pm	1:00pm	2:00pm	3:00pm	4:00pm	5:00pm	6:00pm	
CO	**Cool and Dry Season**	4.00	3.00	5.00	5.00	4.00	4.00	4.00	4.00	6.00	8.00	9.00	10.00	5.50
	Hot and Dry Season	3.00	3.00	2.00	3.00	3.00	4.00	5.00	6.00	8.00	12.00	11.00	12.00	6.00
	Warm and Wet Season	6.00	5.00	5.00	8.00	9.00	7.00	9.00	8.00	8.00	11.00	12.00	12.00	8.33
	Warm and Dry Season	4.05	3.75	5.00	7.50	9.50	12.00	13.00	10.00	9.25	8.50	9.50	10.25	8.53
H_2S	**Cool and Dry Season**	0.00	1.00	1.00	0.00	1.00	1.00	0.00	0.00	1.00	1.00	1.00	1.00	0.67
	Hot and Dry Season	1.00	1.00	1.00	2.00	2.00	3.00	3.00	3.00	3.00	3.00	2.00	3.00	2.25
	Warm and Wet Season	1.00	1.00	1.00	1.00	0.00	1.00	0.00	0.00	1.00	1.00	1.00	1.00	0.75
	Warm and Dry Season	0.00	1.05	1.10	1.25	1.45	1.30	1.10	1.20	1.15	1.15	1.25	1.30	1.11
NO_2	**Cool and Dry Season**	0.10	0.20	0.20	0.20	0.10	0.20	0.20	0.20	0.20	0.10	0.20	0.20	0.18
	Hot and Dry Season	0.10	0.10	0.10	0.20	0.10	0.10	0.10	0.10	0.20	0.30	0.10	0.20	0.14
	Warm and Wet Season	0.10	0.10	0.10	0.00	0.00	0.00	0.10	0.50	0.80	1.00	1.10	0.90	0.39
	Warm and Dry Season	0.10	0.22	0.21	0.11	0.33	0.20	0.11	0.31	0.31	0.10	0.20	0.21	0.20
SO_2	**Cool and Dry Season**	0.00	0.00	1.00	0.20	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.17
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.10	0.03
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.10	0.03
	Warm and Dry Season	0.00	0.00	1.00	0.20	0.10	0.30	0.10	0.10	0.20	0.10	0.11	0.10	0.19
FL	**Cool and Dry Season**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	0.00	0.00	0.00	0.00	1.00	1.00	0.00	0.00	0.00	1.00	1.00	1.00	0.42
	Warm and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NH_3	**Cool and Dry Season**	0.00	1.00	0.00	0.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.25
	Hot and Dry Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Wet Season	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Warm and Dry Season	0.00	1.10	0.00	1.00	1.00	0.50	0.00	0.00	0.00	0.00	0.00	0.00	0.30

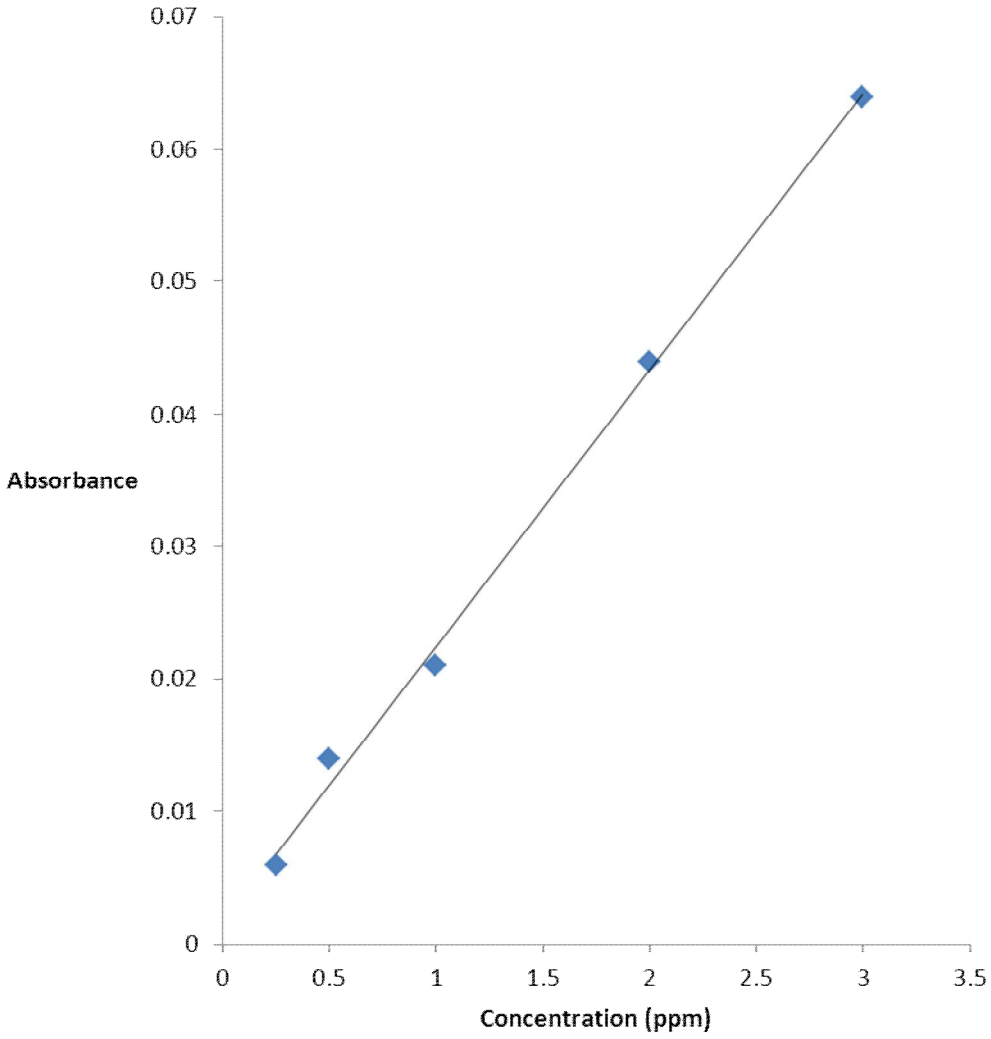
SA: Seasonal Average

Appendix XLI

Mean atmospheric concentrations (ppm) of air pollutants across the seasons at control site

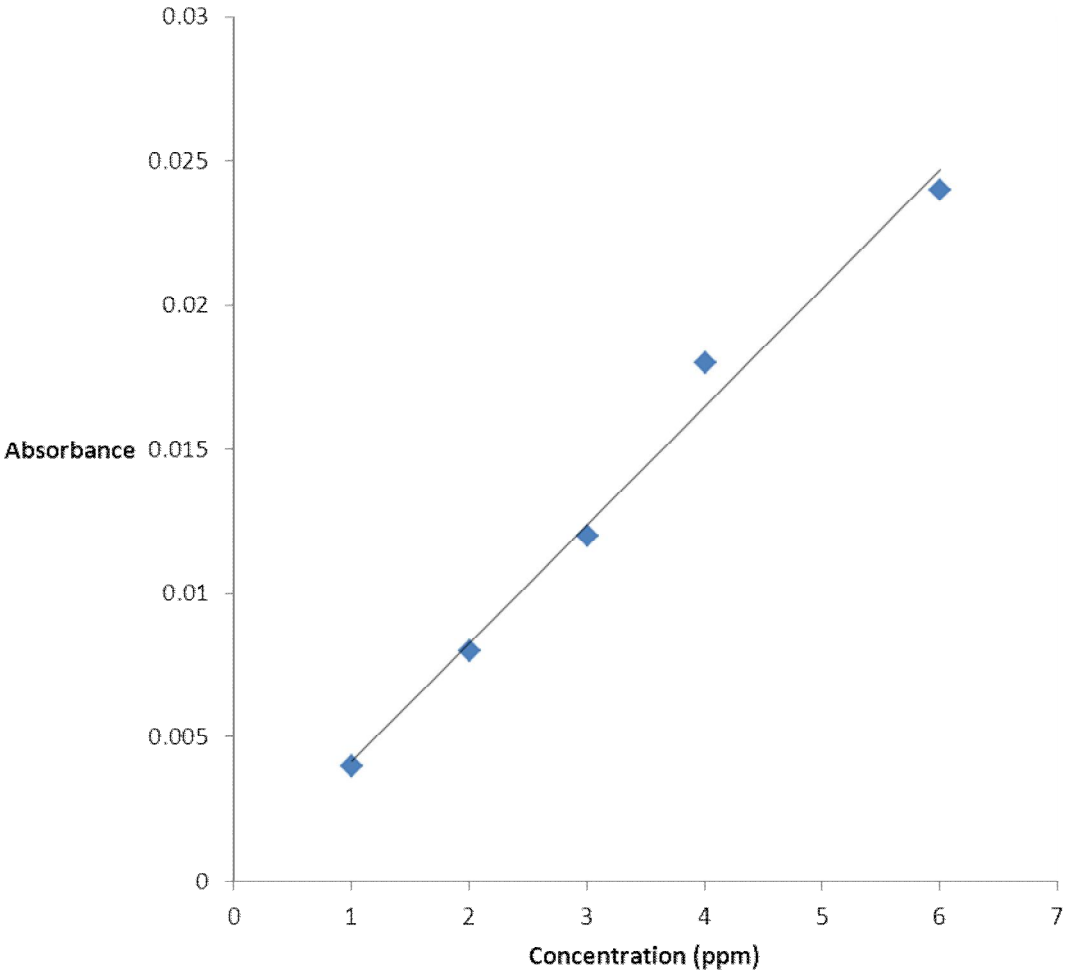
Season	Pollutant					
	CO	H_2S	NO_2	SO_2	FL	NH_3
Cool and Dry Season	0.00	0.00	0.02	0.00	0.00	0.00
Hot and Dry Season	0.01	0.00	0.00	0.00	0.00	0.00
Warm and Wet Season	0.01	0.00	0.00	0.00	0.00	0.00
Warm and Dry Season	0.00	0.00	0.07	0.00	0.00	0.00

Appendix XLII



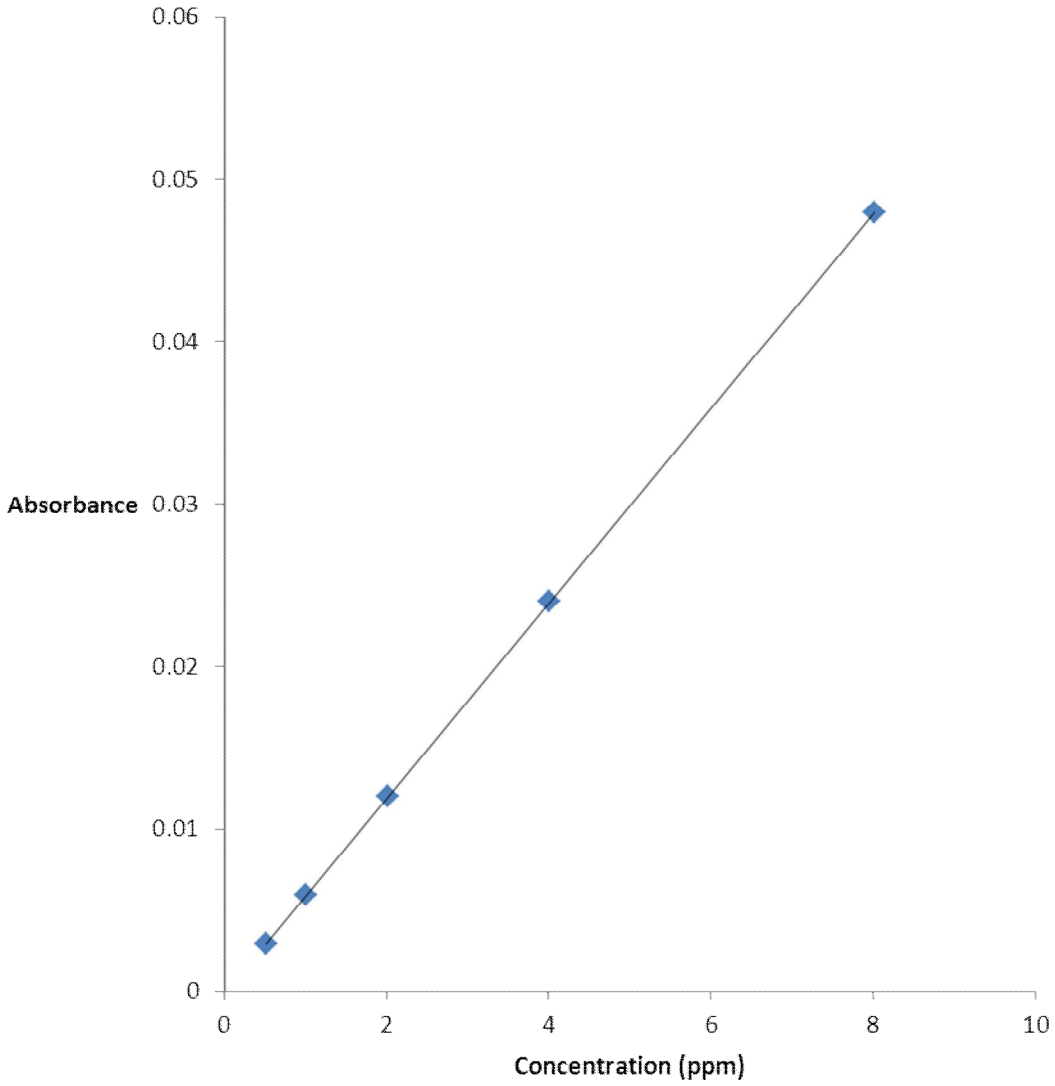
Calibration curve for the determination of Cd

Appendix XLIII



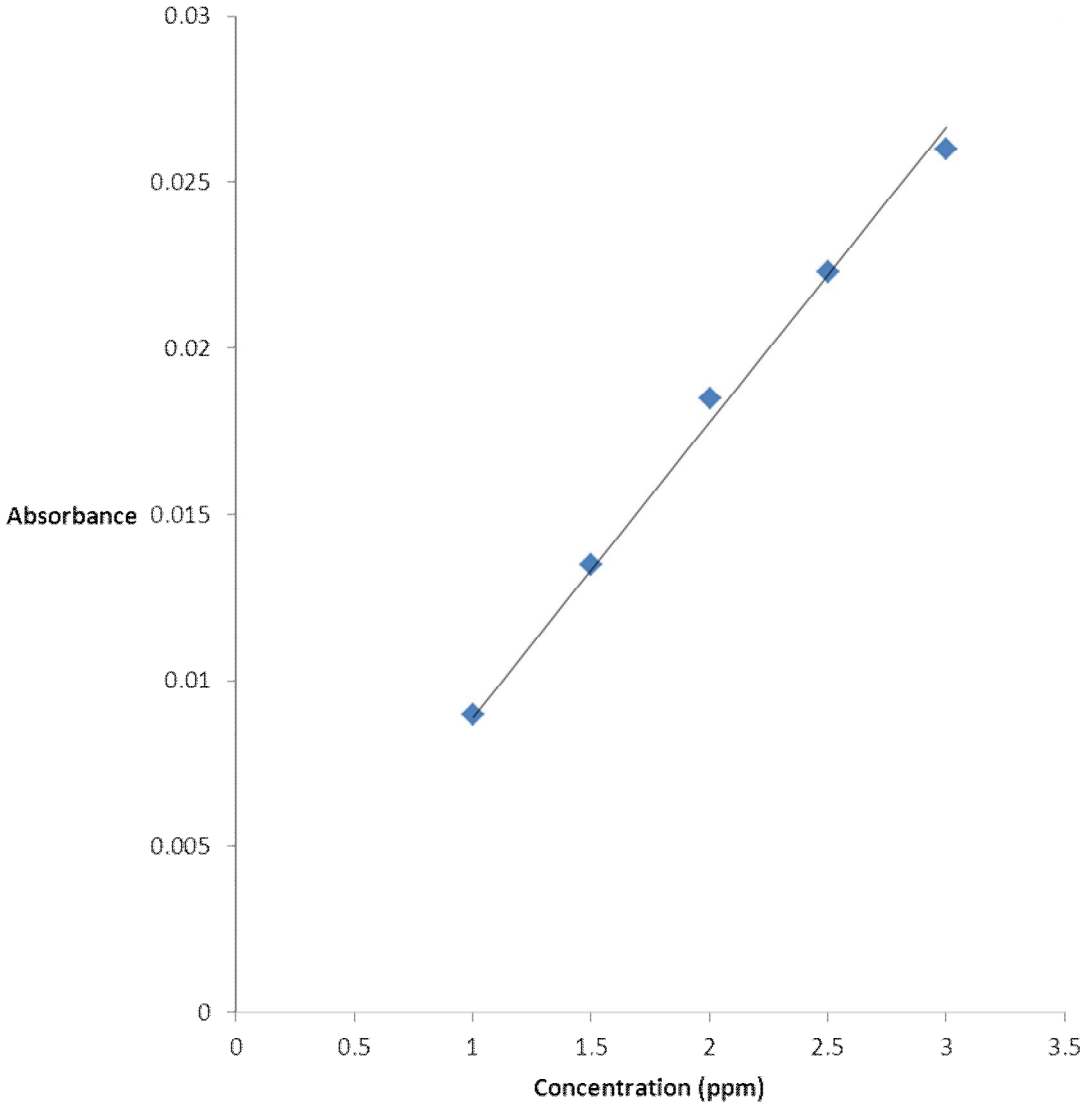
Calibration curve for the determination of Cr

Appendix XLIV



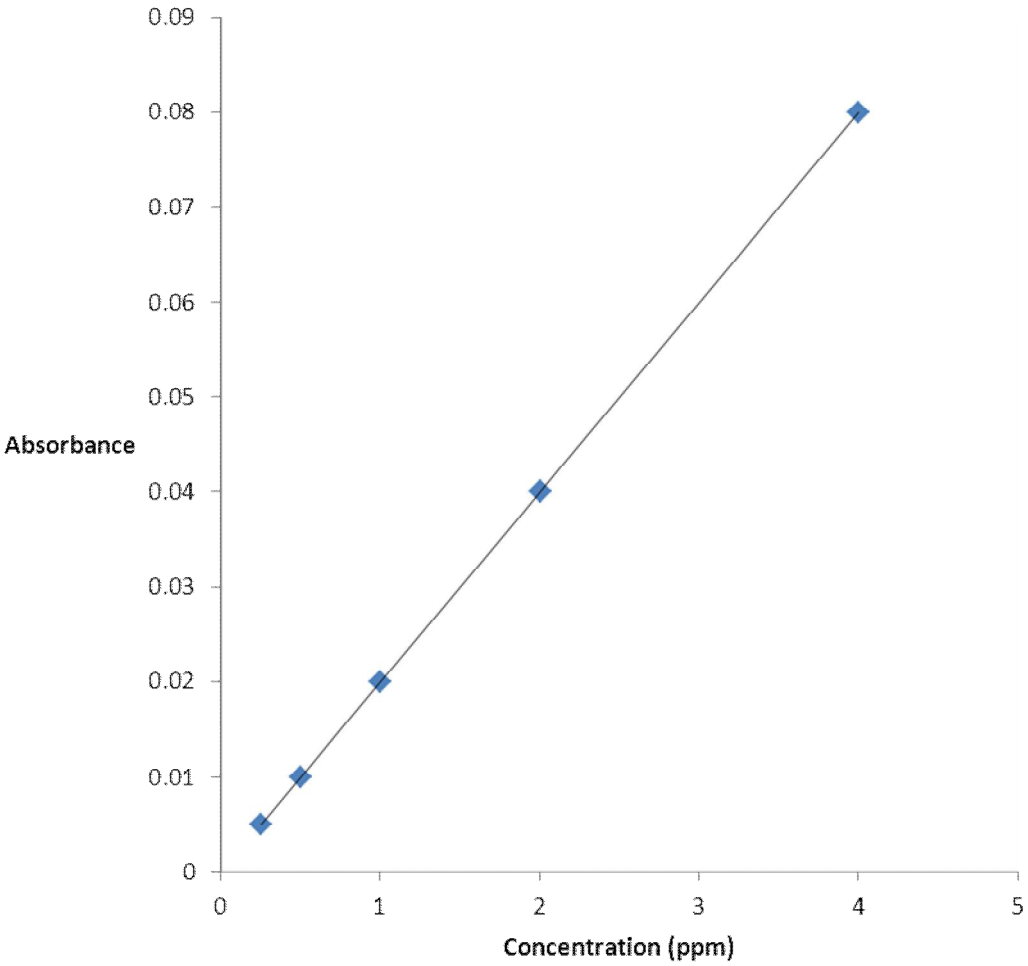
Calibration curve for the determination of Ni

Appendix XLV



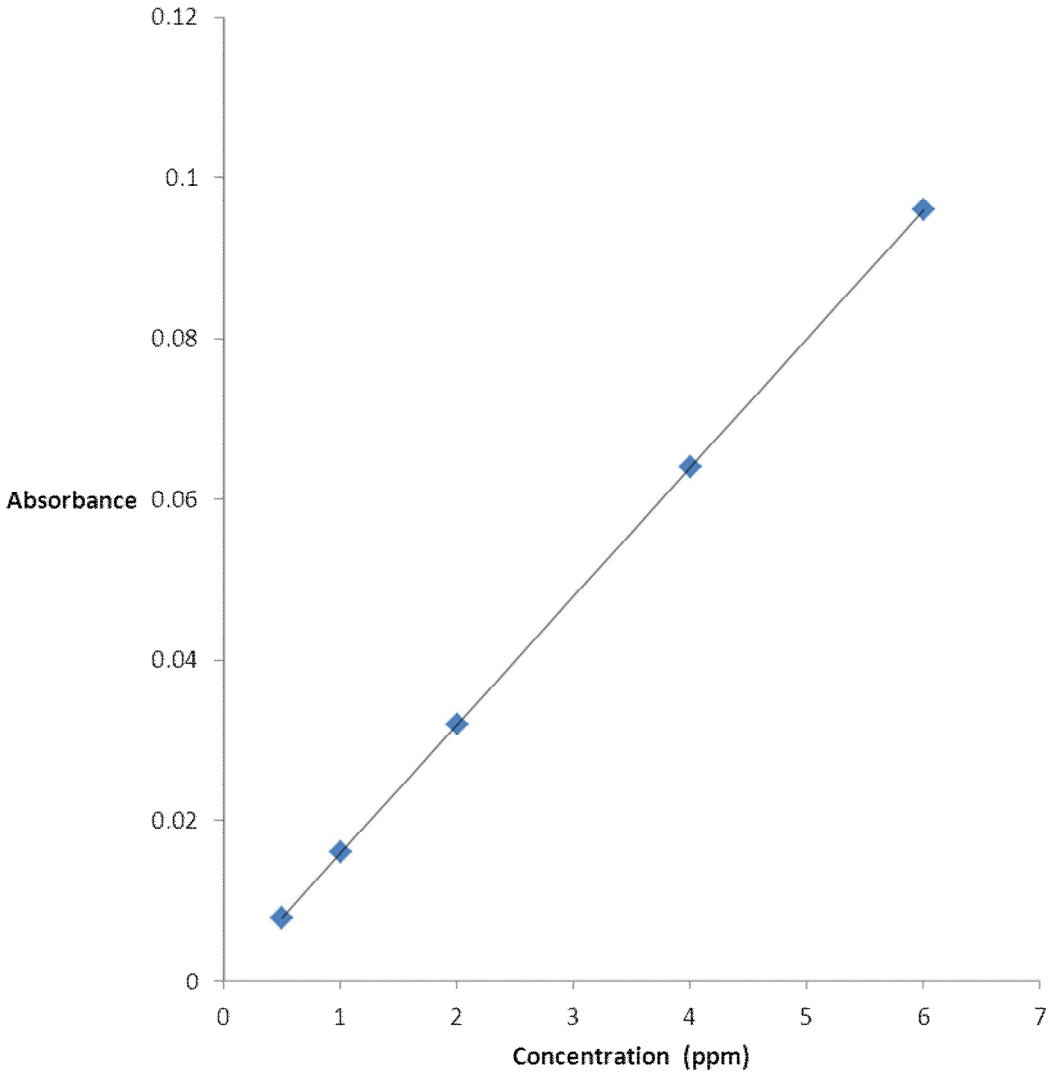
Calibration curve for the determination of Pb

Appendix XLVI



Calibration curve for the determination of Cu

Appendix XLVII



Calibration curve for the determination of Zn